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USERS MANUAL FOR THE SAPRC ATMOSPHERIC CHEMICAL MECHANISM GENERATION SYSTEM

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February 18, 2024

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ABSTRACT

MechGen is a computer program that derives fully explicit mechanisms for the reactions of many types of emitted organic compounds and their oxidation products when they react in the atmosphere in the presence of oxides of nitrogen and other pollutants, and optionally uses the results to derive lumped mechanisms suitable for use in atmospheric models. The scientific basis for how the chemical reactions and rate constants are derived or estimated is given in a separate paper (Carter et al, 2024), and a paper discussing the algorithms used and test cases is in preparation. The system is publicly accessible using a web-based or terminal-based interface, and can be used for generating explicit mechanisms for individual compounds and to view associated documentation, with a telnet login being used to derive mechanisms for multiple compounds, multi-generation mechanisms, and portions of lumped mechanisms for airshed models, as well as to program and manage the system. This document discusses how to access the online system and use it to generate explicit and lumped mechanisms, including mechanisms with user-defined lumping and explicit reaction assignments. In addition, this document describes how users can obtain and install their own copies of this software so they can use it for advanced capabilities such as deriving multi-generation mechanisms, deriving mechanisms and deriving new lumping methods and using them to derive lumped atmospheric reaction mechanisms for airshed models.

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1. INTRODUCTION

1.1. Background

The SAPRC atmospheric chemical mechanism generation system (MechGen) is a computer program that is accessible online to derive fully explicit mechanisms for the reactions of many types of volatile organic compounds and their oxidation products when they react in the lower atmosphere in the presence of oxides of nitrogen and other pollutants. This system is currently freely available online at http://mechgen.cert.ucr.edu, but can also be downloaded for installation on a users' computer. MechGen can be used for analysis of current predictions for the atmospheric reactions of organic compounds and laboratory or ambient data, or for the development of condensed mechanisms for use in atmospheric models. The term SAPRC is used because it has been used for many years to derive the various versions of the SAPRC atmospheric chemical mechanisms for airshed models (e.g., Carter, 1990, 2000, 2016, 2019a,b, 2023a,b, Carter and Heo, 2013) and VOC reactivity assessment (Carter, 1994, 2010a, 2013a), the most recent being SAPRC-22 (Carter, 2023a). Documentation of the scientific basis of the chemical estimates and assignments that MechGen uses to derive the mechanisms is under peer review (Carter et al, 2024), and documentation of MechGen as a software system is in preparation. This document serves as a basic instruction manual on how to access and use this system as it is currently available online at http://mechgen.cert.ucr.edu. In addition, this document also describes how advanced users can to install their own versions of this system and use additional capabilities that are available to those with their own copy of the system.

MechGen can be used to generate reactions of volatile organic compounds with OH, O_3, NO_3, O^3P, by photolysis, or by unimolecular reaction, as applicable depending on the compound, and also the reactions of the organic radicals or intermediates they form under atmospheric conditions. It is designed to generate mechanisms for lower tropospheric modeling only, so its mechanisms are applicable primarily for temperatures at or near 298 K and pressures at or near 1 atmosphere. It is currently not designed for estimating mechanisms for combustion or low temperature or pressure systems. The reactions can be generated in either in "single step" mode to see the predictions and documentation for a single reaction, or in "react completely" mode to also react the intermediates formed to obtain a complete mechanism leading to stable products. The stable products formed can then be reacted separately to determine their mechanisms leading to secondary products as a separate step, if desired.

MechGen is similar to the Gecko-A system of Aumont et al (2005) in that it can estimate and generate atmospheric chemical mechanisms of organic compounds and that it is also available online (at https://geckoa.lisa.u-pec.fr/). The main difference is that Gecko-A is designed to derive complete, multi-generation mechanisms that include the complete reactions of secondary and tertiary products in order to investigate the full complexity of the chemical system, while MechGen is designed primarily to derive mechanisms for single compounds, for use in deriving condensed mechanisms for models, as well as obtaining predictions and documentation information for single reactions. (It also has the capability of deriving multi-generation mechanisms, but because of resource requirements this capability is only available to authorized users, and is not available online.) The chemical bases for the estimation methods currently used in Gecko-A have been documented previously (e.g., Aumont et al, 2018; Jenkin et al, 2018a,b, 2020; Kerdoici et al, 2014), and were derived independently of those used by MechGen (Carter et al. 2024), though some of the estimation methods used in MechGen have been informed by those recently developed for use in Gecko-A (Carter et al, 2024). Therefore, the two systems give somewhat different predictions for some reactions that are particularly uncertain, and in some cases predict different speculative reactions, each of which would result in somewhat different predictions of mechanisms for many compounds.

This document is intended to serve as a practical users guide for those who may wish to use or investigate the use of MechGen in their research. It describes how to access and use the MechGen system as it is currently configured online, and also gives brief discussions of the major concepts and methods employed for basic mechanism generation operations. This system has additional capabilities that require that users obtain their own copy of the system to run on their computers, so this document also describes how to download and configure copies of the system and how to use the additional capabilities that are available to users of their own copy of MechGen, or users who have been authorized to use the additional capabilities.

1.2. Software System

MechGen is currently incorporated into an online MOO system, which was originally developed as a programmable text-based virtual reality system (MOO, 1997, 2014, 2016). This type of text-based system is no longer widely used for online virtual reality experiences and the programming system is no longer being developed or supported, but features of the MOO object-oriented programming language, which is very similar to Python, made it much better suited for mechanism generation applications than Fortran or other programming languages that the author happened to be familiar with at the time MechGen was initially developed. In principle this system could be converted to Python or another platform whose underlying programming system is still being supported, allowing it to be maintained in the future as a collaborative effort, but this has not yet been started. However, the MOO system has online access capabilities that make it relatively straightforward to program to permit multiple users to access it online at the same time. The MOO software system is discussed in more detail in Section 9.1.

The normal operation for MechGen and other MOO systems is to run continuously, with users, programmers, and administrators accessing the system using a terminal or Telnet interface. In addition, MechGen, like some other MOO systems, also has the capability to be accessed using a web browser, providing a subset of their capabilities for general users. However, some advanced capabilities of MechGen require that users run their own copies of the system on their own computers, or that they obtain authorization from the administrators of the systems as installed. Section 9 discusses how users can obtain, install, and configure their own copy of MechGen and utilize some of its advanced capabilities.

1.3. Basic Concepts

Although it is not necessary to understand the details of the methods and programming system do use MechGen, a general knowledge of the terms, concepts, and program objects is useful to understand this document and the MechGen system. These concepts and terms that are used throughout this document are listed and briefly described in Table 1. The following points are particularly important for users to understand.

User refers to anyone who accesses the MechGen system, and also how they are represented within MechGen. Although there are different types of users, unless indicated otherwise the discussion in this document will refer to non-administrative MechGen users who have created user accounts using the web interface as discussed in Section 2. MechGen user accounts are available online to anyone without cost and the need to provide personal information, though it is necessary to have an account and password so that the multi-user MechGen system can distinguish between different users, who could be accessing it at the same time, and it is necessary to obtain authorization to fully utilize the system (see Section 9.3). Each user is assigned a different reactor, which is the programming object that processes the commands and manages the reactants created by that user.

Table 1.   Descriptions of terms and concepts used throughout this document.

Terms	Description
MOO	This is an acronym for "Multiuser Object Oriented", a software platform originally used for text-based virtual reality systems in the '90's, upon which the MechGen software is based.
Web interface	This is the method for accessing MechGen through a web interface, currently available at http://mechgen.cert.ucr.edu. This is freely available and the best way to explore the capabilities of the system and to obtain documentation. However, because of resource and software limitations it cannot be used for generating mechanisms for large molecules or using advanced features useful for mechanism development.
Telnet interface	This is the method for accessing MechGen through a terminal interface, which requires a login and password that can be obtained using the web interface. This provides full capabilities of MechGen, but some require authorization or administrative access, and require some learning to use. Note that users of the telnet interface are treated as "players" within the MOO system (see Section 9.1).
MechGen User	This refers to any login to the system through a web or Telnet connection. Web user accounts and optionally Telnet login accounts are created using the web system.
Primary MechGen user	This is a MechGen telnet login that is used to program and update the MechGen system is and can also utilize all the advanced and resource-intensive features of the system (see Section)9. This requires that the user obtain a separate copy of MechGen and run it on their own computer and configure it so they access it as both the primary MechGen user and also as a MechGen administrator.
MechGen Administrator	As discussed in Section 9.1, MechGen is implemented in a MOO system that require that there be at last one MOO user that has complete system administration capabilities needed to configure and maintain MOO systems. (Such users are referred to as "wizards" in MOO parlance.) Note that the primary MechGen user cannot have administrative access because of the way MOO systems handle user permissions. Access to this login also requires that the user obtain a separate a separate copy of MechGen and run it on their own computer and configure it so they access it in this way.
Authorized MechGen User	This refers to a MechGen user with a Telnet login that that has additional capabilities that are not available to regular MechGen users, which are discussed in Sections 9 through 12. The primary MechGen user is already authorized, but other uses with Telnet logins can be authorized by the MechGen Administrator user, as indicated in Section 9.3.
Reactor Primary Reactor Chamber	This is a MOO "room" or web interface software object that processes commands to carry out reactions and handle the results. Each web or Telnet user is assigned a different reactor for this purpose. This is referred to as the "primary reactor" for the user. Authorized users can create additional reactors with differing options and reactants as discussed in Section 9.3, but other users can only access their primary reactor. Options that the user can modify to control mechanism generation or processing are saved as properties of the reactor. Note that reactors are often referred to as "chambers" when using the Telnet interface.

Table 1 (continued)

Terms	Description
Reactant	This refers to a MOO object that contains information about the structure and (once reacted) results of reactions of an organic compound or reactive intermediate. Users can create, react, obtain results from, and delete reactants within their reactor. Each reactant object is assigned a name that is used for selecting it for operations. It is usually either a SAPRC VOC name or a generic name assigned by the system.
Group	The portion of reactant molecules that are treated as single units within MechGen for the purpose of generating mechanisms, each containing no more than one carbon or nitrogen atom but variable numbers of hydrogen or oxygens. Groups recognized by MechGen are listed in Table 2.
Reactant structure	This is a string that MechGen uses to specify the structure of the reactant in terms of the groups within the reactant, the groups they are bonded to, the types of bonds involved, and (where applicable) *cis* or *trans* orientation. MechGen structure strings serve the same purpose as SMILES strings, are described in Section 3.1.
Reactant name Standard name ORG- names RAD- names	Each reactant that is created must have a 2-8 character string that is used to reference the reactant. Compounds that have been represented in current and previous detailed SAPRC mechanisms, and whose reactivities are included in SAPRC reactivity scales (Carter, 1990, 1994, 2000, 2010a,b, 2023a), have been assigned "standard" names, which can be used as an alternative to the structure string when creating reactants. Lists of most compounds with standard names can be obtained using the web system or in the electronic supplement to the SAPRC-22 documentation (Carter, 2023a). Not all reactants have standard names, and in those cases the system assigns either ORG-nnnn or RAD-nnnn names when permanent names or required, or uses temporary names otherwise.
Intermediate	This is a type of reactant that is predicted to react rapidly when formed in the atmosphere, such as a radical, Criegee intermediate, or excited molecule. They are automatically reacted when created using the web interface, or when a "react completely" operation is carried out.
Stable reactant or Product	This is a reactant that is not an intermediate. In order to react it, it is necessary to specify what it is reacting with or how it is reacting. The term "product" is used for stable reactants formed as products of a reaction.
Single step react	This is the process of generating all reactions of a selected radical or stable reactant without reacting the products or intermediates formed. This is the primary means to obtain documentation information about how the reactions were estimated.
React completely, or Fully React	This is the process of generating reactions of a selected reactant and then reacting the reactions of all intermediates formed. Stable reaction products are not reacted. This is necessary to create complete explicit or optionally lumped mechanisms for a compound. The results of these operations are saved on the reactant object for subsequent processing or output options.
Multi-generation reacting	This is the process of generating complete reactions of a selected reactant, and then generating complete reactions of all the stable products formed in non-negligible yields. The result is a "multi-generation" mechanism, as opposed to single generation mechanisms obtained using react completely or fully react operations. See Section 10.

Table 1 (continued)

Terms	Description
Chemical Estimates	The term "estimates" is used to refer to methods used to derived reactions of species and estimate their rate constants using various estimation methods or structure and reactivity relationships (SARs) that are applicable to all compounds with similar structures. These are as documented by Carter et al (2024), and information about them can also be obtained by web users as described in Section 4.6. These can only be modified by the primary MechGen user and programmer.
Chemical Assignments	The term "assignments" refers to assignments of rate constants or branching ratios for reactions of specific compounds based on laboratory or theoretical data or estimates applicable to only that compound. A list of these are included in the supplementary materials for Carter et al (2024), and also can be obtained by web users as described in Section 4.6.
User Assignments	Advanced users can also change or add chemical assignments used when generating mechanisms in their reactor. These are discussed in Section 8.
Explicit Mechanism	This is the mechanism that is initially produced MechGen that consists of the elementary reactions that are generated, before any reduction or lumping processing. These can be "single-generation" mechanisms that have the reactions of a compound but not its stable product, and "multi-generation" mechanisms that include the reactions of the non-negligible products.
Lumping Lumping options	This is the method used to process results of "react completely" operations to produce reduced or lumped mechanisms. These are implemented using "lumping" objects within the MOO system, and each reactor has one assigned to it, which can be changed by the user. The currently available lumping options include "explicit" or minimal lumping, SAPRC-22 standard and full (Carter, 2023a), and SAPRC-11 (Carter and Heo, 2013). See Section 7 for a discussion of lumping and how to change lumping options, and Section 11 for a discussion of how authorized users can create or modify lumping methods.
Explicit Lumping	This is the default lumping option that produced only minimally reduced processed mechanisms (see below). This is the default because all reactions are carried out during a react completely operation if explicit lumping is chosen.
SAPRC-22 lumping	This is the lumping option used to develop the SAPRC-22 mechanisms, and can be selected by the user if they want to revise SAPRC-22 to represent the compound by its own model species, rather by a lumped model species. Note that this mechanism represents some intermediates as lumped model species, so reactions of these intermediates are not generated during a "react completely" process because the results, which in some cases can result in many reactions and products, are not used. There are two versions of SAPRC-22 lumping, one for the standard version and one for the full version, though they both employ the same model species assignments.
Processed Mechanism	This is a minimally reduced mechanism that is derived from the explicit mechanism by removing intermediates with only unimolecular or O_2 reactions by replacing them with the products they form, and by combining parallel reactions into a single reaction with product yields derived from ratios of rate constants. This should give the same predictions as the explicit mechanism when the O_2 concentration and temperature are the same as when the explicit mechanism was generated.

Table 1 (continued)

Terms	Description
Lumped Mechanism	This is a further reduced or lumped mechanism that is derived if a non-explicit lumping method is selected. Lumped mechanism prepared if SAPRC-22 lumping is selected can be incorporated directly into SAPRC-22 mechanisms because all products formed are given as SAPRC-22 model species. Lumped mechanisms compatible with SAPRC-11 can also be prepared using this system.
User Mechanisms	Advanced users interested in generating lumped mechanisms compatible with SAPRC-22 can optionally modify the lumping method so the lumped mechanisms will represent selected compounds explicitly. This is only available if a compatible lumping method is chosen, which is currently only standard SAPRC-22 lumping.
Environmental conditions	Each reactor is assigned a temperature and pressure used to derive rate constants and also "environmental conditions" objects that define concentrations of atmospheric species such as OH, NO, or HO_2 that affect relative importances of competing bimolecular reactions. The latter are used when showing relative yields of products formed in react completely operations in various environments, when deriving multi-generation mechanisms, and optionally for determining which reactions can be ignored during full mechanism generations.
Standard environmental conditions	These refer to four sets of environmental conditions that by default are included among the environmental conditions determining product yields and in full mechanism generations. These represent conditions where O_3 formation is VOC-limited (high NO_x), where the VOC and NO_x are in the transition regime (mid NO_x) or in NO_x-limited (low NO_x) urban conditions, and also nighttime conditions for multi-day, mid NO_x regional scenarios. These can be modified by users of the telnet interface as discussed in Section 6.

An Authorized User is a user who has the capability to utilize the full capabilities of the MechGen system, including resource-intensive operations that are not available to regular users, including generating multi-generation mechanisms as discussed in Section 10, creating or modifying lumping methods as discussed in Section 11, and working with mixtures as discussed in Section 12. The creation of authorized users is discussed in Section 9.3.

Interface refers to the method used to access the MechGen system, which is either through a web site (the "web interface") or through a terminal, command-based interface accessible using Telnet or a similar method (the "telnet interface"). These are discussed further in Section 2.

Reactants are objects in the system used to represent any organic compound or intermediate that MechGen can process. The types of compounds that can be represented are discussed in Section 3.1 and the types of reactions it generates are discussed by Carter et al (2024). Reactants are classified as either stable or as intermediates, where stable reactants represent close-shell compounds that might react with OH, O_3, NO_3, O^3P or by photolysis or in some cases unimolecular reaction, and where it is necessary to specify its mode of initial reaction (e.g., with OH or photolysis) in order to generate its reactions. Intermediates are radicals or very unstable closed-shell compounds with extremely fast unimolecular or bimolecular reactions that are automatically generated. Reactant objects are created by users as a result of reactions and can be used to store results of reactions for subsequent output.

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Reactor refers to an object within the MechGen system that is assigned to each user for the purpose of creating and reacting, and maintaining reactants and changing options affecting how they react and how the results are processed. Each MechGen user has its own reactor so their operations can be carried out independently in this multi-user system, and authorized users can create additional reactors. Users of the web interface interact with the reactor through the main menu and users of the telnet interface interact with it as if it were a virtual "room" where they can give commands and view lists of contents. Either way, reactants are created within the reactor, where they can be reacted, used to output results, or deleted. Note that reactors are often referred to as "chambers" when using the Telnet interface.

Single step react is the process of generating the reactions of only one reactant, without reacting the products or intermediates formed. Although this is necessarily involved in a complete reaction generation process as discussed below, the user can select to have only a single step reaction carried out in order to see documentation on how the reactions and rate parameters were derived along with the results, or to carry out selected reactions in a step-by-step manner. This is the only way to obtain documentation information for specific reactions, though general documentation is also available using the web system as discussed in Section 4.6.

Complete reaction or full mechanism generation is the process of not only generating the initial reactions of the compound or radical, but also generating reactions of the organic intermediates that are formed. This gives complete mechanisms for the starting compounds through formation of stable products or basic inorganic or C_1 species such as OH, HO_2, NO, CO, CO_2, or formaldehyde (HCHO). This is not a useful method to obtain documentation information because the large number of reactions that have to be carried out requires that documentation output be suppressed during full mechanism generation. Note that this is a single generation process because it does not react the stable products formed. This is useful for deriving lumped mechanisms for individual compounds, particularly mechanisms such as SAPRC that use lumped model species to represent many of the stable products (e.g. Carter, 2000, 2010a,b, 2023a).

The multi-generation reaction process involves reacting the reactive stable products formed in complete reaction sequences as well as the intermediates, until only nonvolatile or unreactive products, or basic inorganic species remain. This is the usual operating mode for the GeckoA mechanism generation system (Aumont et al, 2005), and is useful to determine the ultimate fate of the compound and to fully evaluate its impact on particle formation. MechGen can derive multi-generation mechanisms by carrying out complete reactions of all the major unreactive products, but this requires significant computer resources and only available to authorized users. The process of generating multi-generation mechanisms is described in Section 10.

An explicit mechanism is the primary result of a complete reaction process where a compound and the reactive intermediates it forms are reacted. It consists of lists of reactants, products, and rate constant parameters for all the reactions that are generated, with no lumping, combining of consecutive or parallel processes, or other reduction procedures. It is a single-generation mechanism that does not include reactions of the stable products. These are stored as properties on reactant objects as a result of the full reaction process and are available to be output to the user. Lists of intermediates and products in the mechanism, along with information regarding them, are also stored on the reactant object for use in output or post-processing.

A processed mechanism is a minimally reduced mechanism derived from the explicit mechanism, where parallel reactions are combined and intermediates that undergo only fast unimolecular or pseudo-unimolecular reactions with O_2 are removed by replacing them by the species they form in reactions

where they are formed. This results in mechanisms with approximately 2½ times fewer species and almost a factor of 10 fewer reacting intermediates, yet giving the same predictions as the explicit mechanism as long as the temperature, pressure, and O_2 content is constant at reactor defaults (298K and 1 atm air), and the time scale is long enough that the steady state approximation can be employed for radical intermediates. However, the final stable products, of which there can be hundreds for larger molecules, and the numbers of peroxy radical intermediates, of which there can be dozens, are retained. Therefore, these mechanisms are still too large for airshed modeling applications representing highly complex mixtures.

A lumped mechanism is a processed mechanism that is further reduced or lumped so that it is of an appropriate size for practical use in airshed models with complex mixtures. It can be used to add reactions of selected organic compounds to an existing SAPRC lumped mechanism for airshed model applications, with the current version supporting adding reactions to the SAPRC-11 (Carter and Heo, 2013) or SAPRC-22 (Carter, 2023a) mechanisms. The numbers of products formed is reduced by representing most by lumped model species, and the numbers of reactive intermediates are reduced by using various peroxy radical operators (Carter, 2023a), resulting in minimal numbers of reactions and intermediates needed per compound. Generating lumped mechanisms compatible with SAPRC-11 or SAPRC-22 is an option available for users, though the default is only to generate explicit and processed mechanism.

The lumping method is an option that can be selected by the user that controls whether a lumped mechanism is derived and if so the lumping approach employed. The default lumping method is "explicit lumping", which results in deriving only explicit and processed mechanisms, and requires that all intermediates formed be reacted during mechanism generation. Currently web users have the option to select "SAPRC-11 lumping" or SAPRC-22 lumping" as options, which will result in SAPRC-11 (Carter and Heo, 2013) or SAPRC-22 (Carter, 2023a) compatible lumped mechanisms being derived following full mechanism generation. Advanced users can employ the telnet interface to create new lumping methods (see Section 11) and any users can modify the SAPRC-22 method so additional compounds can be represented explicitly (see Section 7.3). Note that current SAPRC mechanisms use lumped model species to represent phenoxy and most acyl peroxy intermediates, so these are not reacted when mechanisms are generated for SAPRC-11 or 22, but instead treated as final products. Therefore, users interested primarily in complete explicit mechanisms should employ the default "explicit lumping" method.

Environmental Conditions refer to parameters defined on the reactor that affect results of reaction generations. These include temperature, pressure, O_2 concentration, and the presence of water, and the Standard Environments that refer to sets of concentrations of reactive atmospheric species (e.g., OH, HO_2, NO_x, etc.) that affect competitions involving bimolecular reactions. The concentrations of reactive atmospheric species are not needed for single step reaction generation but are normally used to determine which processes can be neglected during complete reaction generation (unless the user selects otherwise), and also to derive relative yields of final products predicted for various environments. Standard environments are necessary to obtain listings of product yields and also to determine which products can be neglected when generating multi-generation mechanisms (see Section 10). Several standard environments are available for this purpose as discussed in Section 6, including those representing various NO_x conditions during the daytime, and also nighttime conditions.

2. SYSTEM ACCESS

2.1. Web access

MechGen can be accessed by anyone using the web interface that is currently available at http://mechgen.cert.ucr.edu. Although telnet access is needed to exploit the full capability of the system, web access provides a means for the general user to generate mechanisms of compounds of interest and is the best means for obtaining associated documentation. This also allows the user to obtain explanations of how MechGen generated the reactions and estimated the rate constants involved, and to get lists of generated reactions and products formed when compounds are reacted completely. The system can also be used to obtain information about most of the various types of estimation methods and lists of assigned reactions. However, the web system cannot be used to program the system or make or change any of its basic assignments or to carry out operations requiring authorization, as described in Sections 9 through 12.

When first accessing the MechGen web site, the user is presented with a login page with a form to give a username and a password. Usernames are not case sensitive but passwords, which are required to prevent others from using the same account by just giving your user name, are. It is necessary to have a user account so the system can assign a unique reactor for each user to allow the user's work independent of other users, to modify options, and to save results between sessions. There is no cost or personal information required to create an account, though users can optionally provide their email address and other information about themselves after they logged in if they wish to be periodically updated about changes to the systems or to work on collaborative efforts. Once logged in, the user is presented with a "main menu" where users can create new reactants for mechanism generation or access previously created reactants and results, obtain information about chemistry assignments or estimates, change mechanism generation options, or optionally provide information about themselves, as discussed below.

2.2. Telnet Access

MechGen can be also be accessed with a terminal or command-based interface using a Telnet client. This access method is similar to entering a multi-user text-based virtual reality system that also has programming capabilities, which is what MOO based systems were originally designed for (see Section 9.1 and MOO 1997, 2014, 2016). Telnet access permits mechanism generation operations that are not possible or practical using the web interface, and is necessary for programming and maintaining the system or carrying out complex or highly resource-intensive operations by authorized users. MechGen has multi-user capabilities that it inherited from a Diversity University MOO (2023) and LamdaMoo (2023) core that serve as the host for the system, but MechGen is not currently being used for this purpose so this is not discussed here beyond the brief description in Section 9.1. Several types of user accounts are currently available, but only the following three types are relevant to the MechGen system:

MechGen users: The web system will allow any web user to create a username and password to allow for Telnet access as a non-administrative user of the MechGen system. These users can carry out the mechanism generation operations that are discussed in this document, including, but not limited to, most operations available through the web system. The main exceptions are that certain help or information pages that can be output by the web system are not available to Telnet users.

Web users can enable Telnet access as a MechGen user from the main menu of the web interface. Once telnet login is enabled, you can use a telnet program to connect to MechGen, with the address being

shown on the main menu page after telnet access has been enabled. Once connected, give the command "connect *username userpass*", where *username* and *userpass* are the same as when accessing the web system. You will be able to give commands and receive output using the same reactor that you use during telnet access, which is assigned only to you. Give the command "@quit" to end your telnet session, or just close telnet. The user will enter this same reactor on subsequent logins, and it will contain any reactants and option changes from previous operations using either interface, as is the case with the web system.

Primary MechGen user: This is the single user that has the capability of programming and modifying the MechGen system itself, including inputting or modifying parameters that affect the chemistry assignments and estimates. There is only a single MechGen administrator for any running installation of MechGen, which is currently the author for the online version at http:// mechgen.cert.ucr.edu. However, as discussed below, users can install their own copy of MechGen on their own computer that will allow them to use administrator accounts. The primary MechGen user has all the capabilities of non-administrative users as discussed in this document, in addition to programming and data input capabilities available to this account alone. In MOO parlance, this is a "programmer" user, which is capable of creating programs and properties on objects that the user "owns" or controls, which includes most objects used or created by MechGen operations, but not basic system objects in the MOO system.

Authorized Users: These consist of the primary MechGen user and also other MechGen users who have been granted authorization by a MechGen administrator user (see below) to carry out the complex or resource-intensive operations discussed in Sections 10, 11, and 12.

MechGen Administrators: As discussed in Section 9.1, all MOO systems have users referred to as "wizards" who have the capability of modifying the system and controlling user access. In the case of MechGen, a "wizard" login is only needed for configuration purposes and creating authorized users (see Section 9.3), and is not used for programming or updating the MechGen capabilities.

2.3. Obtaining and Installing MechGen for Single User Access

The online version of MechGen is available for occasional users, but is shared with other users and is not appropriate for projects that have large resource demands, such as generating mechanisms for large numbers of compounds (as required for full mechanism development), generating multi-generation mechanisms, or generating mechanisms for mixtures. For this purpose, it is more appropriate that the user obtain their own copy of the MechGen core database, and also the freeware MOO server software needed to run MOO systems on either Unix or Windows systems that have access to the internet with security settings that allow use network ports for Telnet or web access. This allows anyone to make themselves the primary MechGen user and a MechGen administrator, and make collaborators authorized users. This is discussed in Sections 9.

3. SPECIFICATIONS OF REACTANTS

In order to use MechGen to generate reactions or mechanisms, it is necessary to specify the structure of the reactant to be reacted. Reactants can represent either stable compounds or radicals. Any reactant can be created by giving its structure as discussed in this section, and a large number of stable reactants can be specified using standard names assigned to them.

3.1. Specification by Structure

Structures of reactants within MechGen are specified in terms of portions of molecules treated as single units or "groups", as listed in Table 2, Table 3a and Table 3b. Each group represents a no more than one carbon, nitrogen, or halogen atom and variable numbers hydrogens or oxygens. Oxygens that are bonded to a carbon or nitrogen by a double or dative bond are treated as part of the group defined by the carbon or nitrogen they are bonded to, while those with only single bonds are treated as separate groups (-O- or -OH). The only group with a single hydrogen atom is that used to represent H atoms, an elementary radical group (Table 3b). Groups with radical centers are treated as separate radical groups.

Normally reactants are created by inputting a string indicating the groups they contain, what they are bonded to, and in some cases configuration information. Most reactants can also be created by inputting SMILES strings, but not all types of SMILES designations are currently accepted, and in any case this input is converted to MechGen format for subsequent processing. Examples of reactants in terms of MechGen structures are given in Table 4, which also shows SMILES strings. Note that, as with SMILES strings, there can be more than one valid structure specification and molecules, and Table 4 include some examples of these. However, MechGen uses an algorithm to produce a unique standard structure designation string for any compound, regardless of how it is input or created within the system, and this is the primary means of identifying compounds and their structures within MechGen. A unique string to identify any compound is necessary for the system to determine whether reactants created or generated refer to the same or a different compound. The following points should be noted:

- Although structure input is not case sensitive, the system converts the designations to mostly uppercase as shown on Table 2 and Table 3. Subscripts are not used.

- Neighboring groups in non-branched and non-cyclic structures are separated by either "-", "=", or "#" symbols, depending on whether their bonds are single (or aromatic), double, or triple.

- Branched structures are indicated using "()"'s to additional groups bonded to groups with more than two neighbors, similar to SMILES notation. This notation is used on Table 2 to indicate groups with more than two groups bonded to them. If the bond between the center group and the 3rd or 4th group is a double or triple bond, it is indicated using a "=" or "#" after the "(", as shown for isoprene on Table 4.

- Monocyclic structures are indicated using "*" symbols to indicate groups bonded to other groups using single bonds. The "*" can be before or after the group name during input, but the standard format is after then name. Bi- and polycyclic structures are indicated using "*1", "*2", etc. symbols to indicate groups that are bonded together, and should always be given after the group name but before any bond designation.

- Aromatic and allylic structures can be created by specifying alternating single or double bonds, but in many cases the designation will not provide a unique identification except for highly symmetric molecules. Therefore, the standard designation uses groups with the prefix "a" or "p" as indicated on Table 1, with the aromatic or allylic bonds designated as if they were single bonds.

Table 2.   List of groups and group designations used to specify C_{2+} organic reactants

Non-Radical Groups		Radical Groups	
Alkane		**Carbon-centered radical groups [a]**	
-CH3 or CH3-	-CH()-	-CH2. or .CH2-	-aCH2. or .aCH2-
-CH2-	-C()()-	-CH[.]-	-aCH[.]-
Alkene		-C[.]()-	-aC[.]()-
=CH2 or CH2=	=C()- or -C()=	=CH. or .CH=	-pC[.]- [e]
=CH- or -CH=		=C[.]- or -C[.]=	-CO. or CO[.]-
Alkyne		**Peroxy radical groups**	
#CH or HC#	#C- or -C#	-CH2OO. or .OOCH2-	-CO[OO.] or CO[OO.]-
Aromatic or Allylic [a]		-CH[OO.]-	=CHOO. or .OOCH=
-aCH-	-aC()-	-C[OO.]()-	=C[OO.]- or -C[OO.]=
Oxygenate		**Alkoxy radical groups**	
-CHO or HCO-	-CO-	-CH2O. or .OCH2-	=CH[O.] or CH[O.]=
-OH or HO-		-CH[O.]-	=C[O.]- or -C[O.]=
Nitrate, nitro, nitroso		-C[O.]()-	-CO2. or CO[O.]-
-ONO2 or O2NO-	-NO2 or NO2-	-pC[O.]- [e]	
-NO or NO- [b]			
Amino and stable amine-oxy		**Crigee biradicals [f]**	
-NH2 or NH2-	-N()-	-CHOO {excited}	-C[OO]- {excited}
-NH-	-N[O]()- [c]		
Imine [b]		**N-Containing radicals and excited adducts**	
=NH or NH=	=N- or -N=	-NH. or .NH-	-NH2[O] or NH2[O]-
		-N[.]-	-NH[O]-
Stabilized Criegee Intermediates		**Carbenes**	
-CHOO[syn]	-C[OO]-	-CH[..] or CH[..]-	-C[..]-
-CHOO[anti]	-syn- [d]		
Halogen (X= F, Cl, Br, or I)			
-X or X-			

[a] The "aC" codes are used to indicate carbon centers in aromatic rings and allylic groups.

[b] Reactants can be created with this group but either the system cannot always generate their reactions successfully, and their reactions are beyond the scope of those discussed by Carter et al (2024).

[c] These groups are generated when amines react with O_3. Those formed from tertiary amines are assumed to be stable, while those formed from primary or secondary amines are assumed to react with H-shift reactions. See Carter et al (2024).

[d] Used to indicate which substituent of a disubstituted Criegee intermediate is in the syn position.

[e] These are phenyl, phenyl peroxy, or phenoxy radical centers.

[f] The designation "{excited}" is given at the end of the compound identification, and indicates the level of excitation of the intermediate. For Criegee intermediates, it could be "{*O3Ole}", or "{*O3cycOle}" or, "{*O3alkyne}".

Table 3.　　　　List of elementary or single-group species names recognized by the system.

a) Elementary non-radical products [a]		b) Single group radicals		c) Species that react with organics		d) Species that may react with radicals	
CH4	H2O	HCO.	CH2[..]	OH	O3	O2	HO2.
HCHO		CH3.	CH3O.	NO3 [b]	HV [c]	NO	NO2
CO	CO2	CH3OO.	HCO2.	O3P	Uni [c]	RO2. [e]	
HF	HCl	CH2OO	H.	Cl. [d]		RCO3. [e]	
HBr	HI	CH2OO {excited}					

[a] MechGen does not generate mechanisms for these compounds because they have known mechanism that do not need to be estimated or they are unreactive. Any complete mechanism for atmospheric models should already include their reactions (if applicable) as part of the base mechanism.

[b] Also reacts with peroxy radicals

[c] Virtual species used for reaction generation. Not formed in any reaction.

[d] Reactions of this species are not supported for most types of unsaturated compounds and are not documented by Carter et al (2024).

[e] Refers to the total of all organic peroxy (RO2.) or acyl peroxy (RCO3.) radicals when reacting with a peroxy radical. Not formed in any reaction. These are designated as SumRO2 or SumRCO3 when lumped mechanisms are output.

- Syn/Anti isomerization for stabilized Criegee intermediates indicates which group bonded to the Criegee carbon is on the same side of the O=O bond. This is designated using the [syn] or [anti] terminology for intermediates with only one substituent, with the -syn- pseudo-group being used to indicate the group in the *syn* position in disubstituted intermediates, as shown on Table 2.

- Specification of optical isomerization and cis/trans isomerization of cyclic compounds is not currently supported. Generated mechanisms will be applicable to all such isomers.

- *Cis* and *trans* isomerization about a double bond are indicated using "^" and "v" symbols, analogous to the use of "\" and "/" symbols in the SMILES notation. Note that compounds can be identified without *cis/trans* isomerization, with the results being applicable to either isomer.

The structures do not have to be in the standard form when input into MechGen, but they are converted to the standard form for subsequent processing, and the original input string (whether SMILES or MechGen format) is not retained if it is different.

Reactants that contain only a single group and other elementary species are listed in Table 3. These can be formed in reactions unless indicated differently on the table, or can be used to indicate how a stable compound reacts if listed on the third column of the table. Reactions can be generated for the radical species listed in the second column, but the other are treated as stable products when they are formed.

3.2. Specification by Name

VOC compounds for which mechanisms have been derived in detailed versions of the SAPRC mechanism can also be specified by giving the 2-8 character standard SAPRC name defined for them. Lists of these compounds and their names can be obtained using the web interface clicking on the links to create reactants by "compound type" "from complete list" in the "Create VOC or radical reactant" section

Table 4.   Examples of designations of selected representative compounds and radicals.

Compound	Smiles [a]	MechGen Structures [a]
propane	CCC	CH3-CH2-CH3
propene	C=CC	CH2=CH-CH3 or CH3-CH=CH2
methyl acetylene	C#CC	CH#C-CH3 or CH3-C#CH
2-methyl propane	CC(C)C	CH3-CH(CH3)-CH3
2-methyl-2-ethyl butane	CCC(C)(C)CC	CH3-CH2-C(CH3)(CH3)-CH2-CH3; CH3-C(CH3)(CH2-CH3)-CH2-CH3
isoprene	C=CC(=C)C	CH2=CH-C(=CH2)-CH3 or CH2=CH-C(-CH3)=CH2
2-butenes (mixed cis & trans isomers)	CC=CC	CH3-CH=CH-CH3
cis-2-butene	C/C=C\C	CH3-^CH=CH-vCH3 or CH3-vCH=CH-^CH3
trans-2-butene	C/C=C/C	CH3-^CH=CH-^CH3 or CH3-vCH=CH-vCH3
trans-3-methyl-2-pentene	C/C=C(\C)CC	CH3-^CH=C(vCH3)-CH2-CH3; CH3-CH2-C(^CH3)=CH-^CH3
cyclopropane	C1CC1	CH2*-CH2-CH2* or *CH2-CH2-*CH2
bicyclo [1.1.1] heptane	C1C2CC1C2	CH2*1-CH*2-CH2-CH*1-CH2*2 or CH*12-CH2-CH(CH2*1)-CH2*2
spiropentane	C1CC12CC2	CH2*1-CH2-C*12-CH2-CH2*2 or C*12(CH2-CH2*1)-CH2-CH2*2
toluene	Cc1ccccc1	CH3-aC*-aCH-aCH-aCH-aCH-aCH* or CH3-C*=CH-CH=CH-CH=CH*
naphthalene	c12ccccc1cccc2	aC*12-aCH-aCH-aCH-aCH-aC*1-aCH-aCH-aCH-aCH*2
2-propyl nitrate	CC(C)ON(=O)=O	CH3-CH(CH3)-ONO2 or CH3-CH(ONO2)-CH3
ethylene glycol ethyl ether acetate	CCOCCOC(C)=O	CH3-CH2-O-CH2-CH2-O-CO-CH3
2-propyl radicals	C[CH]C	CH3-CH[.]-CH3
2-propyl peroxy radicals	CC(C)O[O]	CH3-CH[OO.]-CH3
methyl allyl radicals	C=C[CH]C	CH3-aCH[.]-aCH-aCH2 or CH3-CH[.]-CH=CH2 or CH3-CH=CH-CH2.
OH+benzene adduct	OC1C=CC=C[CH]1	HO-CH*-aCH[.]-aCH-aCH[.]-aCH-aCH[.]*
MEK oxide with CH3- in the *syn* position	(not supported)	CH3-syn-C[OO]-CH2-CH3 or CH3-CH2-C[OO]-syn-CH3

[a] The SMILES and first MechGen structure code given are the strings generated by MechGen that are unique for the compound. Subsequent MechGen structures, if given, are alternatives that can be used to create the reactant.

of the main menu (see Figure 1). It can be also obtained from the "DMS" column in Table B-4 in the supplementary materials of the SAPRC-22 documentation (Carter, 2023a). The names are also shown in outputs produced when compounds are created by specifying their structures.

Not all stable compounds that could be created have standard names, though many have been assigned permanent "ORG-nnnn" names, where "nnnn" is a four-digit number when they are created for deriving mechanisms for mixtures as discussed in Section 12. These are displayed when such reactants are listed, but are generally not convenient for specifying reactants for input because they have no relationship to the nature of the compounds. Radicals and stable reactants without standard or ORG names are given temporary names when created or formed in reactions because the system requires that all reactants have names.

4. BASIC OPERATIONS FOR WEB USERS

This section discusses basic operations for creating reactants, carrying out reactions, and obtaining information using the web interface. Although almost all of these have analogues when using the Telnet interface, the basic operations for telnet users are sufficiently different that they are described separately in Section 5.

4.1. Main Menu

When first logged into the system, or after selecting the "Reload Main Menu" link on most other pages, the user is presented with a web page such as shown on Figure 1. This figure shows the page with a reactor with the default settings as it exists when a new user reactor is created, but after three reactants have been created and one fully reacted as discussed below. (Notations such as "[#nnnn]" on this figure and others, refer to internal object numbers in the MOO system that may be useful to the primary MechGen user for debugging but can normally be disregarded.) These sections are as follows, with their contents summarized and the associated actions discussed further below:

- Header Section. Identifies the user and reactor and gives links to reload, log off, or restore reactor defaults. Also indicates the current lumping method that controls how mechanisms are generated and processed.

- Reactant Creation Section. This section has a form to create a reactant given its structure or standard name. A standard name is a 2-8 character name assigned to most of the VOC species are that represented in SAPRC detailed mechanisms, and the names used can be determined by using one of the links in this section.

- Reactant Section. This lists reactants that were previously created by the user and not deleted, if any. It has links to go to the reactant information page for the reactant, discussed in Section 4.2. If the reactant had been completely reacted, it will have links to obtain the results of the reaction. If the list has five or fewer reactants, it would include links to obtain selected results directly without having to go through the reactant information page. Note that radical reactants that may have been created are not shown on this list unless they were completely reacted. The section also includes links to delete all or selected reactants.

- Reactor Options Section. This contains links to change options that control mechanism generation and lumping options. These are discussed in Section 4.5. Restoring reactor defaults sets all these options to those for a new user.

- Obtain Information. This section includes links to obtain general information about the chemical estimation methods, mechanism assignments, or the derivation of SAPRC-22 mechanisms, and also has links to obtain the users manual, as discussed in section 4.6.

- Advanced Options. This contains links to user assignments as discussed in Section 8 or to derive modified versions of SAPRC mechanisms as discussed in Section 7.2.2.

- Files for Download (not shown on Figure 1): This contains file objects that contain data created during Telnet sessions that the user can download. These files are created using "fileout" commands to create files with various types of results as described in this document, and are stored on the host computer in a subfolder assigned to the user. This is useful for downloading output derived during Telnet sessions for users who do not have FTP authorization or access. This is not shown the user has not created such files, or if they all have been deleted.

SAPRC-22 MECHANISM GENERATION SYSTEM
Reactor for user1 [#520] (Reload) (Log out) (Restore defaults)
Lumping method = Explicit mechanism with no lumping [#22447] (type=3) (Change)

Create VOC or radical reactant

- Input the structure, SMILES string, or assigned name for a reactant [   ] [Create]
- Create from the list of SAPRC VOC model species by compound type or from complete list (sorted by atom nos.)

Get information on reactants in contents: (Delete all reactants)

- MEK: CH3-CH2-CO-CH3 [#21660] (reacted with OH) (delete)
  Reactions generated using Explicit mechanism with no lumping
  Explicit mechanism has 97 reactions and 68 species. Show (reactions and products). Send (reactions) or (products)
  Processed mechanism has 43 reactions and 45 species. Show (reactions). Send in (tab-separated format) or in (SAPRC RXN format)

- ORG-1391: HCO-CH(OH)-CH2-OH [#2643] (delete)

- VOC-1: CH3-CH(CHO)-CH(CH3)-ONO2 [#15527] (delete)

Reactor options

- Temperature (^{o}K)= [298] ; Presssure (atm)= [1.00] ; Atm PM ($\mu g/m^3$)= [50] ; O$_2$ in air [20.95%] [← Change]
- H$_2$O is absent (change)
- Minimum 1-step relative yield during complete reaction generation = [0.50%] [← Change]
- Change lumping method, which is currently Explicit mechanism with no lumping
- View or change standard environments. Currently 4 are used for product yields and 3 are used to generate mechanisms.
- Light source code is "STD640Z0". (Info or Change)
- SIMPOL.1 vapor pressure estimates [#7402] (Change)
- Restore reactor defaults

Obtain information

- Show Estimation Methods
- Show assignments in SAPRC-22 Mechanism Assignments (with 541 species)
- Show information related to the SAPRC-22 mechaniism
- Draft users manual (opens a PDF file in a separate window)

Advanced options

- User assignments are disabled (Enable or edit)
- The user mechanism option is not available when Explicit mechanism with no lumping is selcted.

Web user account actions

- Log out
- Change web login password (does not affect Telnet logins): [   ] [Submit]
- Telnet login enabled. Click here to get information on telnet access and commands.
- Completely delete the web and telnet accounts for user1 and associated data and log out.

- Give or edit user information (optional). Clear field to delete. [Submit]
  Name: [   ]
  Email: [   ]
  Other info: [   ]

- Please email Bill Carter at carter@cert.ucr.edu if you have any comments or questions about this system or notice errors in its operation or in its chemical mechanism assignments or estimates.

Figure 1.   Screen shot of the main menu for the web interface with default settings but after three reactants were created and one was reacted, and after optional user information provided. Arrows show lines with links that are discussed in the text.

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Administrative Actions Section. This section appears only when the primary MechGen user logs into the web system and is used to obtain information about the web system as it is running, or for debugging or testing purposes.

User Account Section. This section has links to log out, change user password, enable telnet logins, or completely delete this web and (if applicable) telnet account, or provide optional user information.

4.2. Reactant Information Pages

Reactant information pages are displayed when new reactants are created or existing reactions are selected using the main menu, and also when reaction products are selected in reaction results pages as discussed in Sections 4.3. The contents of these pages depend on whether the reactant is a stable compound or an intermediate, and whether the reactant has previously undergone a "react completely" operation as discussed in Section 4.4. Figure 2 shows an example of such a page for a stable reactant that has not been reacted, and Figure 3 showing an example for a radical. Note that Figure 3 is the same as the page that results following a single step reaction for an intermediate (see Section 4.3), since reactions of intermediates are generated automatically when such a reactant is created or selected. The contents of these pages are as follows:

- Header Section. The top section gives basic information about the reactant, including its structure in both MechGen and SMILES format, estimated heats of formation, vapor pressure and fractions in the particle phase for the conditions of this reactor, the type of compound, and lumping information if applicable.

- Reaction Section (stable compounds). The second section depends on whether the reactant is a stable compound or an intermediate. In the case of stable compounds (e.g., Figure 2), this section gives links to generate single step reactions or complete reactions of the various type that this reactant can undergo, which is reaction with OH, NO_3, and photolysis in the case of MEK, but can also include unimolecular reactions or reactions with O_3, O^3P, depending on the compound. If reactions of this compound have previously been used in deriving a SAPRC mechanism, the page also includes a "Get Reaction Assignments" link to obtain information about the assignments that were used in previous complete mechanism generations for this compound.

- Reaction Section (intermediates). In the case of reactant pages for intermediates (e.g., Figure 3), this section gives the results of a single step reaction of this radical, and a link to react this radical completely. This page is discussed further in Section 4.3.

- Groups and Heat of Formation Section. The third section lists the MechGen groups in the molecule and how they were used to estimate the heat of formation. Estimated heats of formation are used in estimates of rate constants for some types of reactions, as discussed by Carter et al (2024).

- Volatility Section (stable reactants only). The fourth section on pages for stable compounds includes information about how the vapor pressure is estimated, if this is possible for this type of compound and estimation method. The specific information given here depends on the estimation method employed. Vapor pressure estimates are not made for radicals, so Figure 3 lacks this section.

4.3. Generating Single Step Reactions and Reaction Results Pages

Generating single step reactions is the best means to obtain information about reactions of individual compounds or radicals, and obtaining documentation information about how the results were derived or assigned. It also provides a convenient means to browse a mechanism because the results page

MEK: Methyl Ethyl Ketone

CH_3-CH_2-CO-CH_3
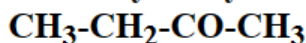
Smiles string: CCC(C)=O
Molecular weight of C_4H_8O is 72.11

No assigned heat of formation.
Estimated heat of formation is -57.13 kcal/mole.
Estimated vapor pressure at 298K is 1.61e-1 atm.
Fraction in particle phase (with PM=50 ug/m3): 1.1e-7.
VOC Type = Ketone

Generate Reactions

React with OH:	(Single step)	(Select to react completely ☐)
React with NO3:	(Single step)	(Select to react completely ☐)
React with HV:	(Single step)	(Select to react completely ☐)

React completely with all, or [React selected completely]

Get reaction assignments

Groups
CH_3-CH_2-CO-CH_3
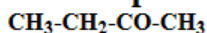
#	Group	Bonded To	Heat of Formation	
1	-CH_3	2	-10.04	C_(C)
2	-CH_2-	1,3	-5.26	C_(C)(CO)
3	-CO-CHx	2,4	-31.79	CO_(C)(C)
4	-CH_3	3	-10.04	C_(CO)

Notes on heat of formation estimate:
- Hf(-CH3[1])= -10.04 C_(C) (Holmes and Aubry (2011))
- Hf(-CH2-[2])= -5.26 C_(C)(CO) (Holmes and Aubry (2011))
- Hf(-CO-CHx)= -31.79 CO_(C)(C) (Holmes and Aubry (2011))
- Hf(-CH3[4])= -10.04 C_(CO) (Holmes and Aubry (2011))

Estimated vapor pressure at 298 deg K is 1.61e-1 atm.

```
Vapor pressures estimated using the SIMPOL1. method.
Estimated for T = 298.00 deg K

Prm Description                    N   Parm   Log(VP)
b0  zeroeth group (constant term)  1   1.842    1.84
b1  carbon number                  4  -0.425   -1.70
b9  ketone                         1  -0.936   -0.94

For CH3-CH2-CO-CH3 at T=298.0K:
Estimated vapor pressure (atm) = 10^-0.79 = 1.61e-1
```

Vapor pressures estimated using the SIMPOL1. method. See J. F. Pankow and W. E. Asher (2008): SIMPOL.1: a simple group contribution method for predicting vapor pressures and enthalpies of vaporization of multifunctional organic compounds, Atmos. Chem. Phys., 8, 2773-2796, www.atmos-chem-phys.net/8/2773/2008/

Figure 2.   Screen shot of the reactant menu for a newly created reactant with default reactor settings, using methyl ethyl ketone as an example. Arrows superimposed on the screen shot show links that are discussed in the text.

RAD-4
$CH_3\text{-}CO\text{-}CH_2\text{-}CH_2O.$

Radical type: A primary alkoxy radical center.
Smiles string: CC(=O)CC[O]
Molecular weight of $C_4H_7O_2$ is 87.10

No assigned heat of formation.
Estimated heat of formation is -40.96 kcal/mole.
Vapor pressure cannot be estimated: Cannot estimate VP for radicals
VOC Type = This is a -CH2O. radical.

React completely

Unimolecular or O2 reactions

CH3-CO-CH2-CH2O. -> CH3-CO-CH2. + HCHO **(5.5%)**

- Decomposition (T= 298K): k= 3.73e+3 s-1.
- k= A*e^-Ea/RT; A= 1.00e+14 s-1; Ea= Base Ea contributions + corrections = 14.22 kcal/mol. A factor estimate based on recommendations of Orlando et al (2003).
- Base Ea contribution for decompositions forming a HCHO carbonyl product = 0.00 kcal/mol. Assigned to be zero (not independent).
- Base Ea contributions for decompositions forming -CH2(.) radicals = 15.51 kcal/mol. Adjusted to fit activation energies derived for decompositions of acyclic saturated hydrocarbon alkoxy radicals.
- Correction for -CO- substituent on the radical formed = -1.29 kcal/mol. Adjusted to fit activation energies for decompositions of various types of acyclic, non-alkyl alkoxy radicals. All the parameters for radicals formed from alkanes were optimized first.
- Warning: This reaction is estimated to be endothermic by 6.85 kcal/mole. However, this is less than the estimated activation energy of 14.22 kcal/mole, so the estimated activation energy is not modified.

CH3-CO-CH2-CH2O. -> .CH2-CO-CH2-CH2-OH **(0.3%)**

- 1,4 H-shift isomerization: k(298K)= 2.25e+2 s-1
- A = 4.00e+10 x 3 = 1.20e+11 cm3-molec-1 s-1. The A factor per H atom used for 1,4-H shift isomerizations is 4.0e+10 sec-1, as recommended by Vereecken and Peeters (2009) for structure-reactivity estimation purposes.
- Base Ea for abstractions from -CH3[1] groups = 7.549 kcal/mol. Activation energies derived from fits of experimental 1,4-H-shift isomerization rate constants for 1-butoxy an 1-pentoxy radicals (Atkinson, 2007).
- Ring strain for 1,4 H-shift isomerizations = 0.000 kcal/mol. No ring strain correction is used for 1,4 H-shift isomerizations.
- Ea correction for substitution by -CO- on the group with the abstracted hydrogen is 0.030 kcal/mole. Correction to the activation energy due to this substituent derived from the correction factor for the effect of this substituent on rate constants for abstractions by OH from various organics.
- Ea correction when a -CO- is in the transition state ring next to a CH3 group with the shifted hydrogen is 4.314 kcal/mole. Adjusted to be consistent with the rate constant for CH3-CO-CH2-CH2O. -> .CH2-CO-CH2-CH2-OH as calculated by Vereecken and Peeters (2010).
- Overall Ea including and all corrections = 11.893 kcal.mole.

CH3-CO-CH2-CH2O. + O2 -> CH3-CO-CH2-CHO + HO2. **(94.2%)**

- O2 reaction (T= 298K, 20.9% O2): k*[O2]= 6.43e+4 s-1
- k= 2.38e-14 * exp(-0.38/RT) = 1.25e-14 cm3 molec-1 s-1; T= 298 K.
- Kinetic parameters are estimated to be approximately the same for reactions of O2 with all alkoxy radicals with -CH2O. groups. The 300K rate constant was derived by averaging the recommended values from measurements for n-propoxy and n-butoxy radicals, with the Arrhenius parameters estimated by assuming that the A factor is the same as that given for 1-propoxy.

Groups
$CH_3\text{-}CO\text{-}CH_2\text{-}CH_2O.$

#	Group	Bonded To	Heat of Formation	
1	-CH₃	2	-10.04	C_(CO)
2	-CO-R	1,3	-31.79	CO_(C)(C)
3	-CH₂-	2,4	-5.26	C_(C)(CO)
4	-CH₂O.	3	-7.89	C_(C)(O*)
			14.02	O*_(C)

Notes on heat of formation estimate:
- Hf(-CH3[1])= -10.04 C_(CO) (Holmes and Aubry (2011))
- Hf(-CO-R)= -31.79 CO_(C)(C) (Holmes and Aubry (2011))
- Hf(-CH2-[3])= -5.26 C_(C)(CO) (Holmes and Aubry (2011))
- Hf(-CH2O.)= -7.89 C_(C)(O*) (Assume no beta substituent effect on BDE's. Set to [C_(C)(O)])

Figure 3. Screen shot of the reactant page for a newly created radical reactant with default reactor settings, using one of the radicals formed in the initial reactions of OH with MEK as the example. Arrows show links that are discussed in the text.

that is produced shows all the organic products as hyperlinks that can be selected to determine how they react. Single step reactions are carried out automatically for intermediates after they are created or selected, while generating reactions for stable compounds requires selecting the appropriate link on the "Generate Reactions" section of the reactant information page that is displayed when the reactant is created or selected (e.g., see Figure 2).

Once a single step reaction is generated, an associated single step reaction results page displayed, which is similar to the reactant information page except that the "Generate Reaction" section is replaced with a section or sections containing the reaction results. These consist of lists of reactions, the fraction that the reactant undergoes the reaction compared to the other listed reactions at the temperature assigned to the reactor, the rate parameters, and documentation giving information about the estimation methods or mechanism assignments used. Examples of single step reaction output for intermediates are shown on Figure 3 and Figure 4, and an example of a selected type of single step reaction of a stable compound is shown on Figure 5.

Note that some types of intermediates are predicted to undergo various bimolecular as well as unimolecular reactions, and all these types of reactions are generated and included on the reaction results pages when these are reacted. Reactions with O_2 are treated as pseudo-unimolecular processes since the concentration of O_2 is assumed to be constant, so they are combined with the output of unimolecular reactions, as shown, for example, on Figure 3. Other types of bimolecular reactions are output in separate subsections of the reaction results section, such as shown, for example, on Figure 4. Note that the percentages for each reaction are relative to other reactions with the same reactants, not the total reaction of the radical, which depends on environmental conditions.

Single step output shows all the reactions that are generated for the particular radical, regardless of whether it is estimated to be negligible compared to the competing processes or not. Therefore, single step mechanism generation can provide information about minor processes or other processes that are not considered during full mechanism generation. However, it should be noted that MechGen will not generate reactions that are estimated never to be important under realistic environmental conditions, such as highly endothermic reactions, reactions involving highly strained transition states, or involving reactions at groups that are estimated to be unreactive for the type of reaction. For example, it will not generate hydrogen shift reactions requiring a 3- or 4-member ring transition state, or hydrogen shifts in peroxy radicals that contain only non-allylic -CH_3 or -CH_2- groups, so such reactions will not be included in single step reaction output for such radicals.

The products of single step reactions generated using the web system are deleted as soon as the results are displayed, so they do not appear among the list of reactants when the user returns to the main menu. However, all the organic radical or stable products of the generated reactants are displayed as hyperlinks in the reaction results pages, and the user can create or react these products by selecting the hyperlink for a product or intermediate of interest. Selecting a radical product will result in radical reaction pages such as shown on Figure 3 or Figure 4, while selecting a stable product will result in a reactant information page such as shown on Figure 2, which can be used to generate selected reactions for this product. In either case, products of these reactions can be selected or selected and reacted to see how they react and what products they form. This sequential single step reaction process can be useful for browsing selected portions of mechanisms.

Radical reactants are deleted once single-step reactions have been generated for them, so they do not appear among the list of previously created reactants in the main menu as discussed in section 4.1, and the information on the radical reactant information page will be lost once the user goes to another

Reactions with NO

CH3-CO-CH2-CH2OO. + NO -> CH3-CO-CH2-CH2O. + NO2 **(92.8%)**

- Alkoxy + NO2 formation (92.8%) (see below).
- k(NO,298K) = 9.13e-12 = 2.55e-12 *exp(0.76 kcal/RT) cm3 molec-1 s-1. The IUPAC (2018) recommendation for the rate constant for NO with ethyl peroxy is assumed for all total peroxy + NO rate constants.

CH3-CO-CH2-CH2OO. + NO -> CH3-CO-CH2-CH2-ONO2 **(7.2%)**

- Nitrate formation (7.2%)
- Nitrate yields for peroxy radicals are assumed to be approximately the same as for all non-acyl peroxy radicals with the same carbon number, except for those with O atom substitutents in the alpha or beta positions. The dependence on carbon number, temperature, and pressure is estimated using the Troe-like parameterization first used by Carter and Atkinson (1989) but updated for this work using slightly different parameterizations and nitrate yield data up to 2014. The parameters were adjusted to fit nitrate yields from secondary alkyl peroxy radicals, but they are also consistent with the more limited data for primary and tertiary alkyl radicals. This is used as the default for all peroxy radicals not containing O atoms in alpha or beta positions. Parameters are alpha (300K, 1atm) = 1.50e-2; beta=0.807; Yinf (298K)=5.207; M0=-2.05; Minf=-14.12; F=0.497; Fac=0.342; Method=ModTroe2. Nitrate yield calculated for 4.0 carbons, 298K, and 1.00 atm = 7.2%.

Reactions with NO2

CH3-CO-CH2-CH2OO. + NO2 -> CH3-CO-CH2-CH2-O-ONO2 **(100.0%)**

- RO2NO2 formation (100%)
- k(NO2) = 8.80e-12 cm3 molec-1 s-1. The IUPAC (2018) recommendation for the high pressure rate constant for ethyl peroxy + NO2 is used to estimate rate constants for higher peroxy radicals. Temperature and pressure dependence is ignored.

Reactions with NO3

CH3-CO-CH2-CH2OO. + NO3 -> CH3-CO-CH2-CH2O. + NO2 + O2 **(100.0%)**

- Alkoxy + O2 + NO2 formation.
- k(NO3) = 2.30e-12 cm3 molec-1 s-1. The IUPAC (2018) rate constant for the reaction of ethyl peroxy radicals with NO3 is assumed to apply to the reactions of NO3 with all peroxy radicals.

Reactions with HO2

CH3-CO-CH2-CH2OO. + HO2 -> CH3-CO-CH2-CH2-O-OH + O2 **(100.0%)**

- Hydroperoxy + O2 formation (100%)
- Product distribution is based on IUPAC (2017) recommendations for HO2 + CH3-CH2OO.
- Total k(HO2) = 1.24e-11 cm3 molec-1 s-1. for nC = 4. Estimated rate constants for reactions of HO2 with peroxy radicals not containing OH groups are derived from fits of rate constants for reactions of HO2 with various hydrocarbon-derived peroxy radicals as a function of carbon number. Rate constants tended to increase approximately linearly with carbon number until carbon number of around 7, above which the rate constants appear to be independent of carbon number. Rate constant derived for 298K, with temperature dependence ignored. k = min[2.03e-11, 2.48e-12 + (2.48e-12 x nC)].

Reactions with RO2

CH3-CO-CH2-CH2OO. + RO2. -> CH3-CO-CH2-CH2O. + O2 + RO. **(50.0%)**

- Reaction with generic peroxy radical forming O2 and two alkoxy radicals. (50%)

(Additional output truncated)

Figure 4.   Screen shot of the portion of the single step reaction results page from a peroxy radical formed in the reactions of MEK with OH, after the reaction of the alkyl radical formed in the first reaction on Figure 2.

Figure 5. Screen shot of the portion of the single step reaction results page from reacting methyl ethyl ketone with OH radicals.

page. Therefore, the user will need to create the radical again to see the reactions of radicals they might have reacted previously.

On the other hand, stable reactants are not deleted once reactions are generated for them, and they will appear on the reactant list when the main menu is displayed. Therefore, if a type of reaction is selected for this product, the user could go back to its reactant information page to generate another type of reaction, if desired. However, this is not the case for radical products or for stable products that are not selected. The reactant will need to be deleted manually using the main menu if it is no longer needed -- failure to do will result in unnecessary clutter on the main menu if many reactants after the system has been used for a while.

4.4. Full Mechanism Generation

The full mechanism generation process involves reacting all radicals formed in the initial reactions, then reacting the intermediates formed that need to be reacted, until only stable or species or basic species that do not need to be reacted remain. This can take a significant amount of time for larger molecules. For example, fully reacting α-pinene with OH, O₃, and NO₃ at the current MechGen site takes

over 7 minutes to complete if no one else is using the system. In order to avoid time-outs, the web system only permits full mechanism generation for compounds with 9 or fewer groups, which usually means 9 or fewer carbons (see Table 2). Even so, the full reaction could take several minutes before results are displayed, so the user needs to be patient with generating full reactions for C_{4+} compounds. It is necessary to use the Telnet interface to generate reactions for larger compounds, which can also be used to generate full reactions of multiple compounds in batch mode (see Section 12).

Full mechanism generations are initiated in the web interface by selecting the appropriate options or links in the "Generate Reactions" section of the reactant menu (e.g., Figure 2). As with single step reactions, it is necessary to choose the initial reactions of the VOC, though in this case more than one initial reaction can be chosen. If the user wants to fully react the reactant with all supported reactions, the "React completely with all" link should be selected. If a non-explicit lumping method (e.g., SAPRC-22 lumping) was previously selected (see Section 7), this link would be "React completely as needed for … lumping", in which case the reactions generated would be those that are included in the lumped mechanism for the lumped model species that would normally represent this compound under that lumping (see Section 7). If the user wants to generate full mechanisms with only one or a subset of the available initial reactions, the "(select to react completely)" boxes should be selected for the desired initial reactions, followed by activating the "React selected completely" control. Note that if the compound has more than 9 groups, the "Generate Reaction" section will not contain any active links to generate full reactions -- only single step reactions can be generated using the web system for such compounds.

Full mechanisms can also be generated for intermediates, with the results giving a portion of a mechanism with all the reactions of the intermediate and of the intermediates it forms. This includes bimolecular as well as unimolecular reactions as applicable. This is initiated using the "react completely" link at the top of the reactant page that appears after a intermediate reactant is created or selected, as shown for example on Figure 3. Note that in this case the intermediate reactant is not deleted from the reactor after the reaction is complete (unlike the case with single step reactions of intermediates), and it will appear in the list of the available reactants once the user returns to the main menu.

Once the full reaction generation is complete a page showing the generated reaction is displayed, together with an indication of relative product yields, information about reduced or condensed mechanisms depending on the lumping options employed (see Section 7), and links for downloading files with the reaction or product lists that can be imported into spreadsheets or used as inputs to software used for model simulations. An example of the portions of such a page is shown on Figure 6 and Figure 7. The top portion of Figure 6 gives a list of all the reactions in the explicit reactions in an abbreviated form, listing the reactions, rate constants at the default temperature, relative branching ratios, and the weighting factor used during full mechanism generation, which is an indication of the estimated approximate upper limit of the importance of that reaction in the overall process[1]. The bottom portion of Figure 6 lists all the predicted products and their estimated relative yields for the standard environmental conditions. Note that organic products that are not elementary species are hyperlinked, and selecting these links will result in creating that product in the reactor and displaying its reactant information page.

Additional output included in the reaction results page following a full mechanism generation gives giving the reduced or lumped mechanisms, which depend on the lumping method that has been chosen (see Section 7). Regardless of the lumping method, the output includes the "minimally reduced

---

[1] This is computed as the maximum of the estimated relative rates of the listed reaction relative to the total of initial reactions for the set of standard environmental conditions used for determining negligible processes during mechanism generation. Environmental conditions are discussed in Section 6.

Full set of reactions with OH

```
Full set of reactions with OH
Rxn    k       Fac  Weight  Reaction
1   3.15e-13   28%   28.4%  CH3-CH2-CH3 + OH -> CH3-CH2-CH2. + H2O
2   7.94e-13   72%   71.6%  CH3-CH2-CH3 + OH -> CH3-CH[.]-CH3 + H2O
3              100%  71.6%  CH3-CH[.]-CH3 + O2 -> CH3-CH[OO.]-CH3
4   8.75e-12   96%   68.7%  CH3-CH[OO.]-CH3 + NO -> CH3-CH[O.]-CH3 + NO2
5   3.70e-13    4%    2.9%  CH3-CH[OO.]-CH3 + NO -> CH3-CH(CH3)-ONO2
6   2.30e-12   100%  45.7%  CH3-CH[OO.]-CH3 + NO3 -> CH3-CH[O.]-CH3 + NO2 + O2
7   9.92e-12   100%  11.1%  CH3-CH[OO.]-CH3 + HO2 -> CH3-CH(CH3)-O-OH + O2
8   7.80e-15    50%   0.0%  CH3-CH[OO.]-CH3 + RO2 -> CH3-CH[O.]-CH3 + O2 + RO.
9   3.90e-15    25%   0.0%  CH3-CH[OO.]-CH3 + RO2 -> CH3-CH(CH3)-OH + O2 + RO-alpha-H
10  3.90e-15    25%   0.0%  CH3-CH[OO.]-CH3 + RO2 -> CH3-CO-CH3 + O2 + ROH
11  1.28e-11    80%  11.7%  CH3-CH[OO.]-CH3 + RCO3 -> CH3-CH[O.]-CH3 + O2 + RCO2.
12  3.20e-12    20%   2.9%  CH3-CH[OO.]-CH3 + RCO3 -> CH3-CO-CH3 + O2 + RCO-OH
13  3.63e+2      1%   1.3%  CH3-CH[O.]-CH3 -> CH3-CHO + CH3.
14  3.56e+4     99% 124.8%  CH3-CH[O.]-CH3 + O2 -> CH3-CO-CH3 + HO2.
15             100%  28.4%  CH3-CH2-CH2. + O2 -> CH3-CH2-CH2OO.
16  8.75e-12    96%  27.3%  CH3-CH2-CH2OO. + NO -> CH3-CH2-CH2O. + NO2
17  3.70e-13     4%   1.2%  CH3-CH2-CH2OO. + NO -> CH3-CH2-CH2-ONO2
18  2.30e-12   100%  18.1%  CH3-CH2-CH2OO. + NO3 -> CH3-CH2-CH2O. + NO2 + O2
```

<div align="center">(portions not shown)</div>

```
36  2.14e-14    35%   0.0%  CH3OO. + RO2 -> HCHO + O2 + ROH
37  1.22e-11    90%   0.3%  CH3OO. + RCO3 -> CH3[O.] + O2 + RCO2.
38  1.35e-12    10%   0.0%  CH3OO. + RCO3 -> HCHO + O2 + RCO-OH
39  9.91e+3    100%   2.3%  CH3[O.] + O2 -> HCHO + HO2.
 *  Photolysis rates calculated using the "STD640Z0" light source [Z=0 solar spectrum used for Carter (1994) reactivity
```

Mechanism Generation options: T=298; P=1.0; O2=0.2095; MinYld=0.0050; Lumptype=3; Environ: HighNOxenv, LowNOxEnv, NightEnv

Products from reacting under standard conditions

Explicit products formed when PROPANE reacts with OH under the following conditions:

```
Condition Description
Mid NOx   Mid NOx standard urban conditions (near EBIR)
High NOx  High NOx urban conditions (near MIR)
Low NOx   Low NOx downwind conditions (NOx = MOIR NOx/10)
Night     Nighttime conditions for multi-day, mid-NOx scenario
```

Products listed in descending order of maximum yield

Mid NOx	High NOx	Low NOx	Night	Explicit product or reacted
100.00%	100.00%	100.01%	100.01%	H2O
92.07%	96.63%	79.10%	64.14%	NO2
88.10%	95.94%	65.00%	64.51%	HO2.
65.33%	67.98%	57.50%	59.78%	CH3-CO-CH3
26.07%	27.13%	22.94%	23.84%	CH3-CH2-CHO
2.77%	2.91%	2.38%	-	CH3-CH(CH3)-ONO2
4.70%	-	18.11%	100.44%	O2
2.80%	-	11.10%	11.12%	CH3-CH(CH3)-O-OH
1.10%	1.15%	0.95%	-	CH3-CH2-CH2-ONO2
0.78%	0.84%	0.63%	0.60%	HCHO
0.66%	0.69%	0.57%	0.58%	CH3-CHO
1.11%	-	4.40%	4.41%	CH3-CH2-CH2-O-OH
0.13%	0.14%	0.12%	0.09%	LostRads
-	-	0.05%	0.07%	CH3-O-OH
0.01%	-	-	0.00%	Total < 0.05%

Minimally reduced processed mechanism

<div align="center">(see Figure 7)</div>

Figure 6.   Portions of the web page displayed following a full reaction of propane with OH showing the explicit mechanism generated with the default (explicit) lumping approach, showing explicit mechanism and overall product yields.

```
                    Minimally reduced processed mechanism

.ACT
PROPANE    ! CH3-CH2-CH3
ACETALD    ! CH3-CHO
ACETONE    ! CH3-CO-CH3
IC3-ONO2   ! CH3-CH(CH3)-ONO2
ORG-0125   ! CH3-CH(CH3)-O-OH
I-C3-OH    ! CH3-CH(CH3)-OH
VOC-0001   ! LostRads
PROPALD    ! CH3-CH2-CHO
ORG-0050   ! CH3-CH2-CH2-ONO2
ORG-0129   ! CH3-CH2-CH2-O-OH
N-C3-OH    ! CH3-CH2-CH2-OH
MEOOH      ! CH3-O-OH


.STS
RAD-1      ! CH3-CH[OO.]-CH3
RAD-2      ! CH3-CH2-CH2OO.
RAD-3      ! CH3OO.


.RXN
R) 2.00e-12 0.342  1.76  ;PROPANE + OH = #.28 RAD-2 + #.72 RAD-1 + H2O
R) 9.13e-12              ;RAD-1 + NO = #.01 ACETALD + #.01 RAD-3 + #.95 ACETONE + #.04 IC3-ONO2 + #.95 HO2 + #.96 NO2
R) 2.30e-12              ;RAD-1 + NO3 = #.01 ACETALD + #.01 RAD-3 + #.99 ACETONE + O2 + #.99 HO2 + NO2
R) 9.92e-12              ;RAD-1 + HO2 = ORG-0125 + O2
R) 1.56e-14              ;RAD-1 + RO2 = #.01 ACETALD + #.01 RAD-3 + #.74 ACETONE + #.25 I-C3-OH + O2 + #.49 HO2
R) 1.60e-11              ;RAD-1 + RCO3 = #.01 ACETALD + #.01 RAD-3 + #.99 ACETONE + O2 + #.79 HO2
R) 9.13e-12              ;RAD-2 + NO = #.95 PROPALD + #.04 ORG-0050 + #.96 HO2 + #.96 NO2
R) 2.30e-12              ;RAD-2 + NO3 = #.01 VOC-0001 + #.99 PROPALD + O2 + HO2 + NO2 + #.01 HCHO
R) 9.92e-12              ;RAD-2 + HO2 = ORG-0129 + O2
R) 2.90e-14              ;RAD-2 + RO2 = #.75 PROPALD + #.25 N-C3-OH + O2 + #.5 HO2
R) 1.60e-11              ;RAD-2 + RCO3 = PROPALD + O2 + #.8 HO2
R) 2.30e-12 -0.715 0.00  ;RAD-3 + NO = HO2 + NO2 + HCHO
R) 1.20e-12              ;RAD-3 + NO3 = O2 + HO2 + NO2 + HCHO
R) 5.21e-12              ;RAD-3 + HO2 = #.9 MEOOH + O2 + #.1 H2O + #.1 HCHO
R) 6.10e-14              ;RAD-3 + RO2 = O2 + #.3 HO2 + #.65 HCHO + #.35 MEOH
R) 1.35e-11              ;RAD-3 + RCO3 = O2 + #.9 HO2 + HCHO
```

Figure 7.   Portions of the web page displayed following a full reaction of propane with OH showing the explicit mechanism generated with the default (explicit) lumping approach, showing the minimally reduced processed mechanism.

processed mechanism" that is derived from the explicit mechanism by removing intermediates with only unimolecular or O_2 reactions by replacing them with the products they form, and by combining parallel reactions into a single reaction with product yields derived from ratios of rate constants. This should give the same predictions as the explicit mechanism when the O_2 concentration and temperature are the same as when the explicit mechanism was generated. This is portion of the output shown on Figure 7 for the propane example.

If a non-explicit lumping method is chosen, then additional output will include the lumped mechanism that was derived from the processed mechanism. This is discussed in Section 7.

The top part of the page shown on Figure 6 has links for downloading the list of products and reactants in the explicit, minimally processed, and (if applicable) lumped mechanisms in various formats. The download options include the following:

Explicit mechanism (Reactions): Reactions, rate constant parameters, and branching ratios in tab-separated format that can be loaded into spreadsheets. Columns in this spreadsheet include reaction number, A, Ea, and B parameters for calculating temperature dependences where k(T)=A*exp(-

Ea/RT)*(T/300)^B (with k and A in units of sec^{-1} or cm^3 molec^{-1} sec^{-1}, and Ea in units of kcal/mole, and R is the gas constant), the weighting factor used during mechanism generation, the rate constant at the default temperature, and the reaction itself. For photolysis reactions, the name of the SAPRC-22 photolysis file is given in the column used for Ea and the overall quantum yield is in the column used for B, and the rate constant is shown for overhead sunlight for standard reaction conditions.

Explicit mechanism (Products): List of products and their estimated yields for the standard environmental conditions. This is in fixed-width text format such as shown, for example, on the bottom part of Figure 6, but without the hyperlinks.

Processed mechanism: reactions in (tab-separated format): List of products and intermediates (steady state species) in the minimally reduced processed mechanism (see Section 7), followed by lists of reactions and rate constants in tab-separated format. The product and intermediate listings include columns with the product or intermediate number, the name used for the product or intermediate in the reaction listings (either a standard SAPRC name or system generated), and the structure. The reaction section includes columns with the reaction number, A, Ea, and B parameters and rate constant at the default temperature (or photolysis file names and quantum yields and photolysis rates for overhead sunlight for photolysis reactions), and the reactions.

Processed mechanism in (SAPRC .RXN format): This gives the processed mechanism in the format that can be used with SAPRC modeling software (Carter, 2020a, 2023b). This is similar to the output is shown on Figure 7, except that lines longer than 80 characters are continued on the following line. Note that selecting the "show (reactions)" link will result in this being shown as a web page, but does not download it.

If a non-explicit (e.g., SAPRC-22) lumping is selected, there will also be links for outputting the lumped mechanism in either tab-separated or SAPRC .RXN format. These outputs are discussed in Section 7. Note that selecting the "(show)" link will show the SAPRC .RXN output as a web page.

The full reaction results data that are used to produce these outputs are saved as properties of the reactant object, and are available for output at a later time until the reactant is deleted from the reactor. Note that these results do not include the documentation information that is produced during the single-step reaction process because of the large numbers of reactions that are usually generated. The reactant will be included in the reactant listing portion of the main menu with a "(Reacted with …)" link that, if selected, will result in re-displaying the reactant results page that results from full reaction generation. If 5 or fewer reactants are in the reactor, there will also be links to download or show selected data without having to go through the reactant results page.

4.5. Modifying Mechanism Generation Options

The options that affect mechanism generation and results processing in the reactor that the user can modify are listed and summarized on Table 5, which also gives the defaults for these options. These can be modified using links or input boxes in the "Reactor options" or "Advanced Options" sections of the main menu. This is done either by selecting links that give menus of available options that users can select, or by modifying input boxes containing the current value of the option, and selecting the "change" control, depending on the type of option. Selecting "Restore reactor defaults" results in the reactor options reverting to the default values as they existed when the user logged in the first time. This also deletes any user assignments or user mechanisms that may have been created, as discussed in Sections 7.3 and 8.2. Note that changing the lumping method or creating or deleting user mechanisms will delete any previous full reaction results that may have been generated.

Table 5.   List of reactor options that can be modified by MechGen users

Option	Default	Description
Temperature	298 K	Default temperature in K
Pressure	1.0 atm	Default pressure in atmospheres
O_2 in air	20.95%	Mole fraction of O_2 in the reaction environment
H_2O	Present	Used to determine if some intermediates (e.g., Criegee intermediates) react with water
Atm PM	50 $\mu g/m^3$	Atmospheric particle levels used to estimate fractions of reactants in the particle phase if their vapor pressures can be estimated
Minimum 1-step yield	0.5%	The minimum yield for a competing process in a single step reaction for it to be considered non-negligible during full mechanism generations
Lumping method	Explicit	Lumping method used when generating full reactions and processing results. Currently available options are "Explicit" or SAPRC-11 or versions of SAPRC-22. See Section 7.
Environmental Conditions	See Section 6	This shows the standard environments used for deriving estimated product yields and allows the user to control whether they are used during mechanism generation to determine which reactions can be treated as negligible. See Section 6.
Vapor pressure estimator	SIMPOL.1	Method used to estimate the vapor pressure that is displayed on the reactant information page for stable compounds. Available options are SIMPOL.1 (Pankow and Asher, 2008) or EVAPORATION (Compernolle et al. 2011). SIMPOL.1 is the default because it can be used with a larger variety of compounds,
	Advanced options	
User mechanisms	No user mechanisms	Users who select a SAPRC lumping method can optionally add versions of the standard SAPRC-22 mechanism with selected reactant and product compounds being represented explicitly. This is discussed in Section 7.
Mechanism Assignments	No user assignments	This option is selected if the user wants to use user assignments that the user can create to add to or replace the standard used by MechGen (Carter et al, 2024). This is discussed in Section 8.

4.6. Obtaining Information

The "Obtain Information" section of the main page includes links to obtain various types of information regarding MechGen and the SAPRC-22 mechanism, including a PDF of this users manual. This includes information regarding estimation methods and assignments and information related to the SAPRC-22 mechanism and how MechGen was used to derive it. These are discussed further below. These outputs are only available using the web interface.

4.6.1. Estimation Methods and Mechanism Assignments

Estimation Methods. Selecting the "Show Estimation Methods" link in the "Obtain Information" section will produce a page containing multiple links that the user can select to obtain information about different types of estimates or SARs, including estimating rate constants or mechanisms for different types of compounds or radicals. This page is shown on Figure 8. Clicking on any of these links will result in pages giving detailed information about how various types of reactions and rate constants are estimated. This information is taken from the documentation of the chemical basis of MechGen as given by Carter et al (2024). Note that this will be updated as MechGen is updated, though currently this is the same as documented by Carter et al (2024). Note that output of estimation method documentation is only available using the web interface.

Mechanism Assignments. Selecting the link to show assignments would normally result in the display shown in Figure 9, which contains links for viewing all assignments or assignments for compounds or types of reactions. It also includes links for downloading the assignments in various formats. This link and the resulting display is different if the user selected to use its own user assignments, which is discussed separately in Section 8. Figure 10 shows the page that results when the user requests assignments be shown for methyl ethyl ketone (MEK), either by requesting assignments for it using the assignments menu shown on Figure 9, or by selecting the "Get reaction assignments" link on the reactant menu. Note that this includes assignments not only for reactions of MEK itself, but also assignments for reactions of intermediates formed when it reacts completely. The latter is shown only if the reactant was reacted previously by some user or (more likely) in the process of deriving the SAPRC-22 mechanism (Carter, 2023a).

The type of output shown on Figure 8 through Figure 10 is also only available using the web interface. However, commands are available to telnet users to list assignments for selected or all reactants, but not assignments used for intermediates formed when generating their full mechanisms.

4.6.2. SAPRC-22 Mechanism

Selecting the "Show information related to the SAPRC-22 mechanism" link in the "Obtain Information" will produce the page shown on Figure 11. The online version of MechGen includes links to show mechanisms for the many compounds whose mechanisms were generated in the process of deriving SAPRC-22, compositions of mixtures for used for various purposes and input used to derive the SAPRC-22 lumping methods, and lists of SAPRC-22 model species[2]. The derivation of lumping methods and the input defining these mechanisms are discussed in Section 11, and the process of preparing mechanisms for lumped model species and deriving complete lumped mechanisms is discussed in Section 12. Additional information includes listings of the mechanism and a link to the SAPRC-22 web page where the mechanism and its documentation can be downloaded.

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[2] The link to show mechanisms for the compounds and mixture compositions used to derive SAPRC-11 are not included in user-installed version of MechGen because of the amount of data required.

Estimation methods used for mechanism generation (version SAPRC-22)

Estimation of rate constants for H-abstraction reactions from organics

- Abstraction by OH
- Abstraction by NO3
- Abstraction by Cl

Estimation of rate constants for additions to organics

- OH addition
- O3 addition
- NO3 addition
- O3P addition
- Cl addition

Discussion of assignments for photolysis reactions

- Aldehydes
- Ketones
- Nitrates
- Peroxynitrates
- Hydroperoxides
- Peroxides

Reactions used for carbon-centered (e.g. alkyl) radicals

- Reactions of stabilized alkyl radicals
- Reactions excited alkyl radicals
- Reactions of OH + aromatic adducts

Estimation of rate constants and other assignments for alkoxy radical reactions

- Reactions with O2
- Beta-scission decompositions
- H-elimination decomposition
- H-shift isomerizations
- Ester and nitrate rearrangements

Estimation of unimolecular reactions of peroxy and acyl peroxy radicals

- Hydrogen shift isomerization (autooxidation) reactions
- Internal addition to conjugated double bonds forming cyclic peroxides or epoxides

Estimation of bimolecular rate constants and mechanisms for peroxy and acyl peroxy radicals

- Reactions with NO
- Estimation of nitrate yields in the reactions with NO
- Reactions with NO2
- Reactions with NO3
- Reactions with HO2
- Reactions with other peroxy or acyl peroxy radicals

Mechanisms assumed for other types of reactive intermediates

- Reactions of Criegee intermediates (formed in O3 + alkene and O2 + carbene reactions)
- Reactions of amine oxide intermediates formed in Amine + O3 Reactions
- Internal addition of peroxy radicals to double bonds (e.g., from OH-aromatic-O2 adducts)

Figure 8.   Page showing links to get information about various estimation methods used when generating mechanisms when no assignment data are available.

Figure 9.   Display created when user selects the link to view or download information on the default assignments used when generating mechanisms.

Mechanism assignments for MEK
CH3-CH2-CO-CH3

Rate Consant Assignments

- k(OH) = k(298)=1.05e-12 = 5.42e-14*exp(1.767/RT)*(T/300)^3.57 [From the Compilation of McGillen et al (2020), as updated to version 2.1.0, June 23, 2021. https://doi.org/10.25326/mh4q-y215]
- k(Cl) = k(298)=3.99e-11 = 3.05e-11*exp(0.159/RT) [From the compilation of McGillen et al (2020), as updated to version 2.1.0, June 23, 2021. https://doi.org/10.25326/mh4q-y215]

Reactions of intermediate radical CH3-CO-CH[O.]-CH3

- CH3-CO-CH[O.]-CH3 -> CH3-CO-CHO + CH3.
  k(298)=9.39e+0 = 5.00e+13*exp(-17.353/RT) [Derived from Eb(DFT) values tabulated on Table 2 of Vereecken and Peeters (2009), calculated using the B3LYP/6-31G(d,p) level of theory. These are used to estimate activation energies by using a linear fit between the activation energies derived from the data tabulated by Orlando et al (2003) assuming an A factor of 5e13 sec-1 x the reaction degeneracy recommended by Atkinson (2007), as discussed in the text. The 298K rate constraint is derived from these estimated activation energies and A factors.]
- CH3-CO-CH[O.]-CH3 -> CH3-CHO + CH3-CO.
  k(298)=2.25e+8 = 5.00e+13*exp(-7.290/RT) [Derived from Eb(DFT) values tabulated on Table 2 of Vereecken and Peeters (2009), calculated using the B3LYP/6-31G(d,p) level of theory. These are used to estimate activation energies by using a linear fit between the activation energies derived from the data tabulated by Orlando et al (2003) assuming an A factor of 5e13 sec-1 x the reaction degeneracy recommended by Atkinson (2007), as discussed in the text. The 298K rate constraint is derived from these estimated activation energies and A factors.]

Reactions of intermediate radical CH3-CH2O.

(additional output not shown)

Figure 10.   Screenshot of page showing mechanism assignments used when generating full mechanisms for the reactions of methyl ethyl ketone.

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[a] Output displayed using online MechGen

Information used by MechGen to derive the SAPRC-22 Mechanism

Compounds, model species, and lumping input used:

- Show mechanisms generated for the 359 compounds used to derive SAPRC-22
- Show mixtures of compounds used to derive mechanisms for lumped model species in SAPRC-22
- List explicitly represented compounds in SAPRC-22
- List model species used in the SAPRC-22 mechanism (with links to show their reactions)
- Show "input-rules" input used to create Standard SAPRC-22 lumping

---

[b] Output displayed using user-installed MechGen (see Section 9)

Information used by MechGen to derive the SAPRC-22 Mechanism

Model species and lumping input used:

- List explicitly represented compounds in SAPRC-22
- List model species used in the SAPRC-22 mechanism (with links to show their reactions)
- Show "input-rules" input used to create Standard SAPRC-22 lumping

---

[c] Output displayed below the above with both online and user-installed MechGen

Mixture databases used (select to see compositions or lists):

- ARBmix-22 Composition of mixture used to derive lumped model species repesenting primary VOC emissions from anthropogenic sources. Obtained from the California Air Resources Board staff in 2022
- ARBbio-22 Composition of mixture used to derive lumped model species repesenting primary VOC emissions from biogenic sources. Obtained from the California Air Resources Board staff in 2022.
- ARBemit-22 Composition of mixture used to derive weightings for formation of products from reactions of biogenic and anthropogenic emissions under representative environmental conditions. Mixture consists of equal mass fractions of ARBmix-22 and ARBbio-22.
- BaseMix List of explicitly represented compounds in the standard mechanism plus those compounds represented explicitly during evaluations against chamber data
- NoUse Compounds not used when deriving mechanisms of mixtures because they were not considered representative of other compounds represented using the same model species or because of problems in generating their mechanisms.

SAPRC-22 mechanism listings

- Base reactions (excluding VOC model species) (Send as file)
- Complete mechanism for airshed models (Send as file)

Open the SAPRC-22 web page with links to download the mechanism and documentation. (Opens in a new window.)

Figure 11. Screenshot of page giving links to information related to the SAPRC-22 mechanisms. Note that the "Show mechanisms generated" and the "Show mixtures of compounds" links appear on the online version of MechGen but not in user-installed versions as discussed in Section 9 because of the amount of data required.

5.   BASIC OPERATIONS FOR TELNET USERS

The Telnet or terminal interface is necessary when working with larger reactants or carrying out the more advanced options available only to authorized users. However, it is not as straightforward to use as the web interface and is not as useful for browsing mechanisms or obtaining information about estimates or assignments. General users can obtain Telnet access to MechGen using the web system as discussed in Sections 2.1 and 2.2. The primary and administrative MechGen users have telnet access when MechGen is first installed, though their login passwords will have to be provided when MechGen is installed, as discussed in Section 9.2.3.

Once telnet access is enabled, a telnet program can be used to connect to MechGen using a terminal interface. Once you are connected you will see an opening login screen with a brief message. Give the command "connect *username userpass*", where *username* is the telnet user's name and *userpass* is the password you provided when creating your web account. If the login is accepted, you will then enter the virtual "reactor" that has been created for you to generate mechanisms or modify options. Give the command "@quit" to end your telnet session, or just close telnet. Note that the telnet password does not have to be the same as your web password, and changing the password using the main menu of the web interface will only affect the web password. The telnet password can be changed using the @password command during your telnet session. This will not change your web password.

Terminal input and output when the user first connects to the MechGen interface is shown on Figure 12. Figure 12a shows the message displayed when the user first connects to the web system, section Figure 12b shows an example of a user giving its name and password and the initial connect message, and Figure 12c shows the environmental conditions and reactants contained in the reactor. The output shown on Figure 12c can also be obtained at any time by giving a "look" command when the user is in the reactor. Note that the user and reactor and its contents are exactly the same as shown on Figure 1, which shows the display if the same user were connected using the web system.

Once logged in, users can carry out a number of actions related to text-based virtual reality experiences, including interacting with other users who are logged into the multi-user system at the same time. Because MechGen is not intended for this purpose, the discussion in this document of use of the telnet interface is restricted to describing operations and actions that are needed to work with MechGen. However, the host MOO system has a help feature, and users can give "help" commands to get information on selected topics, with just "help" giving a list of help topics, and "help newbie" giving basic help to new users. Unfortunately, there are not yet "help" topics related to MechGen, so this feature is not particularly useful for MechGen users.

The reactor that the user entered when first logged in is the only virtual location in the MOO where non-authorized users can carry out the MechGen operations discussed in this document, with each MechGen user having their own separate reactors so they can carry out their operations independently. This is because it is not possible for more than one reaction generation operation to be carried out at the same time in the same reactor. Note that the user's reactor using the telnet interface is the same as used with the web interface. MechGen users are not able to enter reactors created for other users. Authorized

```
   HTTP/1.0 200
   X-moo: This is the SAPRC atmospheric chemical mechanism generation system.    (a)
    For more information, contact Bill Carter at carter@cert.ucr.edu,
    or go to http:\\mechgen.cert.ucr.edu to access the web interface.
    Guest logins allowed but a user account is needed to use the system.
    You can obtain a user account using the web interface.
```

```
connect User1 user1pass
   *** Connected ***                                                            (b)
```

```
   Interior of User1's web chamber (#5940)
   This is a reaction chamber for generating mechanisms for chemical reactions in
    the atmosphere.

   Options for user1's web chamber:
     Lumping Procedure (lumping) .... Explicit mechanism with no lumping
     Minimum 1-step yield (minyld) .. 0.005
     Vapor pressure estimates (VP) .. SIMPOL.1 vapor pressure estimates

   Environmental conditions for user1's web chamber
     Temperature    = 298 deg K (T)
     Pressure       = 1.00 atmospheres (P)                                      (c)
     O2 Content     = 21%.  (O2)
     Atmospheric PM = 50.0 ug/m3  (PM)
     H2O            = absent  (H2O)
     Yield Environs = Mid NOx
     M.Gen Environs = High NOx, Low NOx, and Night
     Light source   = STD640Z0 (light)

   Stable reactants:
     MEK: CH3-CH2-CO-CH3 (reacted with OH) [#19814]
     ORG-1391: HCO-CH(OH)-CH2-OH [#9828]
     VOC-1: CH3-CH2-Br [#1682]
```

Figure 12.   Input and output shown when a user connects to the MechGen Telnet interface. (a) Connect message; (b) user login, giving name and password; (c) display of user's reactor, showing options and contents. Reactor shown is the same as that shown on Figure 1.

users can create additional reactors where they can assign different options and carry out mechanism generation operations separately.

Terminal commands that MechGen users can give when using the telnet are listed and briefly described on Table 6, with Table 7 describing the types of information that can be output. Most correspond directly to operations or links in the web system, but some operations available to telnet users are not available using the web interface. These are only a subset of commands available to Telnet users, and do not include additional commands involving lumping, creating user assignments, or available for mechanism development for advanced users as discussed in Sections 7, 8, and 9, respectively. It also does not include general MOO commands available to any MOO user, for which information can be obtained using the MOO's "help" command. The latter are not generally needed for MechGen users, except for some administrative commands needed to maintain the system (see Section 9).

Unlike the web interface, the telnet interface does not automatically delete radical reactants and products formed following single step reaction commands, so these can build up in the reactor if many single step reaction operations are carried out. As indicated on Table 6, there are several commands that can be used to manage reactants in the reactor. The "look" command includes a listing of the reactants in

Table 6.   Summary of commands that can be given by Telnet users to carry out basic MechGen operations discussed in this document.

Command [a]	Function
General reactor maintenance	
Look	Generate the display summarizing the environmental conditions and listing reactants in the reactor as shown on Figure 12c.
Options	Outputs summary of current reactor options.
Reactants (or "r")	List the reactants in the reactor
Delete-reactants	Delete all reactants in the reactor
Clean (or "c")	Delete reactants that were created by a single step reaction process and not subsequently reacted. Also clears (deletes temporary group properties) in remaining reactants with such properties.
Reset-options	Resets reactor options to defaults, including deleting user mechanisms and user assignments if they were created.
Delete <object>	Deletes a reactant, user-created environments, or other user-created objects such as discussed in sections below.
General reactant maintenance	
Delete <reactant>	Deletes an existing reactant in the reactor, where <reactant> is the name or structure of a previously created reactant in the reactor.
Erase <reactant>	Deletes results of a previous fully react operation for the reactant. Does not clear temporary group properties.
Look <reactant>	Displays the name and structure of a previously created reactant in the reactor and indicates whether and how it has been fully reacted. The groups within the reactant, indicating what other groups they are bonded to and related information, are also listed in the output.
Clear <reactant>	Removes the temporary group properties (see Table 1) on newly created or product reactants to save system resources. Does not delete results of previous complete reactions.
Expand <reactant>	Re-creates temporary group properties on reactants that have been cleared. This is done automatically when reacting reactants, but is useful if it is desired to obtain information about its groups using the "look <reactant>" command.
Reactant creation (Section 5.1)	
Build [<name> as] <structure>	Create a reactant and optionally give it a name. This could be a stable compound or radical. This has no effect if the reactant already exists in the reactor.
DMS <standard SAPRC name> Build <standard SAPRC name>	Creates a VOC reactant that has been assigned a standard SAPRC detailed model species (DMS) name.

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Table 6 (continued)

Command [a]	Function

Reaction generation (Sections 5.2 and 5.3)

React <reactant> [with <what>]	Carry out a single step reaction for a reactant, where <reactant> can be either the name of a previously created reactant, or a standard SAPRC VOC name or a valid structure designation that is used to create a new reactant, and <what> refers to how it reacts (e.g., OH, O_3, "uni", etc), which must be specified when reacting a stable compound, but not radicals. See Section 5.2.
React1 <reactant>	Similar to "React" but only generates a single step unimolecular reaction if the reactant reacts this way. Only applicable to reactants that refer to peroxy radicals.
Fullreact <reactant> [with <what>] (For stable compounds) Fullreact <radical reactant>	Carry out a complete reaction of the reactant, where <reactant> and <what> have the same meaning as in the "React" command, above, except that more than one type of reaction can be specified, and if "with <what>" is not given, then all supported reactions of the stable compounds are carried out as needed for this type of compound and lumping method. Note that <what> can refer to more than one type of reaction, in which case the types are separated by a space. See Section 5.3.

Obtaining information or results

Read <item> on <reactant>	Outputs results of fullreact operations on a reactant to the terminal. The types of results that can be output are listed and briefly described on Table 7.
Read <item> on usermech Read userasns	Used to obtain information about a user mechanism (usermech) as discussed in section 7.3 and 7.3.2, or about user assignments (userasns), as discussed in Section 8.
fileout <item> on <reactant> fileout <item> on usermech fileout userasns	Same as "read" except that output goes to a file on the host computer in a folder for the user, whose contents can be read by those with access to the host computer, or downloaded as a file using "Files for download" section of the main menu in the web system. Fileout (and @ftpout, described below) are more useful than "read" if many lines of output are produced.
@ftpout <item> on <reactant> @ftpout <item> on usermech @ftpout userasns	Same as "read" or "fileout", above, except that the output goes to the MechGen FTP site rather than the terminal, and is available only to authorized users where FTP access has been set up.

Modifying reactor options

| Option <item> is <value> | Used to change reactor options, where <item> indicates which option and <value> refers the new option to be used, which could be a number or a MOO object. These are listed on Table 8. |
| Option <item> is default | Sets select option to reactor defaults, as given on Table 8. If <item>="all", then all options listed there are set to their defaults. |

Table 6 (continued)

Command [a]	Function
Reset-options Option all is default	Restores all options to the defaults, and deletes any user mechanisms or assignments that may have been created.
Stdenvts [options]	Displays information or provides options to modify standard environments used for deriving product yields or to determine negligible reactions during mechanism generation. See Section 6 for a description of the available standard environments and available options.
Lumping [<lumpname>]	Changes the lumping to the named lumping method, if available. If <lumpname> is not given, shows the current lumping method and lists the available lumping methods, offering users the option to select a different method. See Sections 7 and 11.
Usermech [option]	Used to manage user mechanisms, which provide a means for advanced users to represent additional compounds explicitly when working with the standard SAPRC-22 mechanism. See Section 7.3.
Userasns [option]	Provides a means for advanced users to create their own mechanism assignments to be used in addition to or to supercede the MechGen assignments. Additional commands are used to create or delete the assignments. See Section 8.
<center>Basic user commands</center>	
@quit	Ends the telnet session. The reactor options and contents will be the same when you log in again, unless they were subsequently modified using the web interface.
@password [<old> <new>]	Use to change your telnet login password. Does not affect the web password. You will be prompted to give the old then new password if they are not on the command line.
Home	If you find you are getting "I don't understand that" output when giving MechGen commands, your player object somehow exited your reactor. This command moves this back where it belongs.
Help	Gives general information about MOO commands. Currently it is of limited utility for MechGen commands, but this may be improved in future versions.
Do-commands <command 1> <command 2> … .	Provides a means to have MechGen execute a series of commands in batch mode. Giving this command prompts the user to enter multiple commands, terminated by a "." line. Following this the commands will be executed sequentially.
Delete-accounts	Deletes the account, reactor, and reactor contents for this user. The user is prompted to verify this deletion, and is automatically logged out and is unable to log in again after this is completed. The user can use the web system to create a new account if desired.

[a] Commands and are not case sensitive. Items specified by <item> are variable and depend on the context, and are also not case sensitive. Items inside brackets ([item]) are optional.

Table 7.   Description of items terms that can be used to output selected results of fullreact processes using the read, @ftpout or fileout commands.

Item code	Description	Web system analogue
Reactions	The explicit mechanism in fixed-width format	Middle section of Figure 6
Explmech	The explicit mechanism in tab-separated format that can be imported into spreadsheets, containing additional rate constant parameters.	Select explicit "(reactions)" in the reaction results page.
Products	The products formed in the explicit mechanism in fix-width format as shown on the bottom section of Figure 6	Bottom section of Figure 6
Processed	The minimally reduced processed mechanism in tab-separated format, listing species and corresponding structures, then reactions and kinetic parameters.	Select option to output processed mechanism "(in tab-separated format)" in the reaction results page
Procrxns	The minimally processed mechanism in the .RXN format that can be used to implement mechanisms using SAPRC software (Carter, 2020a, 2023a).	Select option to output processed mechanism "(SAPRC .RXN format)" in the reaction results page.

The following are available if a non-explicit (e.g., SAPRC) lumping method used when the mechanism was generated (if explicit lumping is selected, output same as "processed" and "procrxns", respectively)

Tabrxns	The reactions in lumped mechanism in tab-separated format, listing reactions and kinetic parameters.	Select option to output the lumped mechanism in "(tab-separated format)" in the reaction results page
Rxns	The minimally processed mechanism in the .RXN format that can be used to implement mechanisms using SAPRC software (Carter, 2020a, 2023a).	Select option to output the lumped mechanism "(SAPRC .RXN format)" in the reaction results page.

the reactor, and the "reactants" (or "r") command outputs only the reactant list; the "clean" (or "c") command deletes products formed in single-step reactions that have not reacted; the "zap <name>" command deletes a named reactant, and the "zap-reactants" deletes all the reactants in the reactor.

In the figures in the following sections where examples of inputs and outputs to the terminal using the telnet interface are shown, all commands given by the user are underlined, while output produced by the system are indented slightly. When command are shown in the text, options that can vary in the commands, such as names or structures of reactants, are given using the <option> notation, e.g., the input command "Build <structure> is the same as "Build CH3-CH3" if "CH3-CH3" is the structure. Optional input is indicated using brackets, e.g., "React <name or structure> [with <reaction>]", where the "with <reaction>" is optional. Triple dots "…" are used to indicate that additional optional input may be provided but is not required. Note that most user input is not case sensitive, but lower or sentence case will be used in the examples except for specifications of structures or standard reactant names.

5.1. Creating Reactants

New reactants can be created by using one of the following commands when users are in their reactors:

<div align="center">

Build <structure>
Build <standard-name>
DMS <standard-name>
Build <your-choice-of-name> as <structure>

</div>

Here, <structure> is the structure of the reaction either as a SMILES or MechGen structure string such as discussed in Section 3.2, <standard-name> refers to a standard 2-8 character name assigned for many VOCs represented by SAPRC detailed mechanisms (see Section 3.2), and <your-choice-of-name> is any name that the user may assign, which should consist of only alphanumeric characters, "-", or "_". Names that might be interpreted as prepositions in the English language (e.g., "in", "with", "is", or "as") must be avoided because of syntax requirements for MOO commands (the command "help prepositions" give a complete list of names that should be avoided). Note that if the user assigns a name that has an assigned SAPRC name, the system will issue a warning method and use the SAPRC name instead. If no name is given for a structure that does not have a standard SAPRC name, the system will automatically generate "VOC-n" or "RAD-n" as the name, depending on whether the reactant has a radical group as specified on Table 2, with "n" being a sequence number used to distinguish it with other generated names that may be in the reactor.

An example of terminal output following the execution of the "build" command using the telnet interface is shown on Figure 13, which is the same compound as shown on Figure 2 after it was created using the web system. Note that this contains some of the header information and lists of groups as contained in the web output on Figure 2.

```
build CH3-CO-CH2-CH3

  Reactant MEK [#10499] is created with structure CH3-CH2-CO-CH3
  MEK CH3-CH2-CO-CH3 [#10499] (saved)
  Type: Simple Ketones
  VOC type = Ketone (24)
  COs = 1
  Groups:
     g1 [#19918] (&CH3_g)  bonds: g2
     g2 [#17188] (&CH2_g)  bonds: g1, g3
     g3 [#4778] (&ketone_g)  bonds: g2, g4
     g4 [#18696] (&CH3_g)  bonds: g3
  Estimated vapor pressure at 298K is 3.70e+0 atm.
  Fraction in particle phase (with PM=50 ug/m3): 7.5e-9.
```

Figure 13.   Example of terminal input and output following a "Build" command using the Telnet interface, using MEK as the example.

5.2. Generating Single Step Reactions

Single step reactions are carried out using the "react" command, which could be

<div align="center">

React <name or structure> [with <reaction>]

</div>

Where <name or structure> is either the name of a reactant previously created using the "build" command, the standard SAPRC name for a VOC, or a valid MechGen structure identifier, and <reaction> refers to the mode of reaction if the reactant is not a radical. The "with <reaction>" must be specified when reacting a stable compound except when generating unimolecular reactions. In this context <reaction> could be OH, O3, NO3, O3P, Cl, hv, or uni to indicate bimolecular, photolysis, or unimolecular, respectively, and "with uni" is optional when generating unimolecular reactions for stable compounds (e.g., peroxynitrates). As with the web system, single step reactions of stable compounds can be carried out for only one type of reaction at a time.

In the case of radicals, the "with <reaction>" must not be specified, and the "react" command generates all types of reactions the radical can undergo, including bimolecular as well as unimolecular, as applicable. This is the same as the with the web system in this regard. This can result in a fair amount of output for peroxy radicals, since they have a number of bimolecular reactions that they can undergo. If the interest is mainly unimolecular reactions, the "react1 <name or structure>", which generates only unimolecular reactions, instead.

The output of the react or react1 commands is the same as the single step reaction output using the web system, as shown on Figure 3 (central portion), Figure 4, and Figure 5, above. However, unlike the web system the products formed following the react or react1 commands are not deleted and remain in the reactor. (The "clean" (c) command will delete the products but not the reactants.) A list of names, structures, and relative yields of the products that are created, which can include elementary species as well as stable or radical organic reactions, is included with the output following the list of reactions, rate parameters, and documentation information. The products are given temporary names (e.g., S1, S2, …), depending on how many unnamed species are in the reactor. These names can be used in subsequent react or react1 commands to carry out sequential single-step reactions, analogous to the process discussed above in Section 4.3 for the web system.

A simple example showing terminal input and output for a sequential mechanism generation is shown on Figure 14. The first "react" command creates ethane as a reactant by giving its structure and initiates a single step reaction with OH. The reaction and documentation output is the same as when using the web system, but a list of products formed, with their temporary names, is also output. The second "react" command reacts one of the radicals formed, which creates an additional radical. The "reactants" command shows what reactants are in the reactor following these commands, where there were none previously.

5.3. Full Mechanism Generation

Complete reaction generation is initiated using the "fullreact" command, which has a similar syntax as the "react" command discussed above, i.e.,

Fullreact <name or structure> [with <reaction>] [<reaction2> …]

where <name or structure> and <reaction> indicates the type of reaction. This command can be given for both radicals and stable reactants, where "with <reaction>" is not specified for radicals, and more than one type can be specified for stable compounds. As with the web system, full mechanism generation can be initiated for all or a subset of the types of reactions that the compound can undergo, with all types of possible reactions being generated if the "with <reaction>" is not included in the command. (In the case of non-default lumping, discussed in Section 7, only the reactions needed by the lumping method, which can be a subset of the possible reactions, are generated.) If only a subset of the reactions are to be generated, but more than one type of reaction is required, then the types can be listed following the

```
react CH3-CH3 with OH

   Reacting CH3-CH3 with OH

   100.0% CH3-CH3 + OH -> H2O + CH3-CH2.
           2 x Abstraction from -CH3[1]: kRef(CH3)=3.66e-13*exp(-309/T)
           =1.30e-13; T=298.  Rate constants and A factors adjusted to fit data
           for acyclic alkanes. Activation energy derived from estimated A factor
           and rate constant.  F[-CH3]=1.000.  k= 1.30e-13 cm3 molec-1 s-1.
           Estimated rate constant for all pathways multiplied by a factor of
           0.960 to yield the assigned total rate constant.
           Rate info = {2.49318544615544e-013, {2.49318544615544e-013, E_NO ...

   Assigned Total kOH for T=298 and 1.00 atm. = 2.49e-13 cm3 molec-1 s-1.
   From the Compilation of McGillen et al (2020), as updated to version 2.1.0,
    June 23, 2021. https://doi.org/10.25326/mh4q-y215

   2 products formed:
   CH3-CH2. [#17853] (radical S1) (100.0%)
   H2O [#434] (100.0%)

react S1

   Reacting CH3-CH2. with O2

   100.0% CH3-CH2. + O2 -> CH3-CH2OO.
           O2 addition is assumed to be the major fate for most carbon-centered
           radicals.
           Rate info = 1.0 ...

   1 products formed:
   CH3-CH2OO. [#8114] (radical S3) (100.0%)

Reactants

   Stable reactants:
     ETHANE: CH3-CH3 (#19564)

   Reactive radicals:
     S1: CH3-CH2. (#17853)
     S3: CH3-CH2OO. (#8114)
```

Figure 14.   Example of terminal input and output illustrating sequential single-step reaction
generation using the telnet system

"with", separated by spaces. For example, to generate the reactions of propene with OH and O3 but not
NO$_3$ or O3P, the command "fullreact propene with OH O3" can be used.

An example of the terminal input and output involved with the fullreact command is shown on
Figure 15. Unlike the web system, the terminal fullreact command shows the progress of the full
mechanism generation process, which is useful because it can take a noticeable amount of time when
large molecules are reacted. (The process output includes: "steps" -- number of reactants processed;
"rxns" -- number of reactions completed; "Ints" -- number of temporary reactant objects used by process;
"Susp" -- number of process suspensions, necessary to allow other processes to occur at the same time;
"ToGo" -- number of reactants in queue to be processed; "Working on" -- intermediate currently being
processed. Because the continuous output allows users to know if the process is proceeding and time-outs
should not occur. Therefore, there is no restriction on the size of the molecule that can be reacted using
the fullreact command, but the time required may be many minutes for larger reactants. However, the

```
Fullreact PROPENE with OH O3
   Reacting PROPENE with OH and O3
   Steps Rxns Ints Susp ToGo Working on
       3    1    6    8    3 CH3-CH[.]-CH2-OH
       5   11    6   25    3 CH3-CH[O.]-CH2-OH
       7   13    6   30    3 CH3-CH(CH2.)-OH
       9   23    6   46    3 CH3-CH(CH2O.)-OH
      11   25    5   51    2 CH3-CHOO {*O3Ole}
      13   32   12   57    5 CH3-CHOO[syn]
      15   34   11   59    4 HCO-CH2OO.
      17   45   12   73    5 HCO-CH2O.
      19   48   12   78    5 .OOCH2-CO-O-OH
      21   59   12   98    5 CH2OO {*O3Ole}
      23   65   14  100    4 CO[.]-O-OH
      25   67   12  101    2 CH3.
      27   77   12  106    2 CH3O.
      29   79   10  106    0 H.
   Completed reacting PROPENE with OH and O3

   Reactions: 80
   Reactants: 29
   Products:  20
   Lost due to de-minimus yield = 0.4%
   Processed reactions for PROPENE has 33 species and 28 reactions.
   Fullreact and process completed for PROPENE
```

Figure 15.   Example of terminal input and output for full mechanism generation using the telnet interface.

resources available to MechGen that are needed to generate multiple reactions can become exhausted if molecules with more than about 16 carbons or groups are reacted, and the process is aborted with thousands of intermediates left in the reactor.

Note that if the process is aborted during full mechanism generation because of exhausted resources or another error, such as being unable to estimate reactions for some intermediate, there may be large numbers of temporary reactants remaining in the reactor after the process is aborted -- thousands if the process is aborted because of resources being used up. In that case, it is important to give a "clean" ("c") or "zap-reactants" command to clear the reactor. There are no new reactants created in the reactor if the process is successful. The results of the mechanism generation are saved as properties on the reactant object, and are available to be displayed or downloaded (see Table 7) until the reactant is deleted or its reaction results erased using the "erase <reactant>" command. Unlike the case with the web interface, the results of full mechanism generations are not automatically output when the process has successfully completed, other than the summary output as shown on Figure 15. Instead, the results can be output to the user using the commands

Read <output> on <reactant>
or   fileout <output> on <reactant>
or   @ftpout <output> on <reactant>

where <output> is the type of output desired, as indicated on Table 7. The "read" command outputs the results to the terminal; the "fileout" command creates an output file on the host computer that you can download using the web system; and the "@ftpout" command sends the results to the MechGen ftp site. The @ftpout command is only available for authorized users who have access to the MechGen FTP site. If you are not authorized to access the MechGen ftp site, you should use the "fileout" command instead, and then log into the web system to download the file using the "Files for download" section of the main

menu. The name of the output file is given if the "fileout" command is successful. If you downloaded your own copy of MechGen to run on your computer (see Section 9), you can also obtain files created by "fileout" commands directly from the "files\users\<username>" folder, where <username> is your login name.

5.4. Modifying Mechanism Generation Options

The current reactor options are displayed when the user logs in, and can also be displayed by giving the "options" command. Basic reactor options can be modified using the command

<div align="center">

Option <option> is <value>

Option <option> is default

</div>

where <option> can be anything in the "item" column of Table 8, which also gives the acceptable values or ranges of values. Using "default" as the value restores the option to the default, as also indicated on Table 8. In addition to options listed on Table 8, advanced users can enable "user mechanisms" and "user assignments", which are discussed in Sections 7.3 and 8. The commands

<div align="center">

Reset-options

</div>

Or   Option all is default

restores the values of all options listed on Table 8 to the defaults, and also deletes any user mechanisms or assignments that may have been created.

Note that none of these options commands affect any of the reactant objects in the reactor, other than deleting results of previous "fullreact" operations of the lumping or user mechanism is changed.

Table 8. List of reactor options that can be modified using the "option <item> is <value>" command.

Item	Default	Description
T	298 K	Default temperature in K. Must be greater than 0.
P	1.0 atm	Default pressure in atmospheres. Must be greater than 0.
O2	0.2095	Mole fraction of O_2 in the reaction environment. Must be between 0 and 1, and given as a number, not a percentage.
H2O	Present	Used to determine if some intermediates (e.g., Criegee intermediates) react with water. Available options are "present" and "absent".
PM	50 μg/m^3	Atmospheric particle levels used to estimate fractions of reactants in the particle phase if their vapor pressures can be estimated. Must be greater than 0.
Minyld	0.005	The minimum yield for a competing process in a single step reaction for it to be considered non-negligible during full mechanism generations, Must be greater than 0 and less than 0.5, and given as a number, not a percentage.
MGminyld	0.0001	The minimum yield of a product formed during a multi-generation mechanism derivation to be included as a reacting product in the mechanism (see Section 10).
Lumping	Explicit	Lumping method used when generating full reactions and processing results. Currently available options include "Explicit" or "SAPRC22", but others may be available in later versions of MechGen. See Section 7.
VP	vpsimp	Method used to estimate the vapor pressure that is displayed on the reactant information page for stable compounds. Available options are "vpsimp" for SIMPOL.1 (Pankow and Asher, 2008) or "vpevap" for EVAPORATION (Compernolle et al. 2011), but others may be available in future versions of MechGen.
All	see above	Resets all options to default. Also deletes any user mechanisms (Section 7.3) and user assignments (Section 8.3) that may have been created.

6. STANDARD ENVIRONMENTS

Standard environments consist of sets of concentrations of atmospheric species such as OH, NO_x, HO_2, etc that affect competitions between bimolecular reactions in generated mechanisms. They are used for two purposes, as follows:

- Determination of relative yields of products formed in react completely or fullreact operations that are output in the reaction results pages for web users or by using "read products on <reactant>" terminal commands.

- Determination of which reactions may be negligible and can be neglected when a fullreact or react completely command is carried out.

- Determination of which products are negligible and whose reactions can be ignored when deriving multi-generation mechanisms (see Section 10).

Note that these do not determine environmental conditions that are specified by reactor options as listed on Table 5 or Table 8, such as temperature or O_2 content, even those these can also affect relative yields of reactions.

Standard environments used for this purpose can be specified using either the web or telnet system as discussed below. More than one standard environment can be specified, and users can control which, if any, of these are used for determination of negligible yields. At least one standard environment must be specified for the purpose of deriving relative product yields. If more than one is specified, the "products" output gives relative yields for all the environments. This is useful to obtain how product yields change with environmental conditions. Only a single standard environment is used when deriving multi-generation mechanisms (see Section 10).

The minimum 1-step yield, or "minyld" parameter is used during full mechanism generation to determine which of competitive reactions can be ignored, based on estimated relative rates of the competing reactions. Note that this does not affect single-step reaction output, which shows all reactions that may be non-negligible under at least some conditions. Use of standard environments provides a means to estimate relative rates of competing processes involving bimolecular reactions, such as reactions of stable compounds with different oxidants such as OH or O^3P, reactions of peroxy radicals with NO_x or other peroxy radicals, or unimolecular vs. bimolecular reactions of peroxy radicals. If more than one standard environment is selected for use in mechanism generation, the system determines relative yields for all the environments, and compares the *maximum* of these with the minimum 1-step yield parameter to determine which can be ignored. This results in no process being ignored that may be non-negligible for at least one of the environments selected for use.

Users can optionally not use standard environments for determination of which reactions are negligible during reaction conditions, but the default is for them to be used for this purpose. If no standard environments are used, then the all possible bimolecular reactions are included in full mechanism generation, with the minimum 1-step yield parameter being used for competing unimolecular reactions, or reactions with the same species. The resulting mechanism is potentially applicable to a wider range of conditions, but may include many more reactions that are of negligible importance for most applications.

6.1. Determination of Relative Yields

The relative yields of products or intermediates when a selected compound undergoes full mechanism generation is a measure of the importance of the product or intermediates in the reaction of the compound. In the case of stable products, these are defined as the amount of product that would be formed when the VOC completely reacts in the selected environment, neglecting the secondary reactions of the product. In the case of intermediates, it is the amount of intermediate that would be formed if its loss due to its own reactions were not considered (but not neglecting the products and intermediates formed from their reactions when determining the yields of those products), and is a measure of the flux of the system through reactions of this radical. Relative yields of stable products are useful in assessing the atmospheric fate and impact of the compound, while relative yields of intermediates are useful when determining which intermediates and reactions can be neglected during full mechanism generation.

Relative yields depend on environmental conditions because they are affected by competitions between unimolecular, bimolecular and photolysis reactions, whose rates depend on temperature and (for photolysis reactions) lighting conditions, and whose rates in the case of bimolecular reactions depend on concentrations of atmospheric species such as O_2, NO, HO_2, etc. The temperature and light spectrum is specified as a reactor option as discussed in Section 4.5, while the concentrations of relevant atmospheric species and also overall light intensity is specified in the standard environments used for mechanism generation as discussed below in Section 6.2. Once these are specified, the relative yields in a full mechanism generation are derived as follows:

- The "relative yield" of the initial reactant is set at 1 by definition.
- All thermal rate constants are calculated for the temperature of the reactor.
- All photolysis rate constants are calculated using the absorption cross sections, quantum yields for the reaction and for the light spectrum assigned to the reactor, unless the standard environment is specified as being dark, in which case all photolysis rate constants are zero.
- All bimolecular rate constants are converted to unimolecular rate constants using the concentrations of the relevant atmospheric species assigned to the standard environment.
- If the unimolecular or pseudo-unimolecular rate constant for reaction "i" of a reacting species "s" in a full mechanism (whether the initial reactant or an intermediate) is defined as $k_{s,i}$ and yield of product or intermediate "j" from that reaction is given as $a_{s,i,j}$, then the yield of "j" from all the reactions of "s" is given by

$$y_{s,j} = (\Sigma_i\ k_{s,i}\ x\ a_{s,i,j})\ /\ (\Sigma_i\ k_{s,i})$$

- The reacting species in the full mechanism are ordered with the initial reactant first, intermediates formed in the reactions of the initial reactant next, and followed by intermediates formed in reactions of the intermediates that are previously ordered. This is not possible if there are "cycles" where the reactions of an intermediate re-forms itself after one or several steps. These cases are generally not frequent or important, and are dealt with by neglecting certain types of reactions when determining relative yields, as discussed below.
- Therefore, if "s" is the reacting species ordered as indicated above, then its total relative yield, ry_s is given by

$$ry_s = y_{1,s} \hspace{4cm} \text{if s=2}$$
$$ry_s = y_{1,s} + \Sigma_{t=1,s-1}\ ry_t\ x\ y_{t,s} \hspace{2cm} \text{if s>2}$$

where $y_{t,s}$ is the relative yield of intermediate "s" in the reactions of intermediate "t", where t<s. Note that the relative yield is not defined for the initial reactant (s=1) is not used in this way.

- The total relative yields of stable product "j" is therefore obtained from

$$ry_j = \Sigma_s \; ry_s \; x \; y_{s,j}$$

    where $y_{s,j}$ are the yields of this product from intermediate "s", and ry_s is computed as given above.

- If the initial reactant forms itself as a stable product after a series of reactions, i.e., ry_1 calculated as indicated above is nonzero, then this is removed as a product from this overall reaction, and the relative yields for the other products, are increased by a factor of $1/(1-ry_1)$ to compensate for this. This happens for PAN compounds and hydroperoxides, but not most other species.

As indicated above, the algorithm used to derive relative yields does is not designed for cases where there are "cycles" of radical reactions, where a radical reacts to form another radical that in turn reacts to form the starting radical, among its other reactions. Currently, there are two types of chemical systems in generated by MechGen where this can occur: interconversions of phenoxy and phenoxy radicals, and scrambling reactions of hydroperoxy-substituted peroxy radicals. These are handled as follows.

Reactions of phenoxy and phenyl peroxy radicals. These types of radicals are predicted to undergo only bimolecular reactions, and among these are

$$\text{Phenoxy} + O_3 \rightarrow \text{Phenyl peroxy} + O_2$$
$$\text{Phenoxy} + NO_2 \rightarrow \rightarrow \text{Nitrophenol}$$

$$\text{Phenyl peroxy} + NO \rightarrow \text{phenoxy} + NO_2$$
$$\text{Phenyl peroxy} + HO_2 \rightarrow \text{Phenol} + O_2$$
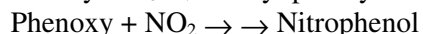
The phenoxy/phenyl peroxy interconversions are not net loss processes, but the reactions forming nitrophenol and phenol (and other competing reactions not shown) are. The relative yields of these two products are determined by the concentrations of O_3, NO_x, HO_2 and other species. The algorithm used to derive product yields should give the correct total yield of these two types of products, but may not give the correct ratio of their yields. Note that this problem does not arise when processing for SAPRC mechanisms (see Section 7.2.2) because all types of phenoxy or phenyl peroxy radicals are represented by lumped species (BZO and BZO2, respectively.)

Scrambling reactions of hydroperoxy-substituted peroxy radical. Based on theoretical results of Vereecken and Noziere (2019), Mechgen assumes that hydroperoxy-substituted peroxy radicals can undergo rapid interconversions, such as, for example

$$HOOCH_2CH(CH_3)OO\cdot \leftrightarrow \cdot OOCH_2CH(CH_3)OOH$$
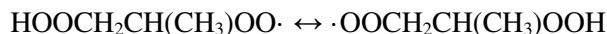
These reactions are not loss processes for these radicals, but will affect the relative yields of products formed when they undergo other reactions. The algorithms for deriving product yields for standard environments may not correctly predict relative yields of those products, though it should predict the correct total yields. The algorithms used for deriving lumped SAPRC mechanisms (see Section 7.2.2) also cannot handle such cases, so these scrambling reactions are neglected when generating mechanisms using SAPRC lumping methods. Note that the inaccurately calculated relative product yields will usually concern isomers with very similar reactivity characteristics that are usually represented using the same SAPRC lumped model species, so probably would not affect predicted yields of lumped SAPRC model species.

The hydroperoxy/peroxy scrambling reactions are not the only cases in atmospheric chemistry where there are rapid interconversions of intermediates that have competing reactions that might affect

relative product yields. This includes formation of OH-aromatic or OH-dialkene adducts that may back-decompose to reactants. However, MechGen assumes that the effects of these processes are incorporated when estimating overall rate constants (Carter, 2021), so it does not consider such equilibria when generating explicit as well as lumped mechanisms. This might result in product yields depending on reaction conditions in ways that MechGen does not currently predict, but the important of this approximation in specific systems has not been assessed.

6.2. Available Standard Environments

Table 9 lists the standard environments that are available for use by all MechGen users, giving the name that Telnet users can employ to specify the standard environments, their default use, brief descriptions, and concentrations of selected species. In addition to O_3, NO, NO_2, and HO_2, the standard conditions also specify concentrations of NO_3, O^3P, and total peroxy and acyl peroxy ("SumRO2") and acyl peroxy ("SumRCO3"). These concentrations (in molecules/cm^3) can be output using the web interface by selecting the "(view or change)" link on the line concerning environments in the Reactor Options section, or by giving the "stdenvts" command using the Telnet interface.

Table 9. List and descriptions of standard environments currently available for use.

Name	Description of conditions	Default use [a]	O_3 (ppb)	NO_x (ppb)	OH (ppt)	HO_2 (ppt)
HighNOxEnv	High NOx urban (near MIR)	Y, G	73	16.8	0.31	~0
MaxO3Env	High ozone urban (near MOIR)		97	7.4	0.48	17
StdEnv	Mid NOx standard urban (near EBIR)	Y	92	4.2	0.45	24
LowNOxEnv	Low NOx downwind (MOIR NOx/10)	Y, G	38	0.7	0.15	29
NightEnv	Nighttime for multi-day, mid-NOx, stagnant	Y, G	119	2.0	0.01	5.2
OnlyNo	Only OH and NO, and NO=1 ppb		0	1	0.1	0

[a] Y = Used for yield determinations; G = Used to determine negligible reactions during mechanism generation. If blank, it is not used by default, but can be selected for use as discussed in Section 6.3.

The conditions used to derive most of the standard environments are based on results of multi-day dynamic model simulations of urban scenarios, using the SAPRC-22 mechanism (Carter, 2023a). These represent various NO_x levels that may occur in moderately polluted urban conditions, and also polluted nighttime conditions. More information on the simulation inputs, and how the simulation results were used to calculate the standard concentrations, is given in Table 10.

6.3. Selecting Standard Environments

Web System. The "Reactor Options" selection of the main menu (see Figure 1) includes a line indicating the number of standard environments currently in use, followed by a "(View or Change)" link. Selecting that link results in a page shown on Figure 16a, listing all the available standard environments and indicating which are used for product yield determination, which are used for mechanism generation, and which are currently unused but are available for use. This shows the default configuration, and the check boxes may be different if changes were made, and there may be additional options if new user-

Table 10.   Methods used to derive atmospheric species in the model simulations used to derive the standard conditions representing urban scenarios.

Simulation duration	6:00 AM local daylight time through 5:00 PM on the fourth day.
VOC and NO_x emissions	Continuous from 8:00 AM to 6:30 PM each day; none at night.
VOC input fluxes	All scenarios used 7.7 millimoles C /m^2/ day, set to approximate current upper limit air quality recommendations for O_3 (see Table 9)
NO_x input fluxes	Adjusted to yield different conditions of NO_x availability, including approximate MIR (maximum incremental reactivity), MOIR (maximum O_3), EBIR (equal sensitivity of O_3 to VOCs and NO_x), as described by Carter (1994). The low NO_x scenario used 10% the MOIR levels. These corresponded to 1.53, 0.87, 0.37, and 0.06 millimoles /m^2/ day, respectively.
VOC speciation	75% anthropogenic and 25% biogenic by carbon, and represented California statewide emissions in 2018, excluding fires.
NO_x speciation	75% NO, 25% NO_2, no HONO .
Background species	2 ppm each of CO and methane, ~50% RH. No aloft pollutants.
Mixing heights	100 M at 6 AM, increasing to 540 M at 3 PM, constant at 540 M until 9 PM, going back to 100 M at 6 AM the next day.
Photolysis rate calculation	Actinic fluxes as a function of zenith angle same as those used in the incremental reactivity calculations of Carter (1994). Zenith angles as a function of time calculated for Los Angeles in the summer.
Derivation of standard concentrations	Standard concentrations for daytime environments were averages of calculation results between 8 AM and 5 PM on days 2 and 4. The averages for the peroxy levels were very low in the high NO_x scenario and set at zero. Averages for the nighttime environment were averages starting at 10 PM through 2 AM starting on days 2 and 3 of the mid NO_x, EBIR scenario.

defined environments are created using the Telnet system, as discussed in Section 6.4, below. These can be changed by checking or un-checking the appropriate boxes and then selecting the "Change" control at the top right of the table. Links are also available for restoring defaults or disabling use of any environments for mechanism generation. Note that if you select only the box for mechanism generation, it will also be selected for product yield determination when the input is processed. Once you have selected "Change" or chosen the other two links, the page will re-appear showing the configuration that you selected.

The page also shows the reactant concentrations and other applicable options for the selected environments. This is the same as the output using the telnet system, discussed below.

Telnet System. The terminal commands that can be used to display or modify the standard environments are listed and briefly described on Table 11. As indicated there, the "stdenvts" command is the primary means to list or change the standard environments used. The "stdenvts" command by itself gives the output shown in Figure 16b, listing the standard environments currently in use for product yield determination, and showing the concentrations of the reactive species and other options associated with

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(a) Web System Output after selecting Standard Environment "(View or Change)" link

Available standard environments and those that are currently used are as follows

Label	Description	Used for * Change
Mid NOx	Mid NOx standard urban conditions (near EBIR)	Yields ☑ Mechgen ☐
High NOx	High NOx urban conditions (near MIR)	Yields ☑ Mechgen ☑
Low NOx	Low NOx downwind conditions (NOx = MOIR NOx/10)	Yields ☑ Mechgen ☑
Max O3	High ozone urban conditions (near MOIR)	Yields ☐ Mechgen ☐
Night	Nighttime conditions for multi-day, mid-NOx scenario	Yields ☑ Mechgen ☑
NO=1 ppb	Conditions with only OH and NO, and NO=1 ppb.	Yields ☐ Mechgen ☐

* "Yields" = used to calculate yields; "MechGen" = used to determine negligible yields during mechanism generation

To change: check or uncheck as desired, then select change, above.. Note that selecting "MechGen" will also select "Yields".
<u>Click here</u> to restore defaults, or <u>click here</u> to disable use of environments during mechanism generation.

Reactant concentrations for selected environments:

```
Species  Mid NOx   High NOx  Low NOx   Night
NO       1.59e+10  9.58e+10  4.12e+9   7.43e+5
NO2      8.63e+10  3.15e+11  1.32e+10  4.88e+10
```

(see below for complete output)

(b) Output of terminal "Stdenvts" command

```
Label       Environment used to derive relative product yields
Mid NOx    Mid NOx standard urban conditions (near EBIR)
High NOx * High NOx urban conditions (near MIR)
Low NOx  * Low NOx downwind conditions (NOx = MOIR NOx/10)
Night    * Nighttime conditions for multi-day, mid-NOx scenario
         * = Also used for mechanism generation

Species    Mid NOx   High NOx  Low NOx   Night
NO         1.59e+10  9.58e+10  4.12e+9   7.43e+5
NO2        8.63e+10  3.15e+11  1.32e+10  4.88e+10
OH         1.11e+7   7.51e+6   3.69e+6   2.86e+5
O3         2.26e+12  1.78e+12  9.20e+11  2.90e+12
NO3        9.92e+6   8.54e+6   1.25e+6   2.25e+9
O3P        2.84e+4   5.50e+4   8.85e+3      0
HO2        6.00e+8      0      7.17e+8   1.27e+8
SumRO2     4.59e+8      0      6.69e+8   2.35e+8
SumRCO3    7.30e+7      0      7.27e+7   1.04e+8
PM         5.00e+1   5.00e+1   5.00e+1   5.00e+1
Lights      On        On        On        Off
Species concentrations in molec/cm3. PM in ug/m3.
```

(c) Output of terminal "stdenvts list" command

```
Available standard environments
  StdEnv......Mid NOx standard urban conditions (near EBIR)
  HighNOxenv..High NOx urban conditions (near MIR)
  LowNOxEnv...Low NOx downwind conditions (NOx = MOIR NOx/10)
  MaxO3env....High ozone urban conditions (near MOIR)
  NightEnv....Nighttime conditions for multi-day, mid-NOx scenario
  OnlyNO......Conditions with only OH and NO, and NO=1 ppb.
The first 4 are used by default
```

Figure 16.   Web and terminal system output displaying currently selected and available standard environments for product yield determination and mechanism generation.

Table 11.   Terminal commands that display, select, or create standard environments used for deriving product yields and mechanism generation.

Command	Description
Stdenvts	Displays current standard environments and indicates which are used for mechanism generation
Stdenvts nogen	No standard environments are to be used for mechanism generation. Does not change those used for product yields
Stdenvts gen	The standard environments used for product yields are also being used for mechanism generation, except that only the last 3 are used if four are used for product yields since it is assumed that the first represents intermediate conditions
Stdenvts default	The four default standard environments, as indicated on listed on Table 9, are used for product yields, with the last three used for mechanism generation.
Stdenvts list	Lists and briefly describes all the available standard that can be used.
Stdenvts <name1>[/NG] [<name2>[/NG] …] This is used to determine which standard environments are to be used for determining product yields and which are also used for mechanism generation. The names must match an environment name shown using the "Stdenvts list" command (case insensitive), or a name listed in Table 9. The code "/NG" (case insensitive) is appended, without a space, following any standard environment name that is *not* to be used for mechanism generation; otherwise it is used for both purposes. Spaces must separate the names and codes for the different standard environments.	
Create-stdenvt <envtname> as <label>	Creates a new standard environment for use only by this user, and prompts the user for lines of input giving a short description that serves as its full name, lines giving an optional multi-line description, a space, then lines with names and concentrations of atmospheric species, as shown on Figure 16b. <envtname> is required and is a short name or alias for the environment and must not be recognized as a name or alias for any other object in the reactor. <label> is optional and is a short label output when concentrations in this environment, and <name> is used for this purpose if not given. This can also be used to modify the name, description, concentrations or options in an existing standard environment that this user previously created. If successful, the user-created standard environment will be created as an object in the user's reactor, will show up in "stdenvt list" commands, and can be selected for use in product yield derivations or mechanism generation using the "stdenvt" command.
Look <envtname>	Shows available information about the named standard environment, including full description, oxidant concentrations, and fractions of peroxy radical reactions, and other information
Delete <envtname>	Deletes the user-created standard environment and removes it from the list of available standard environments and (if applicable) those selected for use.

each. If any of these are also used for mechanism generation there will be a "*" next to the description on the list of standard environments near the top of the page. The output shown on Figure 16 is for the default standard environment configuration; it would be different if changes were made. Note that the "stdenvts" output only shows the standard environments currently in use.

The "stdenvts list" command lists all the standard environments that are available for use, with the output for the default configuration shown on Figure 16c. There may be additional environments on the list if the user created any as discussed below in Section 6.4. The left column of this list gives the short names for the standard environments that must be used if they are to be selected for use.

To select a different set of standard environments, or change which are used for mechanism generation or not, use the command

Stdenvts <envname1>[/NG] <envname2>[/NG] …

where the <envname>'s refer to selected names as shown on the "stdenvt list" output and the optional /NG qualifier following the name (without an intervening space) indicates that it is *not* to be used for mechanism generation. For example, the command

stdenvts StdEnv/NG HighNOxEnv LowNOxEnv NightEnv

is equivalent to restoring the defaults of the system, and has the same effect as using the "stdenvts default" command. Note that the standard environment names and the "/NG" option are not case-sensitive, nor is the "stdenvt" command itself. Once this command (or the "stdenvts default" command) is executed, the system will then give the same output as the "stdenvts" command showing the new configuration (similar to Figure 16). The "stdenvts nogen" or "stdenvts gen" can also be used to toggle between using the currently selected environments for mechanism generation or not, as indicated on Table 11.

6.4. Creating New Standard Environments

Although only the primary MechGen user is able modify the standard environments listed in Table 9, users of the telnet interface are able to create their own standard environments that they can use and edit. Note that this option is not currently available to web users, but environments created using the telnet interface will be available to the same user when subsequently using the web interface. The command to create or edit a user-modifiable standard environment is as follows:

Create-stdenvt <envtname> as <label>

Here <envtname> is a unique short name used to identify the environment in "stdenvt" commands and for other purposes, and <label> is used to identify the environment in outputs such as shown on Figure 16a and b. Note that <envtname> cannot be also be an identifier or name for any other object in the reactor or available to the user, other than a previously created standard environment. If it refers to a previously created user standard environment then the input to this command will be used to modify that environment, rather than creating a new one.

Once that command is given, the user is prompted for additional lines of input, and the command will fail with no new standard environment created or existing environment modified if the expected input is not provided. The additional expected input is as follows:

First line:	A short description of the environment that will be output in lists of the environments such as shown on Figure 16.
Optional lines:	Additional information about the environment that is displayed using the "look" command.
Space:	The space is required to separate the name and optional additional information lines from the remainder of the input giving the reactant concentrations and options.
Remaining lines:	Lines with the name of a species and its concentration or level. Allowable gas-phase species names are "NO", "NO2", "OH", "O3", "O3P", "HO2", "SumRO2" (total non-acyl peroxy radicals), "SumRCO3" (total acyl peroxy radicals), and "HV", used to indicate relative light intensity, and "Hours" used to indicate reaction hours to use when deriving multi-generation mechanisms (see Section 10). Additional species or option names are not allowed.
Termination:	A single "." is used to indicate that this is the end of the input. If this is not given, the system will process anything else the user may type as input to this command.

The input lines are not processed, and error messages (if applicable) will not be displayed until the termination line (".") is input. However, the "create-stdenvt" input can be aborted by giving the "@abort" input line, which will cause the command to fail and normal processing of terminal input to resume.

The defaults for all the species are zero, so if the species are not present it is not necessary to include lines giving their concentrations or values as zero. Note also the following:

- The "HV" option indicates light intensity, with 0 being dark and 1 being full overhead sun. Fractions between 0 and 1 are also permitted, though not used in the default available environments.

- The "Hours" input is used to indicate reaction hours when results of multi-generation mechanisms are processed. A discussion of use of MechGen for multi-generation mechanisms is beyond the scope of this document (see Section 10). It does not affect product yields outputs of fullreact commands as discussed in previous sections.

If any errors occur when processing the input there is no new environment created, or, if an existing environment is referenced then it is not modified. If the command is successful, the new environment is added to the list of the user's available standard environments, and it will be included in web or "stdenvts list" outputs such as shown on Figure 16a or c.

The user-created standard environment(s) will be created as objects within the reactor, and will show up on "look" terminal command, along with other contents of the reactor such as reactants. (They will not show up on the main menu of the web interface.) These can be deleted using the "delete" command (included in Table 6), which will also remove the environment from the list of available environments and (if applicable) from environments selected for use. Note that if the deleted environment is the only one selected for use, the standard environments used will revert to the defaults as indicated on Table 9.

7. GENERATING LUMPED MECHANISMS

Detailed explicit mechanisms such as produced using MechGen "react completely" or "fullreact" operations are generally much larger than needed for practical atmospheric or laboratory modeling applications, both because of the computer demands required for implementing such large mechanisms, and because most modeling applications do not require this level of detail. The term "Lumping" is used here to refer to the process of reducing the mechanism to a size more appropriate for the application, while retaining as much chemical accuracy as possible, and also retaining its relationship to the fundamental chemistry involved. Examples of such applications include use of atmospheric chemical mechanisms in airshed models to predict the effects of VOC and NO_x emissions on formation of ozone and other secondary pollutants, and use of such mechanisms to derive reactivity scales for predicting effects of individual VOC on secondary pollutants (Carter, 1994). Such applications generally do not require the level of chemical detail contained in explicit mechanisms, and, if an appropriate reduction or lumping approach were used, the differences between lumped and explicit mechanisms for predictions of interest could be well within the uncertainty of the chemical estimates and assumptions employed when the detailed mechanism is generated.

The SAPRC family of atmospheric chemical mechanisms is an example of lumped mechanisms designed for use in urban and regional models for predicting formation of secondary pollutants from VOC and NO_x emissions reacting in sunlight (e.g., Carter, 1990, 2000, 2016, 2019a,b, 2023a,b, Carter and Heo, 2013) and deriving VOC reactivity scales measuring the effects of individual compounds on formation of secondary pollutants such as ozone (e.g., Carter, 1994). Starting with SAPRC-90 (Carter, 1990), versions of these mechanisms have been derived using versions of MechGen, using various approaches to lump individual compounds into a smaller number of lumped model species, and using various approaches to reduce the numbers of model species and reactions required to represent reactions of intermediates. The latest version of these mechanisms is SAPRC-22 (Carter, 2023a), and that was derived using the chemical estimation methods and assignments documented by Carter et al (2024) and the MechGen system that is described in this document. In principle the MechGen system could also be used to derive mechanisms using other lumping approaches, but that is not supported by the current system (see Section 7).

The lumping methods currently supported by MechGen are summarized on Table 12. These include "explicit" or no lumping, which is the default, and lumping for two versions of SAPRC-22 or for the SAPRC-11 mechanism. The user can control the lumping method employed as indicated previously and discussed further below. Authorized users can also create and use new lumping methods as discussed in Section 11, but only the primary MechGen user can make them available for all users. The differences between these methods that are currently available to all users are discussed in the following section.

The choice of the lumping method affects how results of react completely or "fullreact" operations are processed, and the outputs that can be obtained. The affected outputs are the "Lumped mechanism" outputs shown on the reaction results pages and links on those pages and the main menu of the web system, or the "tabrxns" or "rxns" output using the telnet system, as shown on Table 7. The choice of the lumping method also affects which reactions are generated during "react completely" or "fullreact" operations, since reactions of radicals that are represented using lumped model species in the lumped mechanisms, such as phenoxy or acyl peroxy radicals using SAPRC lumping methods, are not generated if such a lumping method is in effect. This is because their subsequent reactions are not considered when the explicit mechanism is processed for lumping, and generating these reactions results in unnecessarily large mechanisms that in some cases may cause problems with the mechanism reduction algorithms employed. For that reason, users who are primarily interested in complete explicit mechanism

Table 12.   Summary of lumping methods that are currently available

Short Name	Description
Explicit	No lumping of VOC products formed, and all non-negligible reactions are generated. However, the system uses the results to derive a minimally reduced "processed" mechanism that combines competing reactions of the same reactants into a single reaction and eliminates intermediates that undergo only unimolecular or pseudo-unimolecular reactions with O_2 that give the same predictions of the explicit mechanism at the reactor default temperature and pressure.
SAPRC22	This is the lumping method used to derive the standard version of the SAPRC-22 mechanism as described by Carter (2023a). Selected important compounds are represented explicitly, but most are represented using a limited number of lumped model species. Various chemical operator methods are used to minimize the numbers of reactive intermediates needed to represent the effects of varying NO_x and peroxy radical levels on product formation.
SAPRC22F	This is a modified version of SAPRC-22 described by Carter (2023a) that uses a somewhat more accurate method to represent effects of varying NO_x and peroxy levels on product formation, at the expense of requiring use of a significantly larger number of model species for this purpose. It gives essentially the same predictions as standard SAPRC22 of ozone and total radical levels and products formed from most compounds, but can give some differences in product yields from terpenes and several other compounds that may affect predictions of SOA precursors. See Carter (2023a) for a discussion of the differences.
SAPRC11	This is the lumping method used to derive the SAPRC-11 mechanism (Carter and Heo, 2013), which is almost the same as that used for SAPRC-07 (Carter, 2010a,b). It is similar to that used for standard SAPRC-22 except that SAPRC-11 uses a more approximate chemical operator approach to represent effects of product formation on NO_x and peroxy radical levels, which is not able to handle cases where there are competitions between unimolecular and bimolecular reactions of peroxy radicals. To handle these cases, this lumping approach uses an "Effective NO" concentration of 0.5 ppb to determine relative rates of unimolecular reaction compared to reactions with NO. This can be useful to derive estimates of reactivities of new compounds for SAPRC-07 or SAPRC-11 reactivity scales.

generations should employ the "Explicit" lumping option. Note, however, that the choice of lumping method does not affect single-step mechanism generation.

7.1. Selecting the Lumping Method

Web Interface. The top portion of the main menu indicates the lumping method that is currently selected and has a link that can be used to change the method used. This information and link is also given in the "Reactor options" section of the main menu. Selecting this link will give a page listing the available lumping methods, indicate which is currently selected, and have links allowing you to select a different one. Note that changing the lumping method will result in react completely results being erased for all reactants in the reactor. This is because these results may not be valid for the new lumping method.

<u>Telnet Interface</u>. The "option" command can be used to change the lumping method, as indicated on Table 8. The syntax of the command is

<p style="text-align:center">Option lumping is <lumping></p>

Where <lumping> must exactly match the short name of a lumping method such as shown on Table 12. No change is made if <lumping> does not match the short name of an available method. "Option lumping is default" restores the method to the default, which is explicit lumping. In addition, the "lumping" command, if given by itself, will indicate which lumping method is currently in effect, and give the user a list of numbered available lumping methods, and then ask the user to select a number to chose the method to be used. There will be no change made if the user provides no input or gives input other than the numbers in range.

7.2. Currently Available Lumping Methods

7.2.1. Explicit Lumping

Selecting "Explicit" as the lumping method means that you are choosing to have the system do no additional lumping beyond creating the minimally reduced mechanism that is created regardless of the lumping method employed. This is the default because this method results in all non-negligible reactions being generated during a complete reaction operation, and as such is most appropriate if complete explicit mechanisms are the primary interest of the user.

However, using explicit lumping method where all non-negligible reactions are generated could in some cases result "cycles" where reactions of an intermediate may ultimately result in formation of the same intermediate following several steps. As discussed above in Section 6.1, the algorithm used to derive product yields for the selected standard environments cannot properly handle such cycles of reactions, and will give inaccurate yields of products formed in the reactions involved. Currently, these only involve predictions of relative yields of products formed from reactions of phenoxy and phenyl peroxy radicals and of hydroperoxy-substituted peroxy radicals, but in both cases the overall effects are relatively minor. There are also cases in atmospheric chemistry where there are rapid interconversions of intermediates when OH or NO_3 adds to double or aromatic bonds, but the effects of these are incorporated when estimating the overall rate constants for these reactions (Carter, 2021).

If explicit lumping is in effect, the react completely and "fullreact" operations will not produce lumped mechanism output other than the for the minimally-reduced "processed" mechanism discussed above. Web users will not see links for outputting lumped mechanisms. Telnet users can still obtain "tabrxns" or "rxns" output (Table 7) discussed in Section 5.3, but the output will be exactly the same as "processed" or "procrxns" output, giving the minimally processed mechanism.

7.2.2. SAPRC Lumping

MechGen also provides optional lumping methods that can be used to derive lumped mechanisms that are compatible with versions of the SAPRC mechanism. As indicated on Table 12, these include two methods used for the SAPRC-22 mechanism (Carter, 2023a), which is the most recent SAPRC mechanism and the one derived using MechGen as documented by Carter et al (2023a) and discussed in this document. Standard SAPRC-22 lumping (named "SAPRC22") is compatible with the version that is recommended for general use in airshed modeling because it is much more efficient and has fewer intermediate model species than the "full" version of SAPRC-22 (named "SAPRC22F"), and gives essentially the same results in most cases. Choosing SAPRC22F lumping is primarily useful for sensitivity studies of condensation effects. See Carter (2023a) for more complete discussion of SAPRC-

22 and the differences between the two versions. The differences between the two SAPRC-22 lumping methods are also discussed in Section 11.1.1, below.

The system also provides an option to use the lumping method employed in the SAPRC-11 mechanism (Carter and Heo, 2012), which is essentially the same as used for SAPRC-07 (Carter et al, 2010a,b). Note that although lumped mechanisms derived using MechGen using SAPRC11 are compatible with the SAPRC-11 in that all the product model species formed in the lumped reactions are incorporated in those mechanisms, the resulting mechanisms for individual compounds or mixtures will be different than those used in SAPRC-11 because of updates to the estimation methods and assignments used in deriving the explicit mechanisms that are used as inputs for lumping that were made between the time SAPRC-11 was developed, compared to the current methods and assignments described by Carter et al (2023a). However, mechanisms derived by MechGen using SAPRC-11 lumping can be added to models using SAPRC-11 or SAPRC-07 if it is desired to have additional species represented explicitly in those models, such as, for example, estimating MIR or other reactivity values for compounds not on current SAPRC-07 or SAPRC-11 reactivity scales.

It should be noted that although SAPRC-11 and SAPRC-07 are very similar, there are differences. The main difference is that the reactions of aromatics are revised in SAPRC-11 to improve predictions of environmental chamber results, but this does not affect the lumping approach except for compounds that are unsaturated dicarbonyl ring-opening products. The differences that do affect lumping are as follows:

- Glycolaldehyde and acrolein are represented explicitly in the version of SAPRC-07 implemented in CMAQ, while they are lumped with acetaldehyde or with methacrolein and α-unsaturated aldehydes, respectively, in SAPRC-11. Mechanisms derived in MechGen using SAPRC11 lumping that form these products can be still be used with versions of SAPRC-07, but these two products would be represented by lumped species rather than explicitly.

- SAPRC-11 represents phenol explicitly (as PHEN) and uses separate model species to represent the three cresol isomers (as CRES) and uses a separate model species (XYNL) for all other phenolic compounds. These are all represented using the model species "CRES" in SAPRC-07 mechanisms. To be compatible with SAPRC-07, any PHEN and XYNL products should be replaced by CRES.

- The yields of the "AFG" model species used in SAPRC-07 and SAPRC-11 to represent unsaturated ring-opening products are derived by adjustments to fit chamber data in aromatic-NO_x chamber experiments (e.g., Carter, 2010a, Carter and Heo, 2012), and cannot be derived using the general estimation methods implemented in MechGen for SAPRC-22. Aromatic mechanisms derived using MechGen with SAPRC11 lumping will in most cases give yields of AFG products that are not consistent with those used in SAPRC-07 or SAPRC-11, and will either underestimate or (more often) overestimate the predicted effects of these compounds on radical levels. The SAPRC-22 approach implemented in MechGen for deriving aromatic mechanisms that does not require compound-by-compound adjustments, while still giving generally satisfactory predictions of available chamber data for most compounds (Carter, 2023a).

Because of incompatible treatments of the highly reactive aromatic ring-opening products, it is recommended that models using SAPRC-07 and SAPRC-11 *not* use aromatic mechanisms derived using MechGen with SAPRC11 lumping. However, mechanisms for non-aromatics should provide the best available estimate on how to represent such compounds explicitly in models using SAPRC-07 or SAPRC-11. For this reason, SAPRC11 lumping is provided as an option for MechGen users, despite the inability of MechGen to derive optimized mechanisms for aromatics for use with SAPRC-11.

All the lumped SAPRC mechanism represent acyl peroxy radicals using a limited number of model species, using MECO3 for acetyl peroxy, RCO3 or R2CO3 for higher saturated acyl peroxy, MACO3 for acyl peroxy radicals with double bonds, and BZCO3 for aromatic acyl peroxy radicals. Therefore, reactions of acyl peroxy radicals are not generated when carrying out complete reaction or "fullreact" operations using SAPRC lumping, and these radicals are output as final products, whose subsequent reactions are assumed to be incorporated in the base mechanism using lumped model species.

Likewise, the reactions all types of phenoxy radicals, i.e., all radicals that have which have -pC[O.] groups (Table 2) are represented using the "BZO" model species, whose reactions are incorporated in the base mechanism and thus their subsequent reactions are not generated. Note that this eliminates the "cyclic" problem in product yield estimation that results from interconversions of phenoxy and phenyl peroxy radicals in explicit mechanisms (see Section 6.1). SAPRC-22 also uses a BZO2 model species to represent phenyl peroxy radicals, but their only mode of formation in MechGen is from reactions of phenoxy radicals, so they are only formed in mechanisms generated with explicit (i.e., no) lumping.

The lumped mechanisms derived if a SAPRC lumping option is selected are displayed following a "react completely" operation using the web system, or by selecting appropriate links in the main menu or reactant results pages, or can be obtained using "tabrxns" or "rxns" output as indicated on Table 7 using the Telnet system. The differences between the "Tab-separated" or "tabrxns" output and the "RXN format" or "rxns" concern only the format of the output, but not the information contained, which consists of lists of reactant and intermediate model species that are not in the base mechanism and the generated lumped reactions and their rate constants. Note that the "RXN" or "rxns" output is compatible with mechanism preparation input used with the SAPRC modeling system, which is freely available for user download (Carter, 2023b).

"RXN" outputs using propene as the example compound are shown for the three SAPRC lumping methods on Figure 17. Note that propene is represented explicitly in both versions of SAPRC-22 using the model species "PROPE", while it is not represented explicitly in SAPRC-11, so its standard MechGen name is used with that mechanism. If the compound is explicit in the base mechanism and does not have a standard or ORG name (see Section 3.2), the name "VOC-n" is used, where n is a number that depends on what other species are in the reactor. It is also possible to assign model species names to compounds that are not explicitly represented in the lumped mechanism, using "user mechanism" options discussed in the next section.

Lumped SAPRC-22 mechanisms may require use of intermediate model species that are not part of the base mechanism, where use of the steady state approximation is appropriate. These are listed following the ".STS" line in the RXN output file. These are named by adding suffixes to the model species name used for the reactant, as shown on Figure 17a and b. Note that SAPRC22 only requires one additional species to represent reactions of propene, while SAPRC22F requires five. The maximum number of intermediate species is equal to the number of initial VOC reactions using standard SAPRC22 lumping, but can become quite large using SAPRC22F for larger molecules with complex mechanisms. Note that no additional intermediates are required for SAPRC11 lumping, so there is no ".STS" output line in Figure 17c.

The reaction listing format is the same regarding the lumping method, with the format for RXN files being as discussed in the SAPRC model software documentation (Carter, 2020a). The format in the tab-separate output is similar. Note that the formats used for lumped mechanisms are the same as the RXN or tab separate format for the minimally processed mechanisms that are obtained regardless of which lumping method is used.

```
                              (a) SAPRC22 Lumping
.STS
PROPE_O3

.RXN
R) 1.20e-11 -0.417 -0.62 ;PROPE + OH = #.97 xHO2 + #.97 RO2C + #.03 RO2XC + #.97 xHCHO + #.97 xMECHO + #.03 zRHNO3 + yROOH +
                          SumRO2
R) 5.77e-15 3.736  0.00  ;PROPE + O3 = PROPE_O3 + #.3 OH + #.17 HO2 + #.16 xHO2 + #.03 MEO2 + #.21 HCHO2 + #.12 MECHO2 +
                          #.22 RO2C + #.5 HCHO + #.05 xHCHO + #.05 MEOH + #.5 MECHO + #.09 H2 + #.22 CO + #.24 CO2 + #.09 CH4 +
                          #.25 SumRO2
R) 2.53e+0               ;PROPE_O3 = #.05 xOH + #.16 xPACID + #.05 CO2
R) 2.55e-12 -0.755 0.00  ;PROPE_O3 + NO = NO + #.06 xHO2 + #.17 xHCHO + #.22 CO
R) 4.60e-13 2.295  0.00  ;PROPE + NO3 = #.97 xNO2 + #.68 xHO2 + #.29 RO2C + #.71 RO2XC + #.29 xHCHO + #.29 xMECHO + #.68 zRCNO3 +
                          #.03 zRDNO3 + yRPNO3 + SumRO2
R) 1.02e-11 0.556  0.00  ;PROPE + O3P = #.25 ETCHO + #.25 ACET + #.5 ALK2

.RENAME PROPE PROPENE
```

```
                              (b) SAPRC22F Lumping
.STS
PROPE_R1
PROPE_R2
PROPE_R4
PROPE_R3
PROPE_R5

.RXN
R) 1.20e-11 -0.417 -0.62 ;PROPE + OH = #.85 PROPE_R1 + #.15 PROPE_R2 + SumRO2
R) 5.77e-15 3.736  0.00  ;PROPE + O3 = #.22 PROPE_R4 + #.3 OH + #.17 HO2 + #.03 MEO2 + #.21 HCHO2 + #.12 MECHO2 + #.5 HCHO +
                          #.05 MEOH + #.5 MECHO + #.09 H2 + #.22 CO + #.24 CO2 + #.09 CH4 + #.25 SumRO2
R) 4.60e-13 2.295  0.00  ;PROPE + NO3 = PROPE_R3 + SumRO2
R) 1.02e-11 0.556  0.00  ;PROPE + O3P = #.25 ETCHO + #.25 ACET + #.5 ALK2
R) 9.13e-12             ;PROPE_R1 + NO = #.97 NO2 + #.97 HO2 + #.97 HCHO + #.97 MECHO + #.03 RHNO3
R) 2.30e-12             ;PROPE_R1 + NO3 = NO2 + HO2 + HCHO + MECHO
R) 1.44e-11             ;PROPE_R1 + HO2 = ROOH
R) 1.69e-13             ;PROPE_R1 + SumRO2 = #.5 HO2 + #.5 HCHO + #.5 MECHO + #.25 KET2 + #.25 ALK5
R) 1.60e-11             ;PROPE_R1 + SumRCO3 = #.8 HO2 + #.8 HCHO + #.8 MECHO + #.2 KET2
R) 9.13e-12             ;PROPE_R2 + NO = #.97 NO2 + #.97 HO2 + #.97 HCHO + #.97 MECHO + #.03 RHNO3
R) 2.30e-12             ;PROPE_R2 + NO3 = NO2 + HO2 + HCHO + MECHO
R) 1.44e-11             ;PROPE_R2 + HO2 = ROOH
R) 9.14e-14             ;PROPE_R2 + SumRO2 = #.5 HO2 + #.5 HCHO + #.5 MECHO + #.25 RCHO + #.25 ALK5
R) 1.60e-11             ;PROPE_R2 + SumRCO3 = #.8 HO2 + #.8 HCHO + #.8 MECHO + #.2 RCHO
R) 9.13e-12             ;PROPE_R3 + NO = #1.26 NO2 + #.68 HO2 + #.29 HCHO + #.29 MECHO + #.68 RCNO3 + #.03 RDNO3
R) 2.30e-12             ;PROPE_R3 + NO3 = #1.3 NO2 + #.7 HO2 + #.3 HCHO + #.3 MECHO + #.7 RCNO3
R) 9.92e-12             ;PROPE_R3 + HO2 = RPNO3
R) 1.56e-14             ;PROPE_R3 + SumRO2 = #.15 NO2 + #.35 HO2 + #.15 HCHO + #.15 MECHO + #.25 zRHNO3 + #.6 RCNO3
R) 1.60e-11             ;PROPE_R3 + SumRCO3 = #.24 NO2 + #.56 HO2 + #.24 HCHO + #.24 MECHO + #.76 RCNO3
R) 6.02e+7 10.052 0.00  ;PROPE_R4 = PROPE_R5 + SumRO2
R) 2.55e-12 -0.755 0.00 ;PROPE_R4 + NO = NO2 + HO2 + #.94 HCHO + #.06 GLY + #.94 CO
R) 2.30e-12             ;PROPE_R4 + NO3 = NO2 + HO2 + #.94 HCHO + #.06 GLY + #.94 CO
R) 7.44e-12             ;PROPE_R4 + HO2 = #.15 OH + #.15 HO2 + #.14 HCHO + #.01 GLY + #.85 HPCRB + #.14 CO
R) 2.90e-14             ;PROPE_R4 + SumRO2 = #.5 HO2 + #.47 HCHO + #.25 GLCHO + #.28 GLY + #.47 CO
R) 1.60e-11             ;PROPE_R4 + SumRCO3 = #.8 HO2 + #.75 HCHO + #.25 GLY + #.75 CO
R) 2.55e-12 -0.755 0.00 ;PROPE_R5 + NO = NO2 + #.25 OH + #.75 HO2 + #.25 HCHO + #.75 PACID + #.25 CO2
R) 2.30e-12             ;PROPE_R5 + NO3 = NO2 + #.25 OH + #.75 HO2 + #.25 HCHO + #.75 PACID + #.25 CO2
R) 1.27e-11             ;PROPE_R5 + HO2 = #.19 OH + #.11 HO2 + #.04 HCHO + #.96 PACID + #.04 CO2
R) 9.14e-14             ;PROPE_R5 + SumRO2 = #.13 OH + #.37 HO2 + #.13 HCHO + #.87 PACID + #.13 CO2
R) 1.60e-11             ;PROPE_R5 + SumRCO3 = #.2 OH + #.6 HO2 + #.2 HCHO + #.8 PACID + #.2 CO2

.RENAME PROPE PROPENE
```

```
                              (c) SAPRC11 Lumping
.RXN
R) 1.20e-11 -0.417 -0.62 ;PROPENE + OH = #.97 xCCHO + #.97 xHCHO + #.97 xHO2 + #.03 zRNO3 + #.97 RO2C + #.03 RO2XC + yROOH
R) 5.77e-15 3.736  0.00  ;PROPENE + O3 = #.5 CCHO + #.21 HCOOH + #.17 HO2 + #.25 OH + #.27 CO2 + #.09 H2 + #.22 CO + #.5 HCHO +
                          #.17 CCOOH + #.03 MEO2 + #.09 CH4 + #.05 MEOH + #.05 xHCHO + #.01 xCO + #.12 xHO2 + #.16 RO2C +
                          #.12 xMGLY + #.04 xOH
R) 4.60e-13 2.295  0.00  ;PROPENE + NO3 = #.29 xCCHO + #.29 xHCHO + #.71 zRNO3 + #.68 xHO2 + #.97 xNO2 + #.29 RO2C + #.71 RO2XC
R) 1.02e-11 0.556  0.00  ;PROPENE + O3P = #.5 ALK2 + #.25 RCHO + #.25 ACET
```

Figure 17.   SAPRC lumped mechanisms derived for propene.

7.3. User Modified SAPRC-22 Mechanisms

MechGen provides the capability to modify the SAPRC22 lumping method to have it represent selected individual compounds explicitly, rather than using lumped species, in lumped mechanisms that are generated. This is not necessary when using outputs of "react completely" or "fullreact" procedures for single compounds because they are already represented explicitly in the output, but is necessary if it is desired to have important products formed in reactions of the selected compound(s) also represented explicitly. Users can then output the mechanisms generated for the selected compounds and their explicitly-represented products, with or without the other reactions in the base SAPRC-22 mechanism, which can serve as inputs to SAPRC mechanism simulation software (Carter, 2020a, 2023b). If the user selects to include the base reactions, the mechanism output will include the inorganic + C_1 reactions in the base SAPRC-22 mechanism, plus reactions of the SAPRC-22 model species that are needed to represent any other organic products or intermediates the selected compounds or products may form. This capability is available through both the web and Telnet interface, but is currently only available when standard SAPRC22 lumping is selected, though in principle it could be incorporated using other SAPRC lumping methods if there is sufficient interest.

This process is referred to as preparing a "users mechanism" that consists of providing a list of compounds to be represented explicitly. The process of preparing users mechanisms involves the following steps:

- Select SAPRC22 as the lumping method if it is not already selected. The web system will have no link to create users mechanisms, and the "usermech" terminal command will fail, if SAPRC22 has not been selected.

- Use web interface or terminal commands to create the users mechanism by providing the list of explicitly represented compounds or organic products, giving the model species name to use for them if necessary. Note that it is necessary to specify a model species name for the compound if it does not have a standard MechGen or ORG name (see Section 3.2). This will add the compounds to the reactor. If they already exist in the reactor, results of previous "react completely" processes will be deleted, because the lumping method has been modified. These are referred to as the "user mechanism compounds" in the subsequent discussion.

- React all the selected compounds. This can be done on a compound-by-compound basis as discussed in Sections 4.4 or 5.3, though there are web and telnet commands to react user mechanism compounds more conveniently. However, this should be done only after all the compounds in the users mechanism have been specified, because the results of previous reaction generations are deleted when new user mechanism compounds are added.

- Once all the user mechanism compounds are reacted, web links or terminal commands can be used to output the users mechanism species lists and reactions in text files in the RXN format useable by the SAPRC modeling software. The format of these files is the same as those output using the lumped mechanism RXN format files as discussed above in Sections 4.4 or 5.3.

As indicated above, each compound in the users mechanism must have a model species name to use when representing it in the lumped mechanism. As discussed in Section 3.2, many compounds have standard SAPRC names, and these are used for compounds that have been assigned for such names. If the user specifies a different name when creating a user mechanism with that compound, the user-specified name is ignored and the standard name is used instead. However, the model species name is required input if the reactant does not have a standard SAPRC name, even if the compound has been assigned a permanent ORG-nnnn name. The web system will add the reactant but not process the user mechanism further until a name is input, while the telnet system will reject input that does not provide name input

when it is required. In this case, the user must come up with a name that satisfies the following requirements:

- 2-8 characters in length, consisting only of alphanumeric characters or "_". MechGen converts all alphabetic characters to uppercase.

- The name must not match any model species name used in the SAPRC-22 mechanism, nor any name assigned to another compound in this user mechanism.

- If the name has an "x", "y", or "z" as its first character, the rest of the name must not match any SAPRC-22 model species name or any other user mechanism name. In addition, the names cannot have "_OH", "_O3", "_N3", "_OP" or "_HV" as suffixes. This is because such names may conflict with chemical operator names used in SAPRC-22.

Note that the SAPRC mechanism preparation programs (Carter, 2020a) treat names as case-sensitive, so case matters in names assigned to user mechanism species. However, the match operations that MechGen uses to determine if a proposed name is already in use is not case sensitive, so names that differ only in case with SAPRC-22 or other names also must be avoided.

Three options are available for outputting users mechanism reactions in a RXN file once the mechanism is complete and reacted, as follows:

1. The RXN file contains only the reactions of the users mechanism species. An example of such output is shown on Figure 18, which shows a user mechanism with n-butane and selected major products created as shown on Figure 19c in Section 7.3.1 and Figure 20 in section 7.3.2, below.

2. The RXN file also contains the portions of the base standard SAPRC-22 mechanism representing the reactions of the inorganics and C_1 compounds and the reactions of the products and intermediates formed in the reactions of the user mechanism species or intermediates that are not part of the users mechanism. This is sufficient for providing all the mechanism preparation input to produce mechanisms that can simulate reactions of the user mechanism compounds and the products that they form. However, it is not sufficient if the model application will require representation of reactions of other C_{2+} organic compounds.

3. The RXN file contains the complete standard SAPRC-22 mechanism as well as the reactions of the user mechanism species. If any user mechanism species is represented explicitly in the base mechanism, it is not included in the base mechanism portion of the output. Note that if any other organic compounds form any of the user mechanism species, they are represented using the lumped SAPRC-22 model species assigned to them. If it is desired that they be explicitly, the additional compounds(s) will need to be included in the user mechanism.

If a user mechanism has been created, the lumping method is modified such that if any user mechanism species are formed as products when any compound is fully reacted, they are represented explicitly using their associated model species name in the lumped version of the mechanism that is produced, not by the lumped model species normally used for it in the default lumping. However, the lumping results are not affected if the user mechanism compound is already represented explicitly in the base mechanism. This remains the case until the user mechanism is deleted or until a different lumping method is selected. Selecting a different lumping method results in deleting the user mechanism, and it is no longer available even when the lumping method is restored to its previous value.

User mechanisms can be created and their results obtained using either the web or telnet interface, and a user mechanism created with either interface is available to both. These are implemented as objects in the users reactors, and only affect operations in that reactor. Therefore users mechanisms

```
! User mechanism in User1's mechanism creator generated using Standard SAPRC-22 lumping
!
.ACT
= NC4 + MEK + 1C4RCHO + 2C4-ONO2 + C4P1
!
.STS
= z2C4-ONO2 + x1C4RCHO + xC4P1
!
.RXN
! User mechanism
!
R) 2.09e-12 -0.083 1.82  ;NC4 + OH = #.02 x1C4RCHO + #.09 xC4P1 +
                          #.06 z2C4-ONO2 + #.59 xHO2 + #.33 xETO2 +
                          #1.02 RO2C + #.08 RO2XC + #.33 xMECHO + #.48 xMEK +
                          #.01 zR1NO3 + #.01 zRHNO3 + #1.1 yROOH +
                          #1.1 SumRO2
!
R) 5.42e-14 -1.767 3.57  ;MEK + OH = #.29 xHO2 + #.55 xMECO3 + #.08 xR2CO3 +
                          #.94 RO2C + #.07 RO2XC + #.12 xHCHO + #.54 xMECHO +
                          #.29 xRCHO + #.07 zRCNO3 + #.91 yHPCRB +
                          #1.01 SumRO2
R) PF=MEK-06 QY=1.75e-1  ;MEK + HV = #.15 MEO2 + #.85 ETO2 + #.85 MECO3 +
                          #.15 R2CO3 + SumRO2 + SumRCO3
!
R) 2.75e-13 -2.649 2.65  ;1C4RCHO + OH = #.01 OH + #.01 xOH + #.08 xHO2 +
                          #.9 R2CO3 + #.13 RO2C + #.01 xHCHO + #.04 xMECHO +
                          #.05 xETCHO + #.04 xPACID + #.05 CO + #.01 CO2 +
                          #.01 ALK3 + #.05 yHPCRB + #.13 SumRO2 + #.9 SumRCO3
R) 1.70e-12 2.981  0.00  ;1C4RCHO + NO3 = HNO3 + R2CO3 + SumRCO3
R) PF=C2CHOabs           ;1C4RCHO + HV = HO2 + #.96 xHO2 + #.96 RO2C +
                          #.04 RO2XC + #.96 xETCHO + #.04 zR1NO3 + CO +
                          yROOH + SumRO2
!
R) 8.60e-13             ;2C4-ONO2 + OH = #.32 xNO2 + #.4 NO2 + #.24 xHO2 +
                          #.72 RO2C + #.04 RO2XC + #.63 xMECHO + #.4 MEK +
                          #.15 xRHNO3 + #.08 xRCNO3 + #.04 zRDNO3 +
                          #.76 yRPNO3 + #.76 SumRO2
R) PF=IC3ONO2           ;2C4-ONO2 + HV = NO2 + #.59 HO2 + #.41 ETO2 +
                          #.41 MECHO + #.59 MEK + #.41 SumRO2
!
R) 3.12e-11             ;C4P1 + OH = #.14 HO2 + #.16 xHO2 + #.7 R2CO3 +
                          #.16 RO2C + #.01 RO2XC + #.12 xHCHO + #.14 RCHO +
                          #.04 xRCHO + #.12 xPACID + #.01 zRCNO3 + #.04 CO +
                          #.04 yHPCRB + #.17 SumRO2 + #.7 SumRCO3
R) 1.85e-14             ;C4P1 + NO3 = HNO3 + #.1 HO2 + #.9 R2CO3 + #.1 RCHO +
                          #.9 SumRCO3
R) PF=C2CHOabs          ;C4P1 + HV = HO2 + #.96 xHO2 + #.96 RO2C +
                          #.04 RO2XC + #.96 xRCHO + #.04 zRHNO3 + CO + yROOH +
                          SumRO2
!
! Operators in user mechanism
!
R)    SAMEK R2NO        ;z2C4-ONO2 + NO = NO + 2C4-ONO2
R)    SAMEK R2H2        ;z2C4-ONO2 + HO2 = HO2
R)    SAMEK R2N3        ;z2C4-ONO2 + NO3 = NO3 + KET2 + HO2
R)    SAMEK R2R2        ;z2C4-ONO2 + SumRO2 = SumRO2 + #.5 KET2 + #.5 HO2
R)    SAMEK R3R2        ;z2C4-ONO2 + SumRCO3 = SumRCO3 + KET2 + HO2
!
R)    SAMEK R2NO        ;x1C4RCHO + NO = NO + 1C4RCHO
R)    SAMEK R2H2        ;x1C4RCHO + HO2 = HO2
R)    SAMEK R2N3        ;x1C4RCHO + NO3 = NO3 + 1C4RCHO
R)    SAMEK R2R2        ;x1C4RCHO + SumRO2 = SumRO2 + #.5 1C4RCHO
R)    SAMEK R3R2        ;x1C4RCHO + SumRCO3 = SumRCO3 + 1C4RCHO
!
R)    SAMEK R2NO        ;xC4P1 + NO = NO + C4P1
R)    SAMEK R2H2        ;xC4P1 + HO2 = HO2
R)    SAMEK R2N3        ;xC4P1 + NO3 = NO3 + C4P1
R)    SAMEK R2R2        ;xC4P1 + SumRO2 = SumRO2 + #.5 C4P1
R)    SAMEK R3R2        ;xC4P1 + SumRCO3 = SumRCO3 + C4P1
.
```

Figure 18.   Example of user mechanism reactions using the example mechanism with n-butane and its selected reaction products discussed in the following systems.

and lumping modifications do not affect users mechanisms or lumping for any other user. The following sections discuss the process of working with users mechanisms utilizing the web or telnet interfaces.

7.3.1.   Managing User Mechanisms using the Web Interface

The main menu will indicate which lumping method is in effect, and has links to change the lumping method. This link should be used to change the method to standard SAPRC-22 if it is not already in effect (see Section 7.1). Once standard SAPRC-22 is selected, the main menu will contain a "Manage your users mechanism" link in the "Advanced options" section. It will also indicate the number of user mechanism compounds that it includes at this point, which initially will be zero.

Examples of portions of web pages displayed when selecting the "manage your users mechanism" link are shown on Figure 19. Figure 19a shows the display if there are no compounds in the mechanism. To add a compound, give the name or structure of the compound, using the same format as used when creating a new compound as discussed in Section 3. If the compound does not have a standard name, the model species name can be given following the name or structure of the compound, separated by a space. It is not necessary to give a model species name if the compound has a standard name, and the standard name is used for the model species name even if a different name is input. Model species names will also be rejected if they are used in the base mechanism or already assigned to a different user mechanism species. If the compound has no standard name and one is not specified, the compound is added to the users mechanism but the user will need to give a name before the mechanism is complete, and it will not be possible to add new user mechanism model species that do not have standard names.

Once a compound is added to the users mechanism, it is created in the reactor and the users mechanism page will be updated to show the new compound. An example of a users mechanism display with an incomplete users mechanism for n-butane and its major products where a name is needed for a users mechanism compound is shown on Figure 19b. Note that there is an input box to give the name for the users mechanism compound that does not have a standard name. Once this is input, the page is updated to show the name with the structure of the compound, and there will be links to react all the compounds.

Note that the user has the option to modify the ordering of the compounds on the list by clicking the "(first)" link for the compound to be first on the list. This only affects the ordering of the species and reactions that are output when the users mechanism is complete, and has no effect on the actual mechanisms produced.

After all the compounds desired for the users mechanism have been input as discussed above, the "(react)" link must be selected for each compound, which will cause their reactions to be generated and processed using the modified lumping where the users mechanism product compounds are represented explicitly using their assigned model species names. Once this is completed, the users mechanism display is as shown on Figure 19c, indicating how many species and reactions are in the lumped mechanisms for each, and with links to output the results. There is also a link to send a text file with the terminal commands that telnet users can employ to re-create this users mechanism in case it is deleted. However, users mechanisms created using the web system will also be available to the user when logged into the telnet system, and vise-versa.

(a) Output if no users mechanism defined

Currently no explicit species are specified for User1's user mechanism.

Add structure and (if needed) model species name for an explicit species in the users mechanism.
(Note that many common compounds are already assigned model species names, so names you give will be ignored.)
(Click here for instructions)

| | Add |

(a) Output if a users mechanism is incompletely defined

Explicit species for user1's user mechanism.

Name	Structure	Lumped Rxns	Action
NC4	CH3-CH2-CH2-CH3	(not reacted)	(remove) (view)
MEK	CH3-CH2-CO-CH3	(not reacted)	(remove) (view) (first)
1C4RCHO	CH3-CH2-CH2-CHO	(not reacted)	(remove) (view) (first)
2C4-ONO2	CH3-CH2-CH(CH3)-ONO2	(not reacted)	(remove) (view) (first)
HCO-CH2-CH2-CH2-OH		Name: [ ] Give name	(remove) (first)
Add Species			

(Click here for instructions)

Actions:

- Mechanism is incomplete because some reactants have not reacted or been assigned valid names

- Delete this user mechanism.
- Clear reaction data but keep the species list.

(a) Output if users mechanism is complete and reacted

Explicit species for user1's user mechanism.

Name	Structure	Lumped Rxns	Action
NC4	CH3-CH2-CH2-CH3	1 spec, 1 rxns	(remove) (view) (react)
MEK	CH3-CH2-CO-CH3	1 spec, 2 rxns	(remove) (view) (react) (first)
1C4RCHO	CH3-CH2-CH2-CHO	1 spec, 3 rxns	(remove) (view) (react) (first)
2C4-ONO2	CH3-CH2-CH(CH3)-ONO2	1 spec, 2 rxns	(remove) (view) (react) (first)
C4P1	HCO-CH2-CH2-CH2-OH	1 spec, 3 rxns	(remove) (view) (react) (first)
Add Species			

(Click here for instructions)

Actions:

- Send file with mechanisms for only the above-listed species.
- Send file with mechanisms for these species and the species in the SAPRC-22 mechanism that they form.
- Send the complete SAPRC-22 mechanism with reactions of these species added.

- Delete this user mechanism.
- Clear reaction data but keep the species list.
- Send commands to create this users mechanism using the telnet interface

Figure 19. Examples of portions of web pages used to create or manage a users mechanism for reactions of n-butane and its major products. This is the same mechanism as shown on Figure 18.

7.3.2. Managing User Mechanisms using the Telnet Interface

The telnet interface is necessary for preparing user mechanisms with compounds that are too large to be fully reacted using the web interface, and is more efficient for preparing user mechanisms with many compounds. The commands that can be used to create, delete, react, and output results for user mechanisms using the telnet interface are listed and summarized in Table 13.

As indicated on Table 13, the "usermech create" command is used to provide the list of compounds to be explicitly in the users mechanism, and the model species name to use for it in the lumped mechanism, if it is needed. The compound is specified either by using either its MechGen structure as described in Section 3.1 or its standard SAPRC name if it has one (see Section 3.2). If the compound does not have a standard SAPRC name then the model species name must also be on the input line, separated from the compound structure designation by a space. The command will fail and no user mechanism is created if a needed model species name is not given. Model species names do not need to be specified if the compound already has a standard SAPRC name, and if a different name is given for such compounds then a warning message is output indicating that that the standard name is used instead. If the command is successful, the compounds will be created in the reactor if they do not already exist, and the system will output a summary of the compounds and their model species names in the user mechanism.

Note that the Telnet interface does not provide a means to delete single compounds from the user mechanism, or to add new compounds to the list. The "usermech create" command needs to be run again with all the species input if any changes are desired.

Figure 20 shows two examples of the input that creates a users mechanism with n-butane and selected major products it forms, which is the same user mechanism as Figure 19 for the web system and whose output is shown on Figure 18. Figure 20a shows input when all species are specified using structures, while Figure 20b shows input that designates species specified using standard names when applicable. Note that the 4th compound, $HCO(CH_2)_nOH$, does not have a standard MechGen name, so both its structure and model species name must be given in both cases.

(a) Input using structures for all compounds	(b) Input using names where applicable.

```usermech create```
```CH3-CH2-CH2-CH3 NC4```
```CH3-CH2-CO-CH3 MEK```
```CH3-CH2-CH2-CHO 1C4RCHO```
```HCO-CH2-CH2-CH2-OH C4P1```
```.```
	```usermech create```
	```N-C4```
	```MEK```
	```1C4RCHO```
	```HCO-CH2-CH2-CH2-OH C4P1```
	```.```

Figure 20.   Example of terminal input used to create a user mechanism consisting of n-butane and its major products. This gives the same mechanism as shown on Figure 18.

Table 13. Commands used to create and work with user mechanisms using the telnet interface

Command	Description
Usermech create <reactant1> [<name1>] <reactant2> [<name2>] .	Creates a new users mechanism, deleting any that may previously exist. The "usermech create" command causes the system to prompt for lines giving names or structures for reactants and (if needed) the model species name, separated by a space. A "." line terminates this input. The reactants will be created in the reactor if they do not already exist. Previously generated results of all reactants in the reactor, including those not in the user mechanism, will be deleted. Examples are shown on Figure 20.
Usermech react	Reacts all reactants in the users mechanism. This is necessary before any output can be obtained from the users mechanism
Usermech	Lists compounds and model species names in the users mechanism, and indicated if they have been reacted and the results are available for output.

Read <option> on usermech
Fileout <option> on usermech
@ftpout <option> on usermech

	Outputs lumped reactions produced when reacting all compounds in this user mechanism, optionally including portions of or the entire base SAPRC-22 mechanism that are needed for complete mechanism preparation. These outputs are in the format that can be used as inputs to the SAPRC mechanism preparation program that can prepare mechanisms to conduct simulations using the user mechanism. The "read" commands results in outputs going to the terminal, while "@ftpout" results in the results going to the MechGen FTP site for authorized users. The available options are as follows:
<option> = rxns	Output only the species list and reactions of the user mechanism compounds and intermediate model species (if any) that are not part of the base mechanism.
<option> = needrxns	Also include the base mechanism for inorganics and C_1 species and reactions in the base mechanism that are needed to represent reactions of all the products that they form. This is sufficient to prepare mechanisms to simulate reactions of the user mechanism species, but not necessarily of other compounds represented in the complete mechanism.
<option> = allrxns	Also includes all reactions in the complete base mechanism, which can be used as a new complete version of the mechanism representing the user compounds explicitly. Note that if the base mechanism represents any user compound explicitly, its reactions are replaced by those in the user mechanism.
<option> = cmds	Outputs the "usermech create" input that can be used to re-create this user mechanism in case it is deleted. This may be useful for large user mechanisms.

8.   USER ASSIGNMENTS

Whenever MechGen derives reactions of a given reactant, it first examines whether assignments are available for reactions of the reactant, and if so it uses these to derive the reactions rather than using the general estimation methods that are employed otherwise (Carter et al, 2024). Assignments can include rate constants for various types of reactions that the reactant can undergo, products formed in the reactions, or branching ratios if there are competitive processes. This permits use of available experimental or theoretically calculated data rather than estimation methods when such data are available, and is also useful in specifying mechanisms for unique compounds for which general estimation methods are not useful. Although MechGen provides for the possibility of having alternative mechanism assignment databases, the current system uses the SAPRC-22 mechanism assignments as described by Carter et al (2023a). These assignments can be viewed using the web interface as described in Section 4.6.

Although only the primary MechGen user can modify the default mechanism assignments, other MechGen users can employ "user assignments" to add to or override the default SAPRC-22 assignments. This might be useful for advanced users who wish to derive mechanisms employing rate constants or branching ratios that are not currently assigned or estimated, for the purpose of developing new mechanisms consistent with new data or theories, or modeling experimental data that appear to be inconsistent with default MechGen predictions.

User assignments are disabled by default, but can be enabled using either the web or telnet system as described below. Once enabled, assignments for rate constants or branching ratios can be added to the user assignments. When a reactant is reacted (whether single step or complete reaction) when user assignments are enabled, the system first examines the user assignment set to determine it has assignments for the reactant, and uses these rather than the default assignments if they are found. The default assignment set is used if assignments for the reactant are not included in the user assignments, with general estimation methods being used if no assignments are found for the reactant.

If user assignments are enabled but have no assignments, the generated reactions are the same as would be the case if user assignments did not exist or were disabled. User assignments are referenced and retrieved giving a reactant structure, so user if assignments have been made for a reactant then the default assignments are not used for that reactant, even if they are for a different type of reaction. For example, if the default assignment set has assigned rate constant for reactions with OH, O_3, and NO_3, and a user assignment is given for the OH rate constant but not the others, then the default assignments for the O_3 and NO_3 reactions are ignored, and the rate constants are derived using general estimation methods. For this reason, it is important to determine the default assignments for any reactant before giving any user assignments for the reactant, and then add any of the assignments that are to be retained as part of the user assignment input.

User assignments can be disabled or deleted at any time, after which mechanisms are generated using only the default (currently SAPRC-22) assignments. If they are disabled, the user assignments are not deleted, and will become applicable again if user assignments are re-enabled. However, deleting user assignments results in any previous assignments being lost, and all assignments have to be input when user assignments are next enabled.

8.1. Making Assignments

Assignments are input using single-line ~~assignment commands~~, each specifying either an overall rate constant for the reaction of a compound or the relative rate constant for formation of a particular set of products. These are the same regardless of whether the web or telnet access is used, and are described on Table 14. These commands can be input one at a time using the web system as described in Section 8.2, or as terminal commands using the telnet interface as described in Section 8.3, with the format of the commands being the same in either case. Note that user assignments need to be enabled before giving user assignment input -- this is done automatically in the web system when the link is selected to enable or edit user assignments, or when assignment commands are given to the terminal (Section 8.3)[3].

Several representative examples of the various assignment commands summarized on Table 14 are indicated below. Note that these examples are not necessarily current SAPRC-22 assignments, but are sufficient for illustrative purposes.

Assignments of total rate constants

1) k-assign-OH CH3-CHO is A=5.200e-12 Ea=-0.640 ref=Recommended by Calvert et al (2015).

2) k-assign-NO3 ACETALD is A=1.400e-12 Ea=3.696 REF=From the Compilation of McGillen et al (2020)

3) k-assign-HV CH3-CO-CH3 is phot=ACET-06 qy=0.5 ref=Absorption cross sections and quantum yields in the ACET-06.PHF file from IUPAC (2015), but the overall photolysis rate is multiplied by a factor of 0.5 to better fit environmental chamber data.

Assignments of reactions and rate constants

4) k-assign-rxn CH3-C[O.](OH)-OH = HO-CO-OH + CH3. is A=5.0e+13 Ea=7.367 ref=Derived from theoretical results given by Vereecken and Peeters (2009).

5) k-assign-rxn CO*-CO-CO-O-CO* -> CO2 + CO + CO + CO is fast ref=Assumed to rapidly undergo this endothermic decomposition.

6) k-assign-rxn CH[O.]*-O-O* -> CO + HO2 is fast ref=Expected to be the major process.

Assignments of branching ratios

7) k-assign-rxn CH3-CHO + OH = H2O + CH3-CO. is fac=0.95 ref= based on IUPAC (2009).
   k-assign-rxn CH3-CHO + OH = H2O + .CH2-CHO is fac=0.05 ref=see above.

8) k-assign-rxn HV CH3-CO-CH3 = CH3-CO. + CH3. is fac=1.0 ref=Assume all reaction is C-CO bond scission

9) k-assign-rxn .CH=CH-OH + O2 = HCO-OH + HCO. is fac=0.33 ref=Carter et al (1995).
   k-assign-rxn .CH=CH-OH + O2 = HCO-CHO + OH is fac=0.67 ref=See above.

10) nitrate-assign CH3-CH(CH3)-C[OO.]*-CH2-CH=C(CH2-OH)-CH2-CH2* is fac=0.25 ref=Adjusted to fit chamber data for sabinene.

Table 15 summarizes the types of assignment commands that can be used for the various types of reactions. The following should be noted regarding assignments and assignment input:

---

[3] This is not the case when the primary MechGen user is issuing the assignment commands using the Telnet interface. In this case, the assignments input are added to the currently active assignments, which could be the SAPRC-22 assignments if user assignments are not enabled.

Table 14.   Summary of the command lines for inputting mechanism assignments into the SAPRC
mechanism generation system.

Assignment of total rate constants for atmospheric reactions of stable compounds

k-assign-*(ox) (compound)* is *(kinetic parms)* ref=*(doc)* [a]

where

(ox): an atmospheric oxidant. Currently supported are OH, O3, NO3, O3P, or Cl.

(compound): structure or recognized detailed model species name for a stable compound

(kinetic parms): parameters for calculating absolute rate constants, optionally as follows:
  k=(temperature-independent rate constant in cm, molec, sec units), or:
  A=(A factor in cm, molec, sec units) (not given if T-independent)
  Ea=(activation energy in kcal/mole) or EaT=(activation energy in deg K) (default=0)
  B=(B factor, where $k=A*e(-Ea/Rt)*(T/300)^B$) (default=0)

(doc): a *character* string giving the citation, documentation, or reason for the assignment.

Assignments of photolysis parameters

k-assign-HV *(compound)* is phot=*(phot file)* [QY=*(overall quantum yield)*] ref=*(doc)*

where

(phot file): File with absorption cross-section wavelength-dependent quantum yield data
(overall quantum yield) (optional): wavelength-independent quantum yield. Default is 1.

Assignment of mechanisms, branching ratios, or rate constants for individual reactions

k-assign-rxn *(reactants) = (products)* is *(kinetic parms)* ref=*(doc)* or
k-assign-rxn *(reactants) = (products)* is fac=*(ratio)* ref=*(doc)* or
k-assign-rxn *(reactants) = (products)* is fast ref=*(doc)*

where

(reactants): structures of reactants, separated by " + "'s.
(products): structures of the products, separated by " + "'s
(kinetic parms): same as in 'k-assign-(ox)' if a total rate constant is being assigned, or
(ratio): relative amount of formation of these products from these reactants
fast: This reaction is fast and the only reaction of the reactant(s)

Assignments of nitrate yields in peroxy + NO reactions:

nitrate-assign *(radical)* is fac=*(nitrate yield)* ref=*(doc)*

where

(radical): the structure of a peroxy radical
(nitrate yield): The yield of the organic nitrate in the peroxy + NO reaction, and must be between
  0 and 1. The competing alkoxy-forming reaction is given a yield of 1-(nitrate yield).

Table 15.   Summary of assignment commands that can be used for various types of reactions.

Type of reaction	Command	Discussion
VOC + *ox*	k-assign-*ox*	Gives total rate constant for reaction of a stable compound with an oxidant, where *ox* = OH, O_3, NO_3, O^3P, or Cl.
	k-assign-rxn	Gives reactions and branching ratio (with "fac=" keyword). A "k-assign-*ox*" command is also required to give the total rate constant if branching ratios are assigned. See note [a]
VOC + HV	k-assign-rxn (with "phot=" and "fac=")	Only way to make assignments for photolysis reactions. Photolysis set ("phot="), factor, reaction must be given. QY is optional. See note [a].
Unimolecular or O_2 reactions [b]	k-assign-rxn (with kinetic parms)	Only way to make assignments for unimolecular reactions. Both the rate parameters and the reaction can be given. See note [c].
Fast unimolecular or O_2 reaction	k-assign-rxn (with "fac=" or "fast")	Used to indicate a reaction or set of reactions that dominate(s) over competing processes. This can be used to assign fast unimolecular or O_2 reactions for any species or radical. See note [d].
Peroxy + NO	Nitrate-assign (with "fac=")	Used to assign nitrate yields in peroxy + NO reactions, with the "fac=" input indicating the nitrate yield. The competing reaction is peroxy + NO $\rightarrow$ alkoxy + NO_2.
Other radical bimolecular	N/A	Assignment commands cannot be used to assign rate constants or branching ratios for bimolecular reactions of radicals other than with O_2. See note [e].

[a] One separate "k-assign-rxn" input must be given, specifying the branching radio (as "fac=") for each competing reaction. No kinetic parameter input or "fast" keyword permitted in this context. The branching ratios must sum to 1.0 of the reaction generation will fail.

[b] Applicable to unimolecular reactions of radical species and stable compounds that have assigned rate constants, i.e., not that assumed to necessarily dominate over competing processes. Also applicable to reactions of alkoxy radicals with O_2. Cannot be used for other bimolecular radical reactions.

[c] The kinetic parameters must be given along with the reaction; "fac=" input and the "fast" keyword are not permitted in this context.

[d] The "fast" keyword can be used if the input reaction the only one that occurs. If there are more than one competing process, separate inputs are used for reach reaction, with the "fac=" keyword indicating the branching ratios, which must sum up to 1. "Fac=1" is the same as "fast" in this context.

[e] In some cases, the system may appear to accept assignment commands for bimolecular reactions that are not supported, and show them when user assignments are listed. However, the system will ignore them when generating the reactions. If unsure whether assignments will be used, the user should test them by generating the reaction in single-step mode.

- The species for which the assignment is being made can be designated using either its structure (as used for examples 1 and 3-9) or by its standard compound name (as used for example 2)

- Keywords and reactant designations are not case sensitive. However, the appropriate case should be used in the "ref=" input since this is shown when the results of the reaction are documented following a single step reaction operation.

- The "k-assign-OH", "k-assign-O3", etc. commands are used to assign total rate constants but not products formed or branching ratios, which are derived using general estimation methods unless separate "k-assign-rxn" input is given. If there is more than one reaction pathway, the estimated rate constant for each pathway is multiplied by a factor so that the total rate constant equals the assigned value, and this factor is included in the documentation output for single step reactions. Note that these cannot be used to assign rate constants for radicals, or to assign rate constants for reactions that MechGen does not predict to occur, such as reactions of alkanes with O_3 or photolysis of non-photoreactive species.

- For photolysis reactions, the "phot=" keyword is used to give the name of a photolysis file that gives the absorption cross sections and quantum yields that are included when the reaction is output. The name does not have to refer to a valid photolysis file in the SAPRC-22 mechanism, but such a file would need to be created and used in mechanism preparation input if this is not the case. Specification of an overall, wavelength-independent quantum yield is optional and gives a factor that is multiplied by the photolysis frequency calculated from the data in the photolysis files to use in the model.

- If photolysis assignments are given using the "k-assign-HV" command, it is necessary to also give a "k-assign-rxn" command to indicate the reaction(s) and (if more than one) the branching ratio for the photolysis reaction. For example, example 3 above specifies the photolysis set and overall quantum yield, so example 8 is needed to specify which reaction occurs.

- The "k-assign-rxn" can optionally be used to specify both the rate constant *and* mechanism for the following types of reactions: (1) bimolecular reactions of OH or other species with stable compounds; (2) unimolecular reactions of any type of reactant (e.g. examples 4 and 5, above); and (3) reactions of alkoxy radicals with O_2. It should not be used to assign rate constants for other types of reactions. Note that inappropriate "k-assign-rxn" commands may be accepted and show up in listings of the user assignments, but the generated mechanisms may either ignore this input, or not be as desired.

- Note that "k-assign-rxn" commands are the only means to assign rate constants to unimolecular reactions. The mechanism of the unimolecular reactions must also be given in this command. If there are more than one unimolecular reaction, their rate constants and mechanisms must be given in separate commands.

- If "fast" is used in a "k-assign-rxn" specification for a unimolecular reaction of a reactant compound or radical, MechGen will predict that the specified reaction is the only fate of the reactant, and the reaction is fast enough that it can be assumed to be in steady state, so the rate constant does not affect the mechanism. This is shown in Examples 5 and 6 above for a non-radical and radical reactant. "Fast" can also be used reactions of radicals with O_2, but not for any other type of bimolecular reaction.

- Branching ratios can be assigned using "k-assign-rxn" input where "fac=" is used to indicate the fraction reacting by the specified route. Note that "fac=" input cannot be combined with rate parameter input (e.g., "k=", "A=", "Ea=", "phot="). Unless fac=1, there must be additional "k-assign-rxn" input lines specifying the other modes of reaction for the same reactant, and all the "fac" input values must sum to one. The system will not give warning or error messages during

processing of k-assign-rxn commands if this is the case, but attempts to generate reactions of the reactant will fail. Examples 7 and 8, above show such input, where in each case two input lines are required to complete the assignment.

- Note that if branching ratio assignments are made for reactions of a stable compound, there must be a separate assignment input that assigns its total rate constant. For example, the input shown in example 1, above, must be included with the input shown in example 7.

- On the other hand, if branching ratio input is given for unimolecular or O_2 reactions of a radical, then the reaction is assumed to be fast and no total rate constant is needed. Example 8, above, is example of such input. If rate constant input is desired, then it needs to be assigned along with the specification of the reaction in the "k-assign-rxn" input, as shown in example 4, above.

- The "nitrate-assign" command can be used to derive branching ratios for nitrate formation in reactions of peroxy radical with NO, where the "fac=" input gives the nitrate yield, as shown in example 9, above. The "k-assign-rxn" command cannot be used to specify branching ratios for other bimolecular reactions of peroxy radicals.

Note that assignments of reactions using "k-assign-rxn" will be rejected if the reaction input does not conserve atoms or forms structures that are not recognized by MechGen. It is recommended that user assignments be tested by generating a single-step reaction of the subject reactants to verify that the reactions are generated as desired.

Once a command is successfully entered, the system will display all the assignments for the reactions of the compound, which may include different reactions. Note that all assignments for a given compound need to be given before any reactions are generated using that compound.

All assignments for a reactant can be deleted using the "remove-k-assign" command using the telnet interface or selecting the "(delete)" link when the assignments are shown on the web interface. However, is not possible to delete just some of the assignments for a particular reactant, though assignments of individual rate constants or branching ratios can be modified. Assignments of total rate constants can be modified by giving another k-assign-(ox) command for the compound and oxidant previously input, and factors for "k-assign-rxn" inputs can also be modified as long as the reactions and products are the same as previously input. However, the reactions or products are to be changed, it is necessary to delete all the assignments for the compound before inputting assignments for the modified reactions of the compound. If this is necessary, it will also be necessary to re-input all assignments for the compound that are to be retained.

It is recommended that the telnet interface be used if large numbers of user assignments are desired, since it is possible to input multiple assignments in a single batch operation using this interface, while the web interface requires that all assignment commands be given one at a time. Both interfaces provide means to output the list of all user assignment commands that are currently being used, so they can be re-entered if they are lost or if changes are needed that require deleting previous assignments.

Although the mechanism assignment commands are the same regardless of which interface is used, the procedures for enabling, disabling, listing, or deleting assignments differ depending on the interface, as described in the following sections.

8.2. Managing User Assignments using the Web Interface

User assignments are disabled by default. If disabled, the first line of the "Advanced options" section contains a line indicating they are disabled and providing an "(enable and edit)" link to enable

and create user assignments. Selecting that link will result in a page shown on Figure 21a. It contains a form where a single user assignment command can be entered, as discussed in the previous section and shown on Table 14. Below that are instructions describing assignment commands that can be entered, containing similar information as given in the previous section. If an assignment is entered and accepted, the page will then appear as shown on Figure 21b, where the example assignment is for a rate constant for an ozone reaction. The page has links to disable or delete the assignments, or delete the assignments for selected species, as discussed below. Additional assignments can then be entered, or the user can select the link at the top of the page (not shown on Figure 21) to return to the main menu.

If assignments are enabled and there is at least one assignment, the top section of the main menu page will include a line, right under the line(s) about lumping and user mechanisms (if applicable) stating that user assignments are in effect and indicating how many species have assignments. In addition, the first line in the "Advanced options" section of the main menu will also indicate that user assignments are enabled and give the number of species for which assignments have been made, and provide a link to view, edit, or disable them. Selecting that link will show a page such as shown on Figure 21b.

If there is at least one assignment, the user assignments page will provide links to disable or delete the assignments. In either case, the result will be that subsequent mechanism generations will *not* use these user assignments, and the main menu is displayed with the indication that user assignments are disabled. The difference is that disabling the assignments causes the existing assignments to become active again once assignments are re-enabled, which will happen whenever the "(Enable or edit)" link in the "Advanced Options" section of the main menu is selected. In that case, the resulting display will be similar to that shown on Figure 21b. Deleting assignments will restore the system to its default state where no user assignments exist. Selecting the "(Enable or edit)" link in that case will give the display shown on Figure 21.

The user assignment page will also list any user assignments previously made, grouped by the compounds whose reactions or rate constants are assigned. The list will also include a "(delete)" link that will delete *all* assignments for that compound. Note that a given compound may have several assignments, including various types of rate constants and branching ratios for various reactions, and deleting the assignments for any compound will delete all these assignments. The system stores and retrieves all the assignments using the compound structure string, and does not provide the ability to delete only some of the assignments for a compound. As discussed above, assignment commands giving rate constants or branching ratios can be re-entered if they need to be corrected, but assignments giving reaction products cannot be changed. If such assignments of reaction mechanisms need to be modified, all the assignments for the compound need to be deleted and the ones to be retained will have to be re-entered. This is the case regardless of whether the web or telnet interface is used.

The page also has links to download all the user assignments, either in CSV or command format. The CSV format provides the assignment data in columns giving the type of assignment, the compound or reaction, the branching ratios or rate constant parameters as applicable, and the reference text. The command format gives the assignments in the form of the assignment commands such as described on Table 14. These can be useful if the assignments are lost and need to be re-entered. If more than one, they all can be entered in a single operation using the Telnet interface, but the web interface requires that they be entered one at a time, using the form input shown on Figure 21.

In order to make assignments, it is necessary to create and/or select the user's mechanism assignment set. Once this is done, the Main Menu will have a "(view)" link next to the name of the assignment set near the top of the page and also where will be a "Show or modify your mechanism assignments" link under "Other Actions. If you click on this link, you will see an input box to "Give

User mechanism assignments are enabled

No assignments have been made thus far, so only those in SAPRC-22 Mechanism Assignments will be used.

Give assignment command: (see instructions below)

[   ] [go]

Summary of assignment commands and examples

Assignment of total rate constants for atmospheric reactions of stable compounds:

- **k-assign-*(ox) (compound)* is *(kinetic parms)* ref=*(doc)* [a]**

  (ox): an atmospheric oxidant. Currently supported are OH, O3, NO3, O3P, and Cl.
  (compound): structure or recognized detailed model species name for a stable compound [b]
  (kinetic parms): parameters for calculating absolute rate constants, optionally as follows:
      k=(temperature-independent rate constant in cm, molec, sec units), or:
      A=(A factor in cm, molec, sec units)

(truncated)

User mechanism assignments are enabled

Assignments for 1 species are added to or supercede those in SAPRC-22 Mechanism Assignments.

- Disable these assignments. (They will be available when assignments are re-enabled.)
- Delete all user assignments

Give assignment command: (see instructions below)

[   ] [go]

Download data:

- Download in csv format for spreadsheets
- Download in command format to restore assignments if lost

List of Assignments

CH2=CH-CH2-C(CH3)(CH3)-OH (Delete)

```
o Reaction with O3 (total kO3)
  k(298)=4.27e-18 [Li, W., Dan, G., Chen, M., Chen, Y., Wang, Z., Zhao, Y.,
  Wang, F., Li, F., Tong, S., Ge, M., 2021. "The gas-phase reaction
  kinetics of different structure of unsaturated alcohols and ketones with
  O3." Atmospheric Environment 254, 118394. https://doi.org/10.10]
```

Summary of assignment commands and examples

(truncated)

Figure 21.   Portions of user assignments page that is displayed when the link to enable, view, or edit user assignments is selected.

assignment command" where you can enter or paste a single assignment command line. This must be entered as one line, which may be longer than the input box, so it is recommend that it be pasted into the box if the reference citation is long. Unfortunately, due to network issues that the author does not understand, it is not possible to input multiple lines of assignment commands without losing data, so assignments can be entered only one line at a time.

The assignment input/display page can also give the assignments that have already been entered, though how they are displayed depend on the number of species for which assignments have been made. If there are fewer than 10 species, then all the assignments are displayed. If there are more than 10 and fewer than 50 species then all the species with assignments are listed on a table, and one can select the "(show)" link to see them (they are displayed at the top, then the page is re-loaded). Either way, the assignments for the compound can be deleted using the "(delete)" link. It is generally best to delete all assignments for a compound and re-enter them if mistakes are found that need to be corrected.

The current system does allow use of the web system to make user assignments for more than 50 compounds. If users feels that such a large number of assignments need to be changed, they need to use the telnet system or obtain their own copy of MechGen and make themselves the primary MechGen user and programmer (see Section 9) so they can modify the default assignment used by the system. The primary user can then modify the system default assignments using the same commands as discussed above in Section 8.1 and in the following section, except with no user assignments enabled. In that case, they may wish to rename the default mechanism assignment set to something other than "SAPRC22 Mechanism Assignments".

Users can download the assignments in either csv format for loading into spreadsheets or in command format so they can be re-entered if needed. This can be done with either all SAPRC-22 assignments or with the user's assignments, depending on which set is selected. It your work involves creating many user's assignments, it is recommended to create a backup of these assignments by downloading them in command format so they can be re-created. This may be necessary as general updates to the MechGen system may sometimes result in some user accounts or data being deleted. This allows the assignments to be re-entered after the user account is re-created.

8.3. Managing User Assignments using the Telnet Interface

The terminal commands related to managing user assignments are listed on Table 16. User assignments are disabled by default, but are enabled whenever the user enters an assignment command such as is listed in Table 14 in the users reactor, or gives the "userasns enable" command as indicated on Table 16. The existing assignments (if any) are listed and the status of user assignments is displayed when entering the "userasns" output with no option. The output of a "look" command in the reactor will also indicate whether user assignments are enabled. If enabled, the "options" portion of the output will include a line stating that user assignments are enabled and will give the number of species with assignments. If they are not enabled, the "look" command will not include such a line. However, a user assignment object will be displayed in the list of reactor contents if user assignments have ever been created, regardless of whether they are currently enabled or not. This is the object where the user assignment data are stored.

It is not recommended that multiple assignment commands be made by simply pasted into the system at once because MechGen is based on a multi-user system that allows commands to be carried out essentially simultaneously, which may result in conflicts if more than one command is being processed at the same time. Instead, first give the command "input-asns", and the system will prompt you to enter multiple assignment commands, terminated by a "." by itself. The system will then execute one command

Table 16.   Terminal commands to manage user assignments or output current assignments.

Command	Description
	Manage User Assignments
Userasns	Gives output stating whether user assignments are enabled and lists all the current assignments
Userasns enable	Enables user assignments. This has no practical effect if no user assignments have been made
Userasns disable	Disables user assignments so they are not used in subsequent reaction generations. The existing assignments remain and will come into effect if user assignments are re-enabled
Userasns delete	Deletes all user assignments
k-assign <reactant>	Enables user assignments [a] and displays user assignments for a selected reactant
Show-mechasn <reactant> Show-asn-cmds <reactant>	Shows both user and default assignments for a reactant if any exist, and indicates which are currently being used during mechanism generation (which may depend on whether user assignments are enabled). "Show-mechasn" gives the assignments in an easier to read format such as shown on Figure 21b, while "show-asns-cmds" shows the assignments as commands that can be entered to create the assignments, if needed.
Remove-k-assign <reactant>	Removes all assignments for the reactant
k-assign-*ox* … k-assign-rxn … nitrate-assign …	Enables user assignments and makes an assignment as indicated on Table 14
Input-asns <assignment line 1> <assignment line 2> .	Enables user assignments and prompts user to enter one or more assignment commands as indicated on Table 14, terminated by a line containing only ".". This provides a means to input multiple assignments, such as output when assignments are in command format using the web system (see Figure 21b), or the <outcmd> cmds on userasns" terminal command, where <outcmd> is either "read", "fileout", or @ftpout".
	Output Assignments (<outcmd> could be: "read" to display output to the terminal; "fileout" to output to a file on the host computer, or "@ftpout" to output to FTP for users where FTP access is set up)
Show-asns [<reactant>] show-asncmds [<reactant>]	Shows current assignments for a selected reactant, or for all reactants if no reactant given. "Show-asns" gives the assignments in an easier to read format while "show-asncmds" shows them as assignment commands. Both user and default assignments are shown, if applicable.
<outcmd> cmds on userasns	Outputs the user assignments commands in a format that can be subsequently input using the "input-asns" command, below.
<outcmd> asns on usearans	Outputs the user assignments in an easier to read format, giving the structure of the compounds then the assignments made for them.

at a time, waiting for each to finish before starting on the next. Giving this command will also enable user assignments if they are not already enabled (except when given by the primary MechGen user, where the commands will modify the default assignments if user assignments are not enabled).

As indicated on Table 16, the "show assign" or "show-asn-cmds" commands can be used to give the status of user assignments for any reactant. This outputs the user or default assignments for the reactant if they exist, and indicates which are currently applicable when reactions are generated for this compound, which depends on whether user assignments are enabled. This provides a means to determine if any reactant has default assignments and if so what they are. The output of the "show-asns-cmds" command gives the assignments as commands that can be input into the system if they need to be restored. The latter might be useful if the compound has many assignments, but only one assignment needs to be changed for the user assignments. The default assignments that are to be retained can then be input to the system so they are included among the user assignments for the compound.

8.4. Disabling All Assignments

Telnet users can optionally disable all assignments, including the default SAPRC-22 assignments, by giving the command

Disable-mechasn

This will result in only estimated mechanisms and rate constants being used when mechanisms are generated. This is not recommended when deriving mechanisms for general use, but may be useful if comparisons between estimated and assigned mechanisms are desired. Mechanism assignments can be re-enabled by giving the command

Enable-mechasn

Note that warning messages are given when the user first logs in or gives a "look" command if mechanism assignments are disabled. These commands only affect reactions generated in the reactor where the command is given. Disabling mechanism assignments is not an option for web users.

9. INSTALLING MECHGEN FOR ADDITIONAL CAPABILITIES

The previous sections discuss how anyone can access MechGen online and use it to generate explicit and lumped mechanisms for small to moderate sized compounds and obtain the results in various formats. In addition, MechGen has additional capabilities such as generating mechanisms for larger compounds, generating multi-generation mechanisms, and creating new complete lumped mechanisms for airshed models. These are discussed in the following sections. Unfortunately, because of software limitations, currently the web system does not operate properly when Telnet users are running highly resource operations, such as generating mechanisms for large multiple numbers of compounds. For this reason, unauthorized users are not given the capability of doing such operations when logged into the MechGen system that is available online. These operations need to be done on separate installations of MechGen that are separate from the version available at http://mechgen.cert.ucr.edu.

Therefore, users who are interested in working with the full capabilities of MechGen need to obtain their own copy of the system so they, and their collaborators, can access the system as authorized users who can utilize the full capability of the system. They could also configure their systems for web access, though it should not be relied upon to be always functional when it Telnet users are carrying out resource-intensive operations.

Because of this, the fillies and software required to run stand-alone copies of MechGen are available for download by interested users. This section describes the software system in additional detail as needed to understand how to install and maintain the system, how to obtain and configure the software, and how to authorize selected users so they can employ its full capabilities.

9.1. MOO Software System

MechGen is implemented into a MOO (multi-user object-oriented) system, which are network accessible, multi-user, programmable, interactive systems originally developed for the construction of text-based adventure games, conferencing systems, and other collaborative software (e.g., see MOO, 2014, 2014). Although MOOs are no longer widely used for this purpose and their development is no longer supported, the MOO object-oriented programming language, which is very similar to Python, was found to be much better suited for mechanism generation applications than Fortran or other programming languages that the author happens to be familiar with, so that is why it was used when it was developed. In theory the MechGen software could be converted to Python or another platform whose underlying programming system is still being supported. However, this would be a major effort that has not yet started, so use of MOO software is necessary to utilize MechGen in its current form.

MOO systems consist of two major components, the MOO server and the MOO database. MOO servers are programs that run the systems using a MOO database for input and output. The MOO database is a file that contains all the programs and data structures contained in a MOO. MOO servers must have access the network, and users (called "players" in MOO parlance) normally access the system using the Telnet virtual terminal protocol. Some MOOs, including MechGen, also contain programs that allow the system to be accessed via a web interface using the http protocol, but the Telnet is the primary access method for advanced users and to program the system. Users can then carry out various operations, including programming, within the virtual system, which results in modifications to the MOO database that was read when the server started. The server then saves the modified database from time to time, and saves it when it is shut down, so the changes are available the next time the server is started. Normally MOOs run in memory for extended periods of time, so remote users can access them when needed.

All the programs and databases used by MechGen are contained in the MechGen MOO database, which was built upon the Diversity University MOO database (DUcore) (Wikipedia, 2023a), which in turn was built upon an earlier version of the LamdaMOO database (Wikipedia, 2023b). The MechGen programs and data structures are a subset of those in the overall MOO database, and employ utility subroutines and objects that are part of the core system. The core system also contains programs and objects used in the MOO for virtual reality or user interaction experiences, but most of these are unused in MechGen systems because they are not needed to run MechGen. However, these unused portions of the core have not been deleted from the MechGen database and could still be used if this functionality were desired in the future.

MOO systems utilize various software "objects" within the MOO database that users can interact with or to implement various capabilities within the system. Among these are "player" objects that are connected to each user when logged into the system (with one such object assigned to each user), "room" objects that users can enter and interact with, objects representing virtual things contained in the rooms or can be "held" by the users, and utility objects that contain programs or data utilized by the objects that the user directly interacts with. All objects contain properties and most contain programs or subroutines (called "verbs") that affect how they interact with users or other objects. These are programmed using the MOO programming language (MOO, 1997), an object-oriented language similar to Python, and include verbs invoked directly by users or those that serve as subroutines or functions called by other verbs. Properties on objects can contain various types of data, such as text, numbers, references to other objects, error codes, or lists (sets of various types of data). In the case of MechGen MOOs, the non-player objects can be classified as MechGen objects that implement the MechGen capabilities, or core objects inherited from the host MOO system upon which MechGen was built.

MOO systems can have multiple users who can access the system with a username and password, and some allow "guest" access as well. All MOOs must have at least one system administrator (called a "wizard" in MOO parlance), who has the maximum capabilities needed configure and manage the system, and who can modify all programs and properties within the system. MechGen systems include two additional classes of users: a the single primary MechGen user and programmer who can modify all MechGen objects and can fully utilize all MechGen capabilities, and regular MechGen users who can create their accounts using the web system and access its basic features as discussed throughout this document. Guest access is possible but is disabled by default. The previous sections of this document discuss how anyone can become a regular MechGen user and use it to generate mechanisms and obtain information. However, only the primary MechGen user user, of which there can be only one per MechGen installation because of the way MOO systems handle user permissions, can program or modify the MechGen system. In addition, as currently programmed, only the primary MechGen user and those authorized by an administrator can and employ all of its capabilities of MechGen involving complex or resource-intensive operations, such as carrying out batch operations on multiple reactants or creating multi-generation mechanisms that may involve thousands of chemical species.

Researchers who are interested in utilizing the full capabilities of MechGen and potentially enhancing it for their own purposes can obtain and install their own copy of MechGen to run on their computers, allowing them to access it as the primary MechGen user and allow collaborators to become authorized users. The remainder of this section describes how to obtain, install, and configure MechGen for this purpose. The sections following this describe additional features that only available to the primary user and other authorized users.

Note, however, that a complete discussion of how to program MechGen and update its data and algorithms is beyond the scope of this document. Those who are interested in further development of

MechGen, or reprogramming it into a more widely used programming language, are invited to contact the author concerning potential collaborations.

9.2. Obtaining, Installing and Configuring MechGen Software

The LamdaMOO website at https://www.moo.mud.org contains links that include a MOO FAQ and a MOO programmers manual, and links to where the Unix version of the MOO server software can be obtained. It is recommended that users considering installing MechGen browse the FAQ available there to obtain basic information about such systems. Note that the discussion there is based on the assumption that the MOOs will be used as a system for multi-user interactions, not as a host for a system such as MechGen. However, the information regarding the server, MOO databases, and MOO programming is also applicable to MechGen, and should be read by those considering installing MechGen. Less relevant are details about features of the LamdaMOO core, though MechGen uses some of these features or objects as part of its core system.

MOO server software is freely available for both Unix or Linux-type computers and for Windows systems. MechGen was initially constructed as part of a third-party controlled MOO run using a Unix server, but has been primarily been developed and is now run and maintained using a Windows-based server. Therefore either type of server software can be employed. In addition, the server software should be installed using FUP, the file utility program, that allows running MOOs to write and read files from the host computer, which is used by MechGen as an option to send files with results to users (using the "fileout" command, discussed elsewhere in this document). Most of MechGen operations other than "fileout" will work without FUP, but error messages will appear when MechGen is loaded because some of its programs reference FUP functions. This package is included with both Unix or Windows-based servers.

All the programs, data, and software objects in MOO system are contained in a single MOO database file that is used as both input and output to the server software. In the case of MechGen, the database is in a fill named MechGen.db. The server requires that both an input and output MOO database file be specified. When the server is run, it takes input from the database and then, once the database has been input and verified, the MOO is available for web or telnet access over the network. It then writes an updated database the output file time to time as modifications are made to the running system, and also when the program is shut down. MOO systems are intended to run continuously so they are available to users at any time.

The port used to access the MOO systems with the Telnet interface should be specified when the server is run, the default port number of 7777 will be used. Telnet access is necessary to configure the system as well as run the more advanced MechGen operations discussed in the following sections. In addition, to use the web interface, the system also needs access to port 80, or optionally another port number such as 7000 or 8000 (different from the Telnet port). Port 80 is preferred for use with web access because this is the default port number when a URL is referenced in a browser, otherwise the port number should be appended to the url (e.g., http://MechGen.domain:8000). Use of these ports may require configuring firewall software or obtaining cooperation from network system managers for this type of access to be allowed by the host computer. The server does not take advantage of modern system security protocols when it accesses the network, so system managers may require that it run on computers that are isolated from those used by the host institution before they will allow it to be run on institutional computers.

As indicated on Table 6 in Section 5, the "fileout" command provides a means to write results of various MechGen operations onto files on the computer hosting the MechGen system, to provide a means

for users with access to the host computer to obtain the file directly, and to provide other users who do not have FTP access a means to download the file using the web system. In order for this to work, there must be a subdirectory to the folder containing the MechGen database named "files" and a subdirectory in this "files" folder named "Users". These two subfolders need to be created when MechGen and the server software is installed. The files created using the "fileout" command then go into "files/Users/<user>" folder below the folder where the database file is located, where <user> is the login name of the user giving the command. If these folders do not exist, "fileout" commands will fail with an error message that is not particularly useful indicating the cause.

9.2.1. Installing and Running MechGen on Windows Systems

The Windows-based LamdaMOO server, called WinMOO, was developed and maintained in 1996-2000 by Christopher Unkel, who made the relatively minor changes necessary to port WinMOO from the UNIX version to Win32, and is available at https://suif.stanford.edu/~cunkel/ WinMOO/WinMOO-0.1.0beta8.zip. This also includes the File Utility Program (FUP) extension that MechGen uses. However, it is not necessary to separately obtain and install the WinMOO server and FUP because the necessary files to run MechGen using this server are included with the MechGen database distribution, discussed below.

The Windows MOO server program with the FUP built-in and the MechGen database file are all contained in the file MechGen.zip, which is available at https://intra.engr.ucr.edu/~carter/SAPRC/ mechgen.zip.This zip file that also contains WinMOO server program and a batch file that can run MechGen using this server. If MechGen is to be run on a windows system, then all the contents of the zip file should be extracted into an empty folder. If done properly, this file extraction should also create a subdirectory called "files" containing an empty subdirectory named "users", which is required for the files created or read using FUP. The batch file "MechGen.bat", shown on Table 17, can be run to start the server. If this batch file is run in a DOS window, it will control the window until it shuts down, and the window will display the server log that summarizes its startup and checkpointing operations and its network connections. Closing that window will cause the server to shut down without saving changes

Table 17.   Contents of the batch file "MechGen.bat" included with the distribution of the MechGen database and WinMOO program.

Batch file command	Discussion
if exist MechGen.db copy /Y MechGen.db MechGen.old	Creates a backup of the MechGen database used as input the last time the server ran.
if exist MechGen.new copy /Y MechGen.new MechGen.db	Causes the output file saved when the server was last run to so it will be used as the input this time
SET TZ=PST8PDT	Sets the time zone variable as appropriate for a selected time zone. This example uses Pacific time.
Winmoo -p b8\fup.dll -l MechGen.log -o MechGen.db MechGen.new 7777	Runs the server, using MechGen.db as input, MechGen.new as output, MechGen.log as the log file, and 7777 as the telnet port. The FUP (file utility package) built-in is necessary for the "fileout" command to work.

made since the database was last saved. Typing control-C with the window selected will save the current database and then shut down the server. However, the preferred shutdown method is to log in as as administrative user (see below) and issue the "@shutdown" command.

If MechGen is run as recommended, input will be taken from MechGen.new if that file exists, or otherwise MechGen.db, and the output database will be MechGen.new. In addition the server log is appended to the file MechGen.log. If it is shut down properly and the appropriate batch or command file is used to re-run the server, the database output the last time it is run will server as the input when it is re-run.

9.2.2.   Installing and Running MechGen on Unix or Linux Systems

The LamdaMOO Server that runs on Unix or Linux systems is available from SourceForge (https://sourceforge.net/projects/lambdamoo/), but is also available from Github (https://github.com /verement/lambdamoo). These sources include a REAME file describing the process of installing the server on various Unix or Linux systems, and users should consult these documents for additional information. The FUP extension may need to be downloaded separately if it is not included with the server itself. It also has a README file that should describe how to install it so it works with the server.

Currently the only way to obtain the MechGen database file is to extract it from the files used for Windows installations at https:// intra.engr.ucr.edu/~carter/SAPRC/ mechgen.zip. The file MechGen.db should then be copied to the installation path where it is to be run with Unix server. However MechGen.db as distributed was crated using Windows Systems, and the CRLF sequences need to be removed before it can be used with the Unix/Linux server. The command "tr -d '\015' <input file> <output file> will do this conversion.

The commands and other considerations involved with running the program on Unix/Linux systems are analogous to those used for the Windows system as discussed in the previous section. Additional information regarding installing and running MechGen on Linux systems will be provided in a later version of this document.

9.2.3.   Configuring the MechGen Database

Once the server is started, the user can access the system using the telnet command with the port number specified when the server is run. The system as distributed will have a blank password for the wizard called "owner", allowing the first user accessing the downloaded system to log in just using the command "connect owner", without having to give a password. The system will then demand that the user give a system password that will be assigned to the system wizard user named "MGadmin" and also to the primary MechGen user character named "MechGen". The system will then ask the user to provide configuration input summarized in Table 18, or accept the defaults as indicated there. After that, the "owner" connection will be terminated, future logins as owner will be disabled, and the database will be saved, though the server will continue running. The user can log in as "MGadmin" using the password supplied, if it is necessary to change these configuration options, or to make other system changes as discussed below.

Once properly configured, the MGadmin login would not normally be needed except to create MechGen users or authorize users to have the additional capabilities discussed in the next section. The MGadmin login is also necessary if it is desired to modify portions of the MechGen software that requires wizard capabilities, such as directly accessing the network, making changes to MOO objects or

Table 18.   List of configuration options that can be set when first connecting with a new distribution of MechGen using "connect owner".

Option	Default	Discussion
Password	(no default)	Password to use for users MGadmin and MechGen. Also sets web password for MechGen if web access enabled. This is required input.
IP Address	(not provided)	Enter the IP address if you know it. It is necessary for FTP to work but not otherwise needed.
Site	Localhost	Site name for computer on the web. "Localhost" is adequate for most applications.
Web port	80	The port number to connect to the web system. Default of 80 means it doesn't need to be specified using the browser. Enter "no" if you want web access disabled. If you do not have access to port 80 on the computer you are using (it requires "root" access on Unix-like systems), you should enter another port number. For example port 8000 should be useable for this purpose.
Full MOO name	(see discussion)	Default is adequate for system to run, but can optionally changed. Default is "SAPRC Mechanism Generation System (MechGen), Version 22".
Short MOO name	MechGen-22	Default is adequate for system to run, but can optionally changed.

programs that are not part of the MechGen system, or managing users. However, most of the programs and objects in the MechGen system that are not part of the host MOO system are "owned" (i.e., controlled) by the login for the primary user character "MechGen", and this login (which initially has the same password as "MGadmin", though passwords can be changed) should be used to access MechGen's capabilities and modify its programs or data structures. Although the MGadmin login or other wizard users could modify these MechGen programs or data, this is not advisable because if errors are made it could corrupt the host MOO system or make it inaccessible. In addition the MGadmin login does not have most of the mechanism generation capabilities discussed in this document, at least not without making programming changes to the system.

Table 19 gives the configuration and control commands that can be given using the MGadmin login, including creating and authorizing new users as discussed in the next section. A few of these can also be done using the MechGen login, but those involving user control or general configuration require using the MGadmin login. Once the system is configured, the most common use of the MGadmin login is to create new users and to give selected users authorization to utilize the features discussed in Sections 10 through 12 of this document. Note that if the system is configured for web access through the internet, new users could be created as discussed above in Section 2, though the MGadmin login is required to authorize these users for the full capabilities.

The server program can be shut down using the "@shutdown" command when logged in as either MGadmin or MechGen. The "@shutdown" command itself will wait for 2 minutes to actually shut down the server to give other users of this multi-user system some warning, but usually this warning is not needed for single-user systems. The "@shutdown in 0" command will shut down the system immediately.

Table 19.   Configuration and control commands available when logged in as MGadmin or MechGen

Action	Command		Discussion
	Available to both MechGen and MGadmin		
Change own password	@password (prompts for old then new password)		Only affects telnet password for the user giving the command. Does not affect web user password.

Disable and re-enable web access	MechGen only:
	  Start mechweb
	  Stop mechweb
		Either user:
		  Start &mechweb
		  Stop &mechweb
			The "&" prefix is used to reference system objects that are not held or in the same "room" as the user.

Shut down server (all users logged out)	@shutdown or @shutdown in 0		Default is to shut down after a 2-minute warning.
Save database	@dump-database		The database is saved periodically and upon shutdown, but can also be done on command.
	User Control (available to MGadmin only)		
Create a user or change a user's passwords for both web and Telnet access	User <user> with <password>		<user> is the name of an existing user and new user and <password> is the password for both web and Telnet logins
Deletes a user for both web and Telnet access	Delete-user <user>		<user> is the name of an existing user that is to be deleted. User's chamber also deleted
Control whether a user is authorized for additional capabilities	Authorize-user <user> Unauthorize-user <user>		<user> is the name of an existing web user. The capabilities of authorized users are discussed in Sections 10 through 12.
List MechGen users and indicate their status	Users		Lists users created by web system or commands by MGadmin, and indicates if they are have Telnet access and if they are authorized.
	Configuration Options (available to MGadmin only)		
Enable or disable guest logins	@set $login.guest_login_disabled to 1 @set $login.guest_login_disabled to 0		"0" to enable guest logins, "1" to disable (default)
Enable web access using another port	;listen ($id.mechweb, <port>)		<port> is the port number (a positive integer). Note that the semicolon is part of the command. These are temporary but stay in effect until the system is shut down or an ";unlisten() command is given for the port.
Enable telnet access using another port	;listen(#0, <port>)		
Disable web or telnet access using a port	;unlisten (<port>)		

Table 19 (continued)

Action	Command	Discussion
See which ports are in use (no configuration change)	;listeners()	Shows the ports that are being used and how. #0 refers to telnet access and #6223 to web access.
Change port used for web access on subsequent startups	@set &mechweb.port to <port>	This does not go into effect until the next startup. Use the ";listen()" command to use it immediately.

9.3. Creating and Authorizing Users and Authorized User Capabilities

As indicated on Table 19, the MGadmin login can be used to create and authorize users. Although MOO "wizards" can create users in other ways, it is recommend that the MGadmin login be used to create new users, since otherwise separate steps would be required to configure the new users to work with MechGen. The command to create a new user is

User <name> with <password>

where <name> is the name of the new user and <password> is the telnet and web login password. This also can be used to create a Telnet login for an existing web-only MechGen user or to give new web and telnet password for an existing MechGen user. However, it cannot be used to give reactors or web access to existing users that are not MechGen users -- i.e., not created using the MechGen web system or by the "User" command by MGadmin. It also cannot be used to change passwords for non-MechGen users.

MechGen users can be deleted using the "delete-user <name>" command, where <name> is the name of an existing MechGen user. It cannot be used to delete users MechGen or MGadmin or any non-MechGen user. This deletes both the web and (if applicable) Telnet login for the user and deletes the user's reactor and all its contents.

MGadmin can authorize existing MechGen users so they can carry out the full capabilities of the MechGen system, including the operations described in Sections 10 through 12, and also additional MOO movement operations discussed below. This is done using the "authorize-user <name>" command, where <name> is the name of an existing MechGen user. This does not create new MechGen users but will create a telnet login for this user if it does not already exist. MGadmin can revoke the authorization by giving the command "unauthorized-user <name>". Note that the "unauthorized" operation does not delete the user or its Telnet login. If a user is logged in to the Telnet interface when delete, it is immediately logged out and cannot log back in. If the user is at the web interface, the result of any command will give the web login page. The deleted user could log in again with that name, but any valid password would be accepted and that would only create a new web account with out a Telnet login, and the web reactor will have no contents.

The system does not allow unauthorized MechGen users to exit their reactors and enter other MOO "rooms" because they need to be in their reactors to carry out their MechGen. However MGadmin and authorized MechGen users are allowed to exit their reactors. When MGadmin logs in, the user object enters the "First Room", which is the default login location for most Telnet users who are not MechGen users (i.e., were part of the underlying MOO system or were created by wizards by MOO commands generally used to create new users outside the MechGen system). That "room" contains reactors for the existing authorized users and several exits, named "Webchams", "Lost", or "Webport". "Webchams" is

the room where the reactors for the non-authorized MechGen users are located, and the other two rooms are used for system maintenance and are not discussed further here. Note that authorizing an existing user causes its reactor (chamber) to be moved from the "Webchams" room to the First Room, and unauthorizing the user moves it back. Typing the name of the exit causes the user object to move to that "room" and typing "out" in that room moves the user back. The location of the contents of the rooms and their exits are displayed when the user logs in or enters the room, and also in response to a "look" command.

Authorized users can exit their reactor by giving the "out" command, but they are unable to enter reactors of other users. The command "enter <user>'s" (where <user> is the user's name), will move the user their reactor if the user is where the reactor is located. User can also return to their reactor by giving a "home" command. Authorized users can also create their own reactors using the command

Create-reactor <reactor name>

where <reactor name> is the name of the reactor. The command can be given either in the user's primary reactor or any other reactor the user has created, but not in the First Room or any other MOO location, or other users' reactors. The user can enter the new reactor by giving the command "enter <reactor name>" in the reactor where it is created, and can return to the previous reactor using the "out" command. Users can make any reactor they created their "home" (the location where they appear when they log in or when they type a "home" command) by giving the "@sethome" command. Note that the user's "home" can be set to reactors that users have created or were created for them originally. Use of different reactors permits advanced users to work with generating mechanisms with different reactor options or lumping methods.

The other capabilities of authorized users are related to MechGen operations that are discussed below in Sections 10 through 12.

9.4. Updating Programs, Estimation Methods and Assignments

The primary user, "MechGen", has the capability of modifying or creating MechGen software that controls its operations and how chemical mechanisms are estimated, and modifying or updating the various data structures, lumping methods, and assignments that are used for mechanism generation and associated operations. In addition, the primary user can also carry out the MechGen operations discussed in this document, including the operations available to all users as discussed in Sections 3 through 8 and also the operations available to authorized users discussed in Sections 10 through 12. However, the user "MechGen" does not have the "wizard" status needed to configure the MOO system and control user access, so the "MGadmin" login is used for this purpose, as discussed in the previous section.

It is recommended that the MechGen login not be used unless the user is interested in revising the MechGen software and data or modifying how it makes chemical mechanism estimates. Instead, the web system or the MGadmin login can be used to create users who can carry out basic MechGen operations, and to give selected users authorization to carry out the advanced operations discussed in Sections 10 through 12. Although the MechGen login could also be used to carry out any MechGen operations, there is always the chance that this login could make errors that could modify the system in unintended ways. An example might be giving an assignment command thinking it is for user assignments, but with user assignments actually disabled, resulting in the command modifying the default SAPRC-22 assignments (see Section 8). Using an authorized user login, discussed in the following section, should be sufficient for all the MechGen applications discussed in this document other than modifying the underlying software or data structures.

Making changes to the MechGen software requires knowledge of the MOO programming language, which has not been used for other applications other than developing features for MOOs and is no longer supported. However, it is similar to Python, is well suited for MechGen applications, and should not be difficult for a competent programmer to learn. A greater problem is that it requires an understanding of the MechGen software, which is very extensive and not well documented internally. The current MechGen software has over 45,000 lines of code in ~1200 "verbs" on 87 MOO objects, though not all of these are actually used in the current version. In addition, many of the estimation methods also require input of data giving the parameters that are used by the various structure-reactivity relationships (SARs) and other methods employed. A complete discussion of how to program the system and update all the data it employs is beyond the scope of this document. However, those who are interested in further development of MechGen, or reprogramming it into a more widely-used programming language, are invited to contact the author concerning potential collaborations.

Although a discussion of how to modify the structures used by the various SARs and estimation methods is beyond the scope of this document, it is relatively straightforward for the primary user to update or revise the mechanism assignments that are used in place of estimates or SARs when data are available. Section 8 discusses how regular users can make mechanism assignments to add to or supercede the SAPRC-22 mechanism assignments that are the defaults for all users. The MechGen login can use the same assignment commands as those discussed in Section 8.1 to modify the default assignments. The procedure for this is as follows: (1) Use Telnet to log in as MechGen and enter a reactor where the default mechanism assignments are in effect and user assignments are disabled. (2) Enter an assignment command, using the same format as for user assignments as discussed in Section 8.1. All the assignment commands listed in Table 16 in that section are applicable except for those referencing "userasns", and user assignments are not enabled when these commands are given using the MechGen login. (3) Optionally give a "k-assign <reactant>" command to verify the assignments are as desired. This will result in a change in default mechanism assignments that are applicable for all users. Although the MechGen primary user login can also be used to make user assignments, it is recommended it not be used for this purpose to avoid accidentally changing default assignments for all users.

9.5. Creating New Standard Names for Reactants

As discussed in Section 3.2, most of the reactants present in current emissions or are represented using detailed SAPRC mechanism have standard 2-8 character names to provide a more convenient method to unambiguously reference reactants than using structure strings. These are also necessary for deriving multi-generation mechanisms for reactants (Section 10), representing reactants explicitly when creating lumping methods (Section 11), and are useful when deriving mechanisms for mixtures (Section 12). However, there may be occasions where authorized users may wish to do these operations with reactants that do not have standard names. In these cases, it is necessary for the user to log in as the primary MechGen user to assign standard names to compounds, since this capability is not available to other users.

Table 20 gives the commands that the primary user can employ to assign a standard name to a compound. ("DMS" stands for "detailed model species".) Note that if the compound has already been assigned an ORG-nnnn name (see Section 3.2), the ORG name can be used to create the compound, but it will be given the standard name once created.

Table 20.   Commands that the primary MechGen user can use to create and manage standard names
                 for compounds

Command	Discussion

DMS <name> is <structure> [<option1> <option2> …]
 	
                   Type=<compound type>
                   Desc=<description>
                   Name2=<shortname>
	Assigns <name> as a standard name for a compound with the given structure. For example, for propane <name>="PROPANE" and <structure>="CH3-CH2-CH3"). Options are optional and are as follows:
	
	Compound type (e.g., "Normal alkanes").
	Common name used for the compound (e.g., "Propane")
	Short name (≤6 characters) to be used in lumped models (e.g., "PROP")

DMS <name> is clear	Delete this standard name
Read | fileout | @ftpout DMS	Outputs a list of all standard names with information about the compounds they refer to. Output can go either to the terminal ("read"), to a file on the host system ("fileout") or to FTP.
DMS list	Same as "read DMS"
DMS list <name>	Gives information about the compound named by <name>

10. DERIVING MULTI-GENERATION MECHANISMS

Authorized users have the capability to derive "multi-generation" mechanisms that include not only the reactions of a selected compound and the intermediates it forms, but also the reactions of all the stable products it forms in non-negligible yields. Note that this is different from the "react completely" or "fullreact" operations discussed in previous sections, since these do not react the stable products formed. Because even moderately sized molecules can form many hundreds or even thousands of stable products when they react, generating multi-generation mechanisms is a highly resource intensive operation that currently cannot be carried out using the web interface or by regular MechGen users. This capability requires that the user be logged into the Telnet interface as either the primary MechGen user, or as a user that MGadmin has previously authorized to have these capabilities. In practice, this means that users who desire the full capability of MechGen install their own copy of the system as discussed above in Section 9.

To derive a multi-generation mechanism, it is necessary to specify not only a primary reactant but also a standard environment (see Section 6) giving the conditions under which the compound reacts. It is also necessary to specify a "minimum yield" parameter that is used to determine which products are formed in sufficient yields in the environment to be included in the mechanism, a "reaction time" parameter that determines relative yields of secondary and higher generation products, and a "minimum vapor pressure" that determines which products are too non-volatile to react. If the environmental conditions are not considered, the resulting multi-generation mechanism would be much larger than necessary to predict product formation in practical applications, and for larger molecules may require more time and computer resources that are available in practice. Therefore, multi-generation mechanisms derived by MechGen are functions of the environment where the reactions occur as well as the compounds that are reacted. These can be derived separately for different environments to assess the effects of the environment on these mechanisms and the products that are formed.

In order to derive a multi-generation mechanism, the user must be logged in as an authorized user using a telnet interface, and be in a reactor that has the lumping option (see Section 7) set to "explicit" or "no lumping" and have at least one standard environment selected for mechanism generation, as discussed in Section 6.3. Although more than one standard environment can be used during single generation "react completely" operations, only one standard environment is used to determine which products to include in the multi-generation mechanism. If there are more than one environment selected for mechanism generation, then the first one on the list is used when deriving multi-generation mechanism.

Once the reactor is properly configured, the next step involves creating a multi-generation mechanism (MGmech) object, named "MG-<name>", for a selected reactant, where <name> is the name assigned or specified for the reactant. The command

Create-MGmech <reactant>

can be used to create the MG object for reactants, where <reactant> is either the assigned name or the structure of the reactant. This command fill fail if <reactant> gives a structure that has not been assigned a name. In this case, it is necessary to either assign a name to the reactant as discussed above in Section 9.5, or create and name the reactant using the "build" command (see Section 5.1) before giving the "create-MGmech" command, i.e.

Build <name> as <structure>

Followed by   Ceate-MGmech <name>

In either case, the result is the creation of a "MG-<name>" object within the reactor, where <name> is either the assigned name of the reactant or the one given in the "build" command. MGmech objects are actually types of "reactant container" objects (see Section 12) that contain reactant objects, allowing operations to be carried out on multiple reactants at a time. When the MGmech object is created, the initial reactant is created and moved to the MGmech object. No reactions are generated at this point.

The determination of which products are to be reacted and which are to be added to the "low yield" list is controlled by the selected environment, the and the minimum yield ("minyld"), reaction hours ("rxnhours"), and minimum vapor pressure ("minv[") options of the MGmech object. The minimum yield option, which is 0.0001 (0.01%) by default, is the minimum yield for a product to be included as a non-negligible reactant in the mechanism. The reaction hours option, which is 6 hours by default, is used when estimating how much reactants each of the reactants have reacted for the purpose of determining relative yields of the products that they form. The default minimum vapor pressure is 10^{-13} atmospheres, and compounds with vapor pressures less than this are treated as unreactive products. These can be changed after the MGmech object is created (but before it is reacted and processed) by giving the commands

<div align="center">Minyld MG-<name> is <yield></div>

or   Rxnhours MG-<name> is <hours>

or   Minvp MG-<name> is <atm>

where <yield> is the new minimum yield value, which must be between 0 and 0.5, <hours> is the new reaction hours, which must be positive, and <atm> is the minimum vapor pressure in atmospheres. Note that the former is separate from the "minyld" option for the reactor (see Table 8), which affects determination of negligible yields in when single step or single generation reactions are generated.

The next step involves reacting the initial reactant and all the non-negligible products that they form, then reacting all their non-negligible products, and the non-negligible products they form, until none remain. This is initiated by giving the command

<div align="center">Allreact MG-<name></div>

This operation can take a very long time because even moderately sized reactants can have very large numbers of non-negligible multi-generation products unless a large minyld parameter is used. After each reaction, the products formed and their relative yields in the selected environment are examined, and the non-negligible products are created as reactant objects in the MGmech object and added to the list of products to be reacted, unless they are already on the list. The products formed in negligible yields are added to a separate list of "low yield" products but they are not created as reactants. This continues until all non-negligible products have reacted, which usually takes around 5 or 6 generations. The "allreact" process can take many hours and involve thousands of reactant for larger initial reactants and the default minimum yield parameter.

The relative yield of a product in a multi-generation mechanism is derived as follows:

Generation	Relative yield
Initial reactant	Set to 1
Primary products of the initial reactant	The relative yield from the reactions of the initial reactant in the selected environment

Subsequent generation products Σ (Yield of each reactant forming the product) x (kinetic reactivity of the reactant) x (the relative yield of product from the reactant in the environment), with the sum over all reactants forming the product.

The "kinetic reactivity" of a reactant is the ratio of the reactant that reacts during the specified reaction hours, and is given by

$$\text{Kinetic reactivity} = 1 - e^{-\text{ kPuni(reactant, environment) x 3600 x Rxnhours}}$$

where kPuni is the pseudo-unimolecular loss rate of the reactant in the selected environment, in sec^{-1}, derived from the sum of unimolecular and photolysis rate constants and the rate constants for reactions with the various oxidants which they react (e.g., OH, O_3, etc) and their concentrations in the environment. Note that if the yield x kinetic reactivity of a reactant is less than the minimum yield parameter then all of its products will have negligible yields, so the reactant is added to a list of "slowly reacting" products whose reactions are not generated.

If the "allreact" command did not complete successfully, then only some of the product reactants will have been reacted, and multi-generation mechanism generation will be incomplete. The command

Look MG-<reactant>

will indicate whether this process is completed. If it is not, the "allreact" command can be given again, and the reactants that need to be reacted and processed will then be carried out.

The multi-generation mechanism object is type of "reactant container" object (See Section 12) that can be used for operations on multiple reactants. In this case, the "allreact" command will result in the initial reactant and all the reactant products being created as reactants in this object. Each reactant contains the results of a "fullreact" operation on the reactant, which the programs in the MG-<reactant> object being used to process the results of the single-generation reactions of the various reactants. Normally, these results are processed immediately after the reactants are reacted. However, sometimes there are processing errors and the results will need to be processed again. If processing errors are suspected, give the command

Reset MG-<reactant>

and the processing results will be deleted, but the results of the reactions of the individual reactants will remain. Giving the "allreact" command will result in the results being processed again, but already reacted reactants will not be re-reacted. However, if processing errors resulted in not all reactants being created, any newly created product reactions will have to be reacted as part of this process.

Once the multi-generation mechanism derivation is complete, the results can be obtained using commands of the type:

read [<item> on] MG-<reactant>
@ftpout [<item> on] MG-<reactant>
fileout [<item> on] MG-<reactant>

where "[]"'s indicate optional input, and <item> indicates the type of output. As indicated on Table 6, "read" outputs the results to the terminal, @ftpout outputs the results to the user's FTP site (if available), and "fileout" outputs the results to a file on the local computer that can also be downloaded using the web system. The types of output that can be obtained are indicated on Table 21. Examples of output for a full mechanism generated for ethane are shown on Figure 22 through Figure 27. Note that these output

files would be much larger for larger molecules, so downloading the results using "@ftpout" or "fileout" would generally be preferable to outputting the results to the terminal using "read" unless the terminal output is logged to a file.

Table 21.   Lists of types of output that can be obtained from the results of a multi-generation mechanism generation.

Item	Description
(none)	Outputs a tab-separated ASCII file that can be loaded into spreadsheets summarizing the various types of species in the multi-generation mechanism and gives other summary information. Figure 22 shows the results of a "read MG-ETHANE" command [a]. Note that it includes a summary of volatility categories, though no low volatility products are predicted from ethane.
formedby	Outputs a tab-separated ASCII file that can be loaded into spreadsheets listing first the initial species, then the species that are formed and the species forming them. Figure 23 shows the results of a "read formedby on MG-ETHANE" command.
unirxns	Outputs a tab-separated ASCII file that can be loaded into spreadsheets the reacting compounds than their pseudo-unimolecular rate reactions, with rate constants and product yields computed for the standard environmental conditions used to generate the mechanisms. Figure 24 shows the results of a "read unirxns on MG-ETHANE" command.
rxnfile rxnfile1	Outputs all the reactions of the reacting species that are generated in a format that can be used by the SAPRC box modeling software to conduct model simulations of the reactions of the initial reactants and its reactive products and intermediates. These also include reactions of reactive organic species in the base mechanism The reactions are for a minimally reduced processed mechanism, as discussed in Section 1.3 and indicated in Table 1. "Rxnfile" output gives rate constants in terms of temperature or lighting-dependent parameters where applicable, while "rxnfile1" gives the rate constants for the temperature and lighting conditions defined for the reactor. Figure 25 shows the results of a "read rxnfile MG-ETHANE" command, and Figure 26 shows the reaction results that are different when "rxnfile1" output is requested.
summary	Outputs a summary of reactants that are contained in the MGmech object, which includes the initial reactant and the reacting products formed. This consists of the names, structures, and descriptions (if available) of the reactants, plus the types of reactions the reactants undergo and number of explicit reactions and species formed for those what reacted. The data are given in tab-separated format that can be loaded in a spreadsheet. Figure 27 shows the results of a "read summary on MG-ETHANE" command after being loaded into a spreadsheet, with the blank columns deleted. Note this is the same output that is produced when giving the same command for a reactant container object (see Section 12), since the MGmech object is a type of reactant container within the MechGen system, so it uses some of the same commands.

[a] The results are the same when using "@ftpout" or "fileout" instead of "read".

MG-ETHANE	1	12/8/2023						
Envcond, reaction hours, minimum yield, min vp	d for fullme	6	0.0001	1.00e-13				
Reactant or product	#/Gen	Moles	VP	Name	Rct'd	kUni	Obj	Formed from
Compounds reacted	8	2.79						
Processed reactions	27							
Low reactivity or	0							
Low yield products (atom	1	0.00002						
Failed reactants	0							

	All species		Low Yields					
Volatility categories	Num	Mole Frc	num	Mole Frc
Unknown vp	1	0.00002	1	0.00002
NVOL (vp<0.1 ppb)	0	0	0	0
SVOL-5 (vp=0.1-1 ppb)	0	0	0	0
SVOL-4 (vp=1-10 ppb)	0	0	0	0
SVOL-3 (vp=10-100 ppb)	0	0	0	0
SVOL-2 (vp=0.1-1 ppm)	0	0	0	0
SVOL-1 (vp=1-10 ppm)	0	0	0	0
Volatile (vp>10 ppm)	8	2.79	0	0

Reactants (8)	#/Gen	Moles	VP	Name	Rct'd	kUni	Obj	Formed from		
CH3-CH3	0	1	9.844251	ETHANE	1	3.44e-6	#9569			
CH3-CHO	1	98.9%	0.471504	ACETALD	1	2.06e-4	#19168	CH3-CH3		
CH3-CH2-O-OH	1	6.4%	0.035715	ETOOH	2	8.51e-5	#20459	CH3-CH3		
CH3-CO-O-ONO2	2	62.9%	0.046547	PAN	1	9.66e-5	#4843	CH3-CHO	CH3-CH3	
CH3-O-OH	2	3.7%	0.09494	MEOOH	2	1.39e-4	#8097	CH3-CHO	CH3-CH3	
HCO-CO-O-OH	2	3.5%	0.001755	GLYACID	2	4.42e-4	#17313	CH3-CHO	CH3-CH3	
CH3-CO-O-OH	2	2.6%	0.036637	PAA	2	1.41e-6	#15455	CH3-CHO	CH3-CH3	
HO-O-CO-CO-O-ONO2	3	0.9%	0.000173	PRD-1	2	5.38e-4	#14478	HCO-CO-O-OH	CH3-CHO	CH3-CH3

Base reactants (0)						
HO2	3	164.24%				
NO2	3	4.300252				
CO2	3	0.83449				
OH	3	0.10				
HCHO	3	0.79				
CO	3	2%				
NO3	3	0.8%				

Low yield reactants (1)										
HO-O-CH2-CO-O-OH	3	1.70E-05		ORG-0549				CH3-CO-O-OH	CH3-CHO	CH3-CH3

6 radical intermediates						
CH3-CH2OO.	1	0		RAD-1		
CH3-CO[OO.]	2	-		RAD-2		
.OOCH2-CO-O-OH	2	-		RAD-3		
CH3OO.	2	-		RAD-4		
.OOCH2-CH2-O-OH	2	-		RAD-5		
CO[OO.]-CO-O-OH	3	-		RAD-6		

Multi-generation

Figure 22.   Example of output of a "fileout MG-ETHANE" command after being loaded into a spreadsheet.

```
Products from multi-generation reactions of MG-ETHANE for conditions of Mid NOx standard urban conditions (near EBIR)
Mon Dec 18 16:41:04 2023 PST

no    ID                  Name      Formed by
1     CH3-CH3             ETHANE
2     CH3-CHO             ACETALD   ETHANE    ETOOH
3     CH3-CH2-O-OH        ETOOH     ETHANE    ETOOH
4     CH3-CO-O-ONO2       PAN       ACETALD   PAN      PAA
5     CH3-CO-O-OH         PAA       ACETALD   PAN      PAA
6     CH3-CO-OH           ACETACID  ACETALD   PAN
7     HCO-CO-O-OH         GLYACID   ACETALD   PAA      ORG-0549
8     HO-O-CH2-CO-O-OH    ORG-0549  ACETALD   PAA      ORG-0549
9     CH3-O-OH            MEOOH     ACETALD   PAN      PAA       ACETACID  MEOOH
10    HCO-CO-OH           GLACID    ACETACID
11    HO-O-CO-CO-O-ONO2   PRD-2     GLYACID   PRD-2
```

Figure 23.   Example of output of a "fileout uniprods on MG-Ethane command after being loaded into a spreadsheet

```
Pseudo-Unimolecular reactions of MG-ETHANE and stable products for conditions of Mid NOx standard urban conditions (near EBIR)
Mon Dec 18 16:21:32 2023 PST

                           kUni
no   ID                   (min-1)    Reaction
1    CH3-CH3              1.66e-4    ETHANE = #.97 ACETALD + #.03 ETOOH + #.93 HO2 + #.92 NO2
2    CH3-CHO              9.94e-3    ACETALD = #.62 PAN + #.03 GLYACID + #.01 MEOOH + #.33 CO2 + #.66 NO2 + #.02 OH + #.33
                                    HCHO + #.33 HO2
3    CH3-CH2-O-OH         4.39e-3    ETOOH = #.96 ACETALD + #.02 ETOOH + #.25 OH + #.78 HO2 + #.71 NO2 + #.04 HCHO
4    CH3-CO-O-ONO2        2.03e-2    PAN = #.66 PAN + #.01 MEOOH + #1.64 NO2 + #.34 CO2 + #.01 OH + #.33 HCHO + #.31 HO2
5    CH3-CO-O-OH          8.00e-5    PAA = #.13 GLYACID + #.01 ORG-0549 + #.04 PAN + #.02 MEOOH + #.82 CO2 + #.8 OH + #.8
                                    HCHO + #.85 HO2 + #.91 NO2
6    CH3-CO-OH            4.98e-4    ACETACID = #.27 GLACID + #.01 MEOOH + #.71 CO2 + #.7 HCHO + #.93 HO2 + #.92 NO2
7    HCO-CO-O-OH          2.46e-2    GLYACID = #.21 PRD-2 + #.9 CO2 + #.79 OH + #.68 CO + #.68 HO2 + #.1 NO2
8    HO-O-CH2-CO-O-OH     4.19e-3    ORG-0549 = #.73 GLYACID + #.04 ORG-0549 + #.37 OH + #.23 CO2 + #.23 HCHO + #.65 HO2 + #.79
                                    NO2
9    CH3-O-OH             7.08e-3    MEOOH = #.02 MEOOH + #.98 HCHO + #.08 OH + #.93 HO2 + #.85 NO2
10   HCO-CO-OH            2.50e-2    GLACID = #.69 CO + #.9 CO2 + #1.46 HO2 + #.1 NO2
11   HO-O-CO-CO-O-ONO2    4.70e-2    PRD-2 = #.28 PRD-2 + #.58 NO2 + #1.43 CO2 + #.72 OH + #.57 NO3
```

Figure 24.   Example of output of a "fileout unirxns on MG-Ethane command after being loaded into a spreadsheet

```
! Full mechanism in MG-ETHANE as of 12/08/23
! Minimum estimated yield to react = 0.010%
! Reaction days to calculate amounts reacted = 0.25
! Minimum volatility to react = 1.0e-13 atm.
! Reactions processed using the following environmental conditions:
!    Environments used for fullmech for EPA project (rxn generation)
!     NO        9.79e+9      NO2      7.25e+10     OH        1.38e+7
!     O3        3.37e+12     NO3      1.58e+7      O3P       8.85e+3
!     HO2       9.01e+8      SumRO2   7.36e+8      SumRCO3   1.29e+8
!     HV        1.00e+0
! Base reactions included.
!
! Initial reactant(s) (1)
.ACT
ETHANE    ! CH3-CH3
!
! Reacting products (7)
ACETALD   ! CH3-CHO
ETOOH     ! CH3-CH2-O-OH
PAN       ! CH3-CO-O-ONO2
PAA       ! CH3-CO-O-OH
GLYACID   ! HCO-CO-O-OH
MEOOH     ! CH3-O-OH
PRD-1     ! HO-O-CO-CO-O-ONO2
!
! Products in base mechanism (7)
HO2       ! HO2.
NO2       ! NO2
CO2       ! CO2
OH        ! OH
HCHO      ! HCHO
CO        ! CO
NO3       ! NO3
.
!
! Reacting intermediates (6)
.STS
RAD-1     ! CH3-CH2OO.
RAD-2     ! CH3-CO[OO.]
RAD-3     ! .OOCH2-CO-O-OH
RAD-4     ! CH3OO.
RAD-5     ! .OOCH2-CH2-O-OH
RAD-6     ! CO[OO.]-CO-O-OH
!
! Reactions (27)
.RXN
R) 1.51e-12 1.059 1.92 ;ETHANE + OH = RAD-1
R) 2.55e-12 -0.755 ;RAD-1 + NO = ACETALD + HO2 + NO2
R) 7.44e-12 ;RAD-1 + HO2 = ETOOH
R) 1.28e-11 ;RAD-1 + RCO3 = ACETALD + HO2
R) 2.40e-12 -1.085 0.77 ;ACETALD + OH = #0.95 RAD-2 + #0.05 RAD-3
R) 6.70e-12 -0.676 ;RAD-2 + NO = RAD-4 + CO2 + NO2
R) 7.70e-12 ;RAD-2 + NO2 = PAN
R) 1.91e-11 ;RAD-2 + HO2 = #0.425 PAA + #0.575 RAD-4 + #0.575 CO2 + #0.575 OH
R) 1.44e-11 ;RAD-2 + RO2 = RAD-4 + CO2
R) 2.55e-12 -0.755 ;RAD-3 + NO = #0.251 CO2 + #0.251 HCHO + #0.749 GLYACID +
   #0.749 HO2 + #0.251 OH + NO2
R) 2.30e-12 -0.715 ;RAD-4 + NO = HCHO + HO2 + NO2
R) 3.42e-13 -1.550 ;RAD-4 + HO2 = MEOOH
R) 1.22e-11 ;RAD-4 + RCO3 = HCHO + HO2
R) 6.00e-12 ;ETOOH + OH = #0.025 RAD-5 + #0.156 ACETALD + #0.156 OH +
   #0.819 RAD-1
R) PF=COOH ;ETOOH + HV = ACETALD + HO2 + OH
R) 2.55e-12 -0.755 ;RAD-5 + NO = #2 HCHO + OH + NO2
R) 8.56e+16 27.821 -0.20 ;PAN = RAD-2 + NO2
R) 3.00e-14 ;PAA + OH = #0.742 RAD-3 + #0.258 RAD-2
R) PF=PAA ;PAA + HV = RAD-4 + CO2 + OH
R) 1.17e-11 ;GLYACID + OH = RAD-6
R) PF=MGLY-13 ;GLYACID + HV = CO2 + OH + CO + HO2
R) 6.70e-12 -0.676 ;RAD-6 + NO = OH + #2 CO2 + NO2
R) 7.70e-12 ;RAD-6 + NO2 = PRD-1
R) 5.30e-12 -0.378 ;MEOOH + OH = #0.028 HCHO + #0.028 OH + #0.972 RAD-4
R) PF=COOH ;MEOOH + HV = HCHO + HO2 + OH
R) 8.56e+16 27.821 -0.20 ;PRD-1 = RAD-6 + NO2
R) PF=BACL-11 ;PRD-1 + HV = #2 CO2 + OH + NO3
R) 2.28e-13 ;CO + OH = HO2 + CO2
R) PF=HCHOR-13 ;HCHO + HV = #2 HO2 + CO
R) PF=HCHOM-13 ;HCHO + HV = H2 + CO
R) 5.50e-12 -0.248 ;HCHO + OH = HO2 + CO + H2O
R) 5.80e-16 ;HCHO + NO3 = HNO3 + HO2 + CO
.
! END
```

Figure 25.   Example of output of a "fileout rxnfile on MG-Ethane command

```
                            (Header output same as shown on Figure 25)
! Reactions (27)
.RXN
R) 2.493e-13 ;ETHANE + OH = RAD-1
R) 9.125e-12 ;RAD-1 + NO = ACETALD + HO2 + NO2
R) 7.440e-12 ;RAD-1 + HO2 = ETOOH
R) 1.280e-11 ;RAD-1 + RCO3 = ACETALD + HO2
R) 1.492e-11 ;ACETALD + OH = #0.95 RAD-2 + #0.05 RAD-3
R) 2.098e-11 ;RAD-2 + NO = RAD-4 + CO2 + NO2
R) 7.700e-12 ;RAD-2 + NO2 = PAN
R) 1.914e-11 ;RAD-2 + HO2 = #0.425 PAA + #0.575 RAD-4 + #0.575 CO2 +
  #0.575 OH
R) 1.440e-11 ;RAD-2 + RO2 = RAD-4 + CO2
R) 9.125e-12 ;RAD-3 + NO = #0.251 CO2 + #0.251 HCHO + #0.749 GLYACID +
  #0.749 HO2 + #0.251 OH + NO2
R) 7.693e-12 ;RAD-4 + NO = HCHO + HO2 + NO2
R) 4.686e-12 ;RAD-4 + HO2 = MEOOH
R) 1.215e-11 ;RAD-4 + RCO3 = HCHO + HO2
R) 6.000e-12 ;ETOOH + OH = #0.025 RAD-5 + #0.156 ACETALD + #0.156 OH +
  #0.819 RAD-1
R) 6.57e-6 ;ETOOH = ACETALD + HO2 + OH
R) 9.125e-12 ;RAD-5 + NO = #2 HCHO + OH + NO2
R) 3.387e-4 ;PAN = RAD-2 + NO2
R) 3.000e-14 ;PAA + OH = #0.742 RAD-3 + #0.258 RAD-2
R) 1.00e-6 ;PAA = RAD-4 + CO2 + OH
R) 1.175e-11 ;GLYACID + OH = RAD-6
R) 2.80e-4 ;GLYACID = CO2 + OH + CO + HO2
R) 2.098e-11 ;RAD-6 + NO = OH + #2 CO2 + NO2
R) 7.700e-12 ;RAD-6 + NO2 = PRD-1
R) 1.003e-11 ;MEOOH + OH = #0.028 HCHO + #0.028 OH + #0.972 RAD-4
R) 6.57e-6 ;MEOOH = HCHO + HO2 + OH
R) 3.387e-4 ;PRD-1 = RAD-6 + NO2
R) 4.44e-4 ;PRD-1 = #2 CO2 + OH + NO3
R) 2.28e-13 ;CO + OH = HO2 + CO2
R) 2.28e-13 ;HCHO = #2 HO2 + CO
R) 2.28e-13 ;HCHO = H2 + CO
R) 8.36e-12 ;HCHO + OH = HO2 + CO + H2O
R) 5.80e-16 ;HCHO + NO3 = HNO3 + HO2 + CO
.
! END
```

Figure 26.   Example of .RXN output of a "fileout rxnfile1 on MG-Ethane command.

Reactant	Identity	Description	Lumping	Rwiths	E.Rxns	E.Spec
ETHANE	CH3-CH3	Ethane	explicit	OH	6	13
ACETALD	CH3-CHO	Acetaldehyde	explicit	OH	22	29
ETOOH	CH3-CH2-O-OH	Ethyl hydroperoxide	explicit	OH HV	13	18
PAN	CH3-CO-O-ONO2	Peroxyacetyl nitrate	explicit	uni	12	18
PAA	CH3-CO-O-OH	peroxyacetic acid	explicit	OH HV	17	24
GLYACID	HCO-CO-O-OH		explicit	OH HV	8	15
MEOOH	CH3-O-OH	Methyl Hydroperoxide	explicit	OH HV	9	13
PRD-1	HO-O-CO-CO-O-ONO2		explicit	uni HV	9	12

Output of "summary" on MG-ETHANE as of Fri Dec 8 10:32:01 2023 PST

Figure 27.   Example of output of a "fileout summary on MG-ETHANE after being loaded into a spreadsheet, with unused columns deleted.

11. CREATING OR MODIFYING LUMPING METHODS

As discussed in Section 7, lumping methods control how lumped mechanisms suitable for airshed models are derived from the explicit mechanisms generated in the react completely process. Although standard users cannot create or modify lumping methods, authorized users can create new lumping methods for their use. However, only the primary MechGen user can modify the standard lumping methods available to all users as discussed in Section 7.2, or make new lumping methods available for all users.

Developing lumping methods for MechGen requires creating "lumping objects" and giving commands to input data for its various properties. The required input data include the following:

- Lists of all the model species used for organic reactants and products and their characteristics, including the types of reactions they may undergo (e.g., with OH, O_3, photolysis, etc.), and the photolysis set if the model species undergoes photolysis in the mechanism.

- Structures of the compounds that are represented explicitly for the applicable model species.

- Groups or combinations of groups that determine which types of compounds are represented by lumped model species based on their structural characteristics (see Table 2 for the list of groups that can be used for this purpose). In addition, other molecular characteristics, such as estimated OH rate constant, vapor pressure, atom numbers, photolysis assignments, and types of ring structures can be used for this purpose.

- Options that control the method used to represent reactions of peroxy intermediates need to be specified. Available options include the methods employed in SAPRC-11, SAPRC-16 or 18, and the versions of SAPRC-22. Other methods could be implemented but this would usually require modifying or adding subroutines ("verbs") on lumping objects. Each method has parameters that affect these methods, such as the effective NO concentration, minimum yield for employing less approximate methods, operator names or prefix characters, rate constant ranges for determining "fast" or negligible reactions, and others.

- The types of VOC reactions that can be generated when the lumping method is employed. Current SAPRC lumping methods support unimolecular, OH, O_3, NO_3, O^3P and photolysis reactions, but O^3P reactions can optionally be excluded (as is the case for many mechanisms) and Cl reactions can optionally be included. Note, however, that generating mechanisms for reactions of Cl atoms with many compounds would require adding additional assignments for estimating heats of formation.

- The ordering of model species used when outputting lumped reactions.

Any user can assign or change lumping methods used for their reactor to derive mechanisms using different lumping methods. In addition authorized users can also can create more than one reactor that they can employ, assign different lumping methods or assignment sets, or other options to each, and can chose which reactor to employ by "moving" from one reactor to another. Note that they are limited to the lumping methods that are available to their reactors, which by default are as discussed in Section 7.2.

The commands used to create and manage lumping objects are summarized on Table 22, with additional information concerning options, properties, and model species given in Table 23 through Table 26 and discussed further below. The command "create-lumping <lumping name>" creates the method, adds it as an object in the user's reactor, and makes it an available lumping method for the reactor. However, a separate "lumping" command (see Section 7.1) is needed to make this the method used when generating mechanisms in the reactor, and generally this is not done until the method's options

Table 22.   Summary of commands for creating and modifying lumping methods, and applicable lumping parameters and properties.

Command and input	Discussion
Creation and Deletion	
Create-lumping <name> <description line 1> … .	Creates a lumping control object named <name> that can be specified to control lumping of mechanisms generated in a reactor. The object is located in the user's reactor and is added to the list of lumping methods available to the user.
Delete <name>	Deletes the lumping method and removes it from the list of available lumping methods. The method must have been created by the user and must be located in the user's reactor.
Addlump <name> Rmlump <name>	Addlump makes the referenced lumping method available to all users, and Rmlump removes it from this list of available methods. These commands can only be given by the primary MechGen user.
Specifications of Options, Properties, and Assignments	
Input-rules to <name> Options <option 1> <value 1> <option 2> <value 2> … end Properties <prop 1> <value 1> <prop 2> <value 2> … end ModSpecs <species 1> <info 1> <species 2> <info 2> … end Assignments <species 1> <asns 1> <species 2> <asns 2> … .	The user is prompted for lines of input that to specify options, properties and assignments for the method. The lines of input consist of keywords for the input types, lines of input for that type, followed by line with "end" to indicate end of input of that type or ".", to indicate the end of all input.
	Options Specifies non-default lumping parameters as indicated on Table 23
	Properties Gives values for lumping properties that may differ from the defaults. Properties most likely to be modified are indicated on Table 24.
	ModSpecs List all model species used in the lumped mechanism, and an <info> string giving their non-default properties. The latter consists of lists of <keyword>[=<value>], separated by a space. The keywords and default values associated with them are given in Table 25. See Section 11.3 for more information.
	Assignments Gives information that indicates how model species are assigned to compounds based which groups are in the compound and other properties of the compounds. These are given in the order that the checks are carried out. See Section 11.4 for more information.

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Table 23.   List of lumping options that can be specified using the "Options" section of the "input-rules" to lumping input.

Option and value	Description
Type <type>	Controls how peroxy radicals are treated in the lumped mechanisms as discussed in the text and summarized below. This is required input.
	Type — Description
	Explicit — No peroxy lumping (see Section 7.2.1)
	Standard — As lumped in standard SAPRC-22 (see Section 7.2.2)
	Full — As lumped in full SAPRC-22 (see Section 7.2.2)
	SAPRC07 — As lumped in SAPRC-07 or SAPRC-11, with the "EffNO" parameter used handle unimolecular reactions.
EffNO <conc>	Effective NO concentration (in ppb) used to determine reaction fractions for competitions between unimolecular and bimolecular reactions of peroxy radicals. Applicable only for "Full" or "SAPRC07" peroxy lumping methods. The default is 0.05 ppb.
kRO2slow <kUni> [a]	Unimolecular rate constant for peroxy radical reactions below which unimolecular reactions are ignored. The default is 0.3 sec^{-1}.
kRO2fast <kUni> [a]	Unimolecular rate constant for peroxy radical reactions above which bimolecular reactions are ignored. Default is 200 sec^{-1}.
kRCO3fast <kUni>	Unimolecular rate constant for reactions of acyl peroxy radicals above which the peroxy radical is not assigned to a lumped acyl peroxy radical model species. Not applicable to explicit peroxy lumping methods.
EffNOmid EffNOhigh	The representations of reactions of peroxy radicals using the "Standard" type where there is a competition between unimolecular and bimolecular reactions are derived from product yields obtained using SAPRC07 type lumping at zero, mid, and high effective NO concentrations. These parameters give the middle and low values used for this purpose, in ppb. Defaults are EffNOmid=5 ppb and EffNOhigh=1000 ppb. Only applicable for "Standard" peroxy lumping.
MinYldRO2	Estimated upper limit yield of peroxy radicals below which peroxy radicals are lumped using the "SAPRC07" method when the "Full" peroxy radical lumping method is used. Not applicable to other methods.

[a] These parameters control the mechanism generation process and are applicable regardless of the peroxy lumping type or other lumping options.

Table 24.   Lumping object properties that can be input using the "Properties" section of the "input-rules" input. Note other property values can be input in this section, but this is not recommended,

Property	Description and default values
Supported_rxns [a]	List of types of reactions supported by this lumping method. Default is {"uni", "OH", "O3", "NO3", "O3P", "HV"}. "Cl" can be added to the list to support reactions of VOCs with Cl atoms.
PeroxyReacts [a]	List of types of bimolecular reactions generated for peroxy radicals. Default is {&NO,&NO2,&NO3_rad,&HO2,&LumpRO2S,&LumpRCO3s}, which indicates reactions with NO, NO_2, NO_3, HO_2, generic peroxy radicals, or generic acyl peroxy radicals, respectively. Deleting any of these will result in the corresponding type of bimolecular reaction not being generated.
RO2strs	List of {RO2Cname, RO2XCname, ProdPre, ROOHpre, and RNO3pre} used to define names of model species and operators used for "Standard" SAPRC22 or "SAPRC07" peroxy lumping and for representing low yield peroxy radicals when the "Full" SAPRC-22 method is used. Ignored for explicit peroxy lumping. The default is {"RO2C", "RO2XC", "x", "y", and "z"}, where the first two are used for the NO conversion or consumption operators and the last three are prefixes for products formed after reactions with NO, reactions with HO2, or organic nitrates formed in NO reactions. See SAPRC mechanism documentation reports (refs) for details.
MassMS	List of names of species that are to be represented in units of mass rather than moles, since they represent compounds with widely varying molecular weights. Default is {"NROG", "NVOL"}, for lumped unreactive and lumped non-volatile compounds, respectively.
MixParms	List of two numbers, {SumOK, MaxNcomp} used to determine which and how many product compounds that will be used to derive mechanisms for mixtures based on relative yields of compounds formed when an ambient mixture reacts. SumOK is the mole fraction of compounds in the mixture used that is sufficient for representation, and MaxNcomp is the maximum number of compounds used. Default is SumOK=0.9 and MaxNcomp=15. See Section 12.

[a] These parameters control the mechanism generation process and are applicable regardless of the peroxy lumping type or other lumping options.

Table 25.   Properties of lumped model species that can be specified for each lumped model species in the "ModSpes" section of the "input-rules" lumping input.

Keyword [a]	Property specified and default values
ID=	This gives the structure string for some compound if this model species represents this compound explicitly, and is not used to represent any other compound. Blank by default indicating this may represent more than one compound or is a chemical operator not associated with any individual compound. Formats for structure strings are described in Section 3.1.
nC= nN= MWt=	Number of carbons (nC), nitrogens (nC) or molecular weight (MWT) to be assigned to the model species. Default is zero for each. May not be needed depending on the lumped mechanism.
Rct=	List of bimolecular reactions that the model species can undergo if it represents stable compounds (not radicals or elementary species). Values consist of strings containing "uni", "OH", "O3", "NO3", "O3P", "HV" and/or "Cl", separated by "_" (not spaces). For example, SAPRC lumpings use "OH" for alkenes, "OH_O3_NO3_O3P" for alkenes, "OH_NO3_HV" for aldehydes, and "uni_OH_HV" for PANs. Default is no bimolecular reactions (not applicable or inert). Not used for radical, elementary, or operator species.
RO2prod	Keyword indicating that this model species can be formed after peroxy radicals react with NO, forming an alkoxy radical. No value is given with this keyword. This results in adding an "x<name>" model species to the mechanism, where <name> is the model species name. Default is to create such an additional model species. Not applicable to explicit lumping.
RNO3prod=	Keyword indicating that this model species represents an organic nitrate compound that can be formed following the reactions of peroxy radicals with NO. This results in adding an "z<name>" model species to the mechanism, where <name> is the model species name. Default is to create such an additional model species. The value given is the name of the model species used to represents the products formed when the z<name> model species reacts with NO_3 or other peroxy radicals. Not applicable to explicit lumping.
ROOHprod=	Keyword indicating that this model species represents an organic hydroperoxide compound formed following the reactions of peroxy radicals with HO_2. This results in adding an "y<name>" model species to the mechanism, where <name> is the model species name. Default is to create such an additional model species. The value given is the name of the model species used to represents the products formed when the y<name> model species reacts other peroxy radicals. Not applicable to explicit lumping.
Type=	Code indicating whether this is to be treated as active or in steady state during model simulations, or whether it is to be included in the "SumRO2" or "SumRCO3" species used to compute rates or reactions of peroxy radicals with other peroxy radicals. Default is "Act", indicating active species not constant or in steady state. Other options are "Con" for constant species, "RO2" indicating it represents peroxy radicals whose concentrations are included in "SumRO2", "RCO3" indicating it represents acyl peroxy radicals whose concentrations are included in "SumRCO3", and "SS" indicates it is another type of species to be held in steady state.

Table 25 (continued)

Keyword [a]	Property specified and default values
Rad=	Code indicating whether this model species it to be treated as a radical, which can be "1" indicating this is a radical, "0" indicating that it is not, and "-1" indicating that it may or may not react like a radical depending on the reaction (e.g., O_3). Default is not radical. Note that this is not for mechanism generation or lumping, but is available for future use or optionally checking radical balance.
PHF=	Name of the photolysis set used if this model species undergoes photolysis reactions. Default is blank, indicating that the model species is not photoreactive. See Carter et al (2024) for a discussion of photolysis sets.
QY=	Gives the overall quantum yield of the in the photolysis of the model species, if applicable and not given in the photolysis file. Default is 1.0 for photoreactive species and ignored for others.
Desc=	Optional input giving a description associated with the model species. If provided, this must be the last keyword on the line, and is the only case where embedded spaces are permitted in the value. Default is to make the description same as the name.

[a] An "=" following the name means that the keyword must be given with a value, such as "ID=<structure>". If no "=" is shown, then the keyword is given by itself. The default is used if the keyword is not given.

and parameters are input using the "input-rules to <lumping name>" command as indicated on the tables. The command "delete <lumping name>" deletes the lumping object and removes it from the list of available lumping methods. If this has been selected as the lumping method for the user's primary reactor, the reactor's lumping method is reset to the reactor default, which is "Explicit" lumping.

Note that lumping methods created using the "create-lumping" command are only available as a lumping option for the reactor in which it was created, unless the primary MechGen user creates the lumping object, takes possession of it, makes the new method a core MechGen object, then makes it available go general users, using the following command in a reactor:

Create-lumping <name>
Get <name>
@corify <name> as <unique id>
Addlump <name>   or   Addlump &<unique-id>

where <name> is the name given to the object, and <unique id> is a unique name defined for the object that can be used to reference it regardless of its location without having to know its object number. Note that the @corify command will fail if the unique id name is already in. The "get" command moves the lumping object to the passions of the MechGen primary user, who "holds" most other MechGen system objects. The "@corify" and "addlump" commands will only be recognized as valid commands if given by the primary MechGen user.

A newly created lumping object will have the same options, parameters, and assignments as the system-defined "explicit" lumping method described in Section 7.2.1. Therefore, the "input-rules" command, described in Table 22 and discussed further below, needs to be given in order for this to be used to create lumped mechanism. This gives all the non-default options and assignments associated the lumping method, and referred collectively as "rules" input or lumping rules in the subsequent commands.

Table 26.   List and descriptions of conditions keywords that can optionally be included in the "Assighment" lines in the lumping rules input.

Keyword	Match if …
Keywords with floating point numeric values	
MinKOH=	Rate constant for reaction of OH with this compound is greater than this value.
MaxVP=	Estimated vapor pressure is less than this value.
MinVP=	Estimated vapor pressure is greater than this value.
MaxRO2uni=	Minimum unimolecular rate constant for peroxy radicals.
Keywords with integer values	
MinNg=	The compound has at least as many groups in the molecule as given by this value.
MaxNg=	The compound has no more groups in this molecule than given by this value.
MinC=	The value gives the maximum number of carbons in the molecule.
MinO=	The value gives the maximum number of oxygens in the molecule.
MinCO=	The sum of number of oxygens + number of carbons is greater than this value.
Is_phen=	The compound is a phenol, where the value indicates the maximum number of phenol groups. "Is_phen=2" is used to indicate catechols.
MinGrp:<group>=	
	The value gives the minimum number of groups with the type indicated by <group>, where the group designation is the same as used for the group specification input (as shown on Table 27.
Keywords with text values	
PF=	The compound undergoes photolysis with the absorption cross sections and (if applicable) quantum yields given by the photolysis set named in the value.
Atoms=	The value gives the atomic formula of the molecule, in the format CnHnOnNnCln, where n is the number of atoms of each type in the molecule and atom is not shown if n=0. The atom numbers must be given in this order.
Keywords with no values	
is_HC	The compound is a stable compound with no atoms other than C or H.
is_sat	The compound has only single bonds.
is_cycC10H16	The compound has at least one ring and the formula $C_{10}H_{15}$.. Used for terpenes.
NoRO2uni	The peroxy radical is estimated not to have unimolecular reactions greater than kRO2slow (Table 23).
is_IEPOX	The compound has a 3-member ring with an ether group and at least two -OH groups.
is_furan	The compound is a furan
R3_OO	The compound has a 3-member ring with two oxygen atoms.
is_tetralin	The compound has at least one aromatic ring and one non-aromatic ring.

As shown on Table 22, the "input-rules" command is used to specify the lumping options, properties, list of model species, and model species assignments. That command prompts the user for input, which come in three sections, where the "Options" section gives the lumping options, the "Properties" section gives other non-default property values, the "ModSpecs" section lists all model species used, and the "Assignments" section gives information used to assign compounds to model species. The "ModSpecs" section must be input before this section, but the other sections can be given in any order. Each section consists of lines of input as indicated on Table 22, and are terminated either with a line with "end" to indicate the end of input from that section.

The "input-rules" input used for the standard SAPRC-22 mechanism can viewed using the MechGen web interface by selecting the "Show information used by MechGen to derive the SAPRC-22 mechanism" link in the "Obtain Information" section of the main menu, then by selecting the "Show "input-rules" link in the "Compounds and model species" section of the page that appears. The input for the full version is the same except as indicated except that the "Type" option selected in the "Options" section is "full" rather than "standard".

11.1.   Lumping Options

Table 23 lists the lumping options that can be specified using the "Options" section of the input-rules input. The various types of options are discussed below.

11.1.1. Peroxy Lumping Type options

The "type" option specifies how reactions of peroxy radicals are to be represented in the lumped mechanisms. As indicated in Table 23, the currently supported types are as follows:

"Explicit" type: This option is selected if the reactions of each peroxy radical in the generated mechanism are to be represented explicitly. This is used for the default "Explicit" lumping method, but would not would be used for deriving lumped mechanisms. It may be used if it is desired to have different options regarding which reactions are to be generated.

"SAPRC07" type: This option uses the peroxy radical lumping method employed in the SAPRC-07 and SAPRC-11 mechanism, as described in the available SAPRC-07 mechanism documentation (Carter, 2010a,b). In this method, there are no model species are used to represent individual or lumped peroxy radicals, but instead chemical "operator" model species are used to represent the effects of peroxy radical reactions. This includes two operators, called "RO2C" and "RO2XC" by default, that represent the conversion of NO to NO_2 or the consumption of NO caused by the reactions, and up to three operators for product or intermediate model species that can be formed in the overall reactions of the peroxy radicals. Operators representing the formation of products following one or more NO to NO_2 conversions are designated as "xProd" operators, where "x" is the prefix character used to indicate this type of operator, and "Prod" is the model species name. Operators representing the formation of organic nitrates following the reactions of peroxy radicals with NO are designated as "zRNO3" operators, where "z" is the prefix character for this type of operator, and "RNO2" indicates the name of the model species representing the organic nitrate, of which there may be several depending on the lumping assignments. Operators representing formations of organic hydroperoxides or other products following peroxy + HO_2 reactions are represented by "zROOH" operators, where "z" is the prefix and "ROOH" is the model species name for the types of products formed. The "xProd" operators are also used to approximate the products formed following reactions of peroxy radicals with NO_3 and other organic peroxy radicals or acyl peroxy radicals. Although this requires up to three operator model species for each model species formed in peroxy radical reactions (though usually only a few "z" or "y" operator species are needed), it

does not require model species for individual peroxy radicals, of which there are usually very many in generated explicit mechanisms. If this approach were employed for SAPRC-22 lumping there would be a total of 63 such operators in the SAPRC-22 mechanism for airshed models.

Note that the occurrence of peroxy radical isomerization reactions at lower atmospheric temperatures was not considered when the SAPRC-07 or SAPRC-11 mechanisms were developed. This is not a problem when the unimolecular reactions are so fast that bimolecular reactions can be neglected or so slow that they can be ignored, but is a problem in cases where they are competitive. In order to handle such cases, an "EffNO" parameter (Table 22) is used to estimate overall yields for unimolecular vs bimolecular reactions. Although this is strictly valid only when NO concentrations are close to the chosen value of the EffNO parameter, this is better than ignoring unimolecular reactions entirely.

"Full" type: This is the approach used for the SAPRC-16 and 18 mechanisms (Carter, 2016, 2020b) and the "full" version of the SAPRC-22 mechanism (Carter, 2023a). This is a hybrid of the "Explicit" and the "SAPRC-07" approach, where peroxy radicals are represented either explicitly or using the "SAPRC07" method, depending on the estimated relative importances of the their formation in the mechanism, derived as discussed in Section 6.1. The "MinYldRO2" parameter (Table 22), which has no default and must be specified if the "Full" lumping type is specified, gives the estimated yield of peroxy radicals for them to be represented explicitly. Peroxy radicals formed with lower yields than MinYldRO2 are represented using he SAPRC07 method. This has the advantage of not requiring separate reactions of low yield peroxy radicals, but can still require large numbers of peroxy radical model species in the mechanisms. The "full" version of SAPRC-22 uses MinYldRO2 value of 5%, and requires 239 model species representing individual peroxy radicals, in addition to the 60 operator species used to represent effects of reactions of lower yield radicals.

"Standard" type: This is the approach used in the "standard" version of the SAPRC-22 mechanism, as discussed by Carter (2023a). This is a variant of the SAPRC07 approach and employs the same operators and methods for representing peroxy radicals where unimolecular reactions are negligible. However, instead of using a fixed assigned "EffNO" parameter to derive net product or operator yields when there is a competition between unimolecular and bimolecular reactions, MechGen determines net product yields for three different EffNO values:, zero, EffNOmid, and EffNO high (Table 22) and then adds a separate operator model species representing effects of unimolecular reactions for each reaction forming such peroxy radicals and determines its rate constant, yields, and products that best fit the net yields determined for the three EffNO values. This gives a mechanism that is in principle applicable for a wide range of NO concentrations but requires a much smaller number of additional peroxy model species than the "full" mechanism. The "standard" version of SAPRC-22 requires use of 40 such unimolecular reaction operators in addition to the 63 operators required by the SAPRC07 method. It is preferred for general use because it gives essentially the same predictions as the "full" method (see Carter, 2023a), while requiring almost 200 fewer model species.

11.1.2. Options and that Control the Lumping Process

The "EffNO", "EffNOmid", "EffNOhigh", and "MinYldRO2" parameters affect how peroxy radicals are lumped, depending on the peroxy lumping type selected. As discussed in the previous section and on Table 23, EffNO" is used only for the "SAPRC07" and "full" lumping types, EffNOmid and EffNOhigh are used only for "standard" peroxy lumping types, and "MinYldRO2" is used only for the full lumping types. Their values are ignored if a different lumping type is used.

The "kRCO3fast" option controls the unimolecular rate constant for acyl peroxy radicals above which the radical is not lumped. It is only applicable if model species have been assigned to acyl peroxy

radicals as discussed in Sections 11.3 and 11.4, which is currently the case for all SAPRC mechanisms. This also controls the mechanism generation process (see next section), since reactions of radicals that are assigned lumped species are not generated.

The "MixParms" parameter is used only when deriving complete mechanisms as discussed in Section 12, and does not affect mechanism generation or lumping for individual compounds. It is used for determining which compounds are to be used to determine which mixtures of compounds are appropriate for deriving mechanisms for lumped model species that represent multiple compounds.

11.1.3. Options that Control the Mechanism Generation Process

The "kRO2slow" and "kRO2fast" options give the unimolecular rate constants that determine which reactions are generated for peroxy radicals. If the unimolecular rate constant is less than kRO2slow then unimolecular reactions are ignored, if it is greater than kRO2fast then bimolecular reactions are ignored, and if it is between them then both types of reactions are generated during when complete mechanisms are generated. Thee are applicable regardless of the peroxy lumping approach is employed, including explicit lumping.

As indicated above, the "kRCO3fast" option also controls mechanism generation, but only for lumping methods that represent acyl peroxy radicals using lumped model species. It is not applicable to explicit mechanism generation because no lumped model species are employed. Note that kRCO3fast is generally lower than kRO2fast because the current lumping approaches cannot handle cases where there is a competition between unimolecular reactions of acyl peroxy radicals without all such radicals, and their corresponding PAN analogue formed in their reactions of NO_2, being represented explicitly.

Note that these options only affect the full mechanism generation process as discussed in Sections 4.4 and 5.3. These and other lumping parameters are ignored when single step reactions (see Sections 4.3 and 5.2) are generated.

11.2. Specification of Non-Default Lumping Properties

Table 24 lists the types of properties that might be modified using the "Properties" section of the rules input. Lumping objects have other types of properties that can also be modified using this input, but most of these should normally not be modified by direct user input. These inputs should be included if non-default values are to be used and are not needed otherwise. The default values are also indicated on the table. Note that both the SAPRC-22 lumping options use the defaults for all the properties listed on Table 24, as does SAPRC-11 lumping.

The "Supported_rxns" and "peroxyreacts" properties are used to control which types of bimolecular reactions that may be generated when using the lumping method. The supported_rxns property gives the list of types of bimolecular reactions of stable species, and is included as a lumping option because some lumped mechanism either ignore or do incorporate all types of VOC reactions, such as reactions of O^3P or halogen atoms. The peroxyreacts property gives the list of bimolecular reactions of peroxy radicals that are generated, and is included as a lumping option because some lumped mechanisms ignore peroxy + peroxy reactions, so they do not need to be generated. The default for both is to support all types of such reactions that MechGen can handle, except for reactions of VOCs with chlorine atoms. Although the software and VOC rate constant assignment methods (Carter et al, 2024) support reactions of VOCs with chlorine atoms, unsaturated VOCs tend to form Cl-substituted radicals whose subsequent reactions cannot be generated because of lack of thermochemical estimates required to estimate some of their rate constants (see Carter et al, 2024).

The "RO2strs" property allows use of different operator names and prefixes to use if peroxy radical reactions are lumped using peroxy radical type operators employed in SAPRC-07 and later versions of SAPRC mechanisms. This can be provided if different operator names are to be used, but the default should be used for SAPRC mechanisms. Note that this is ignored for explicit lumping.

The "MassMS" property is used to list those lumped model species that are used to represent concentrations in mass rather than molar units. Although molar units is the default, some model species, such as "NROG" (for unreactive) or "NVOL" (for nonvolatile), are represented using mass units in SAPRC22. This is because the compounds they represent are unreactive and have a wide variety of molecular weights, making mass a more useful quantification.

The "MixParms" option is used when deriving mechanisms for lumped model species based on mixtures of compounds they represent, as discussed in Section 12. This is only used if the lumping method is used to generate complete mechanisms to be used in airshed models representing realistic ambient mixtures.

11.3.   Specification of Lumped Model Species

The "ModSpe" input is used to input names and properties for all the model species that are output in lumped mechanisms, and also to determine the order in which they appear on lists of products formed in the reactions. Most input lines consists of the name of the model species, separated by a space, followed by a list of keywords and (if applicable) values, also separated by spaces. Most keywords have values associated with them, which is separated by the keyword with a "=", with no embedded spaces.

The model species specifications are input in the order that they are to be given in lists of products of reactions that form them, where applicable. Model species names can consist of 1-8 characters, and only alphanumeric, or "_" characters are permitted. Although MechGen is not case-sensitive, case matters in model species names in most simulation programs that will process lumped mechanisms. Usually the alphabetic characters are all upper case, but lower case is permitted, and are used in the "x", "y", and "z" operator species used for SAPRC mechanisms, as indicated in Section 11.1.1.

The keywords and values that follow the model species names in the ModSpe input lines specify the characteristics assigned to the model species, as indicated on Table 25. These do not need to be included if the default values (also given on the table) are used. These include type codes indicating how the model species is to be treated in simulations, what types of reactions it can undergo if it represents non-radical reactants, whether "x", "y" or "z" operators are to be added forming this model species following peroxy radical reactions and how they react, the numbers of carbon, nitrogen, and molecular weights that can optionally be associated with the model species, and photolysis information if the model species undergoes photolysis reactions.

The "ID=<structure> keyword is used when the model species is used to represent a compound explicitly, where the structure must be given in the MechGen standard format as discussed in Section 3.1 (standard names cannot be used in this context). If you are unsure whether a structure designation in the standard form, give the command "ID <structure>" and the output will indicate whether the structure is ok, or whether a different structure should be uses. The ID=<structure> should not be used if the model species is used to for some other purpose than explicitly representing a single compound. In those cases, model species assignments are made based on the input in the Assignments section, as discussed in the following section.

If the name "NoUse" is used for the model species name, it indicates that the compound whose structure is designated using the "ID=" keyword is not to be assigned a model species, and is ignored in lumped reactions where this compound is formed. No other types of keywords are used in these cases. This is used for H2O and O2 in SAPRC mechanisms, since formations of these inert products are ignored when formed in reactions.

11.4.   Assignment of Model species to Compounds

The "<u>Assignments</u>" section of the rules input is used to assign model species to compounds that are not represented explicitly in the mechanism. Most of this input consists of lines containing the name of a model species followed by various keywords that serve to test whether this model species should be assigned to a compound. The model species names must have been previously included in the "ModSpecs" input, and should not be one assigned to a single compound the "ID=" keyword. tests are carried out when MechGen determines how to lump individual compounds, and they are carried out in the order that they appear in the assignments section. Therefore, the ordering of this input is important, since if a compound passes a test specified by an input line, then the lumping is determined and the subsequent tests are not carried out. Note that there can be more than one input line for a given model species if there is more than one test may be sufficient to determine whether a compound should be represented by that model species.

Each keyword in assignments input lines are separated by at least one space, and the keywords, and (where applicable) associated values cannot contain embedded spaces. The following types of keywords are optionally used on the input line to determine whether the compound is to be represented by the specified model species:

- The standard MechGen structure string for a compound, as described in Section 3.1, is optionally used to indicate that the compound with this structure is represented by this model species. Note this model species may also be used for a different compound, as indicated by other assignments input using this model species name, so this is not the same as specifying the structure in the ID= input in the "ModSpecs" input, as discussed above. The structure string must be in the standard format, which can be checked using the "ID <structure>" command. This should be the only keyword if this test is used.

- One or more strings that designate structural groups within the molecule that can be used select compounds with those structural groups. If two or more are given consecutively, the molecule must contain these groups bonded together in the order indicated. As discussed in Section 3.1, each molecule is split into "groups" that consist of portions of the molecule, with one group for each carbon, nitrogen, or halogen atom in the molecule, and oxygen atoms that are not part of carbonyl, nitrate, nitrite, nitro, or nitroso structures. The major types of groups are listed on Table 2 in Section 3.1, and group designations that can be used in assignments input are given in Table 27. The groups must be identified exactly as indicated on Table 27. Note that some of the entries on Table 27 are compound groups that can be used in place indicating two neighboring groups. For example, the input "-CH=C" has the same effect as using the pair "=CH- and =C<". Using compound groups, where available, results in a slight increase in efficiency when mechanisms are processed for lumping.

- Alternatively, group types, as indicated on the first column of Table 27, can be used to indicate any of the groups listed to the left. This can be used as an alternative to including matches involving all of the groups of the same type using the "or" keyword (see below).

Table 27.   List of group specifications that can be used to assign model species based on groups in the molecule.

Type [a]	Groups					
	Stable compound groups					
alkane [b]	-CH3	-CH2-	>CH-	>C<		
alkene	=CH2	=CH-	=C<	-CH=C	-C=(C)-	CH2=C
N/A	=C=					
aro	-aCH-	-aC<	aC(aro)(aro)-aro			
alkyne	#CH	#C-				
carbonyl	-CHO	-CO-	-CO-O			
oxygen	-OH	OH-CO	OH-O-CO			
oxygen	-O-	-O-CO	-O-OH	-O-CHO	-O-O	O(CO)-ONO2
N/A	-ONO2	-ONO	-NO2	-NO	>N[O]-	
amino	-NH2	-NH-	-N<			
N/A	=NH	-N=	#N			
N/A	-F	-Br	-Cl	-I		
	Radical groups that may be lumped [c]					
N/A	-CO[OO.]	-N[.]- [d]	aC[O.](aro)-aro	aC[OO.](aro)-aro		

[a] Specifying the type will give a match for all the groups to the left. "N/A" means that there is no type designation that can be used with these groups.

[b] A "C" code is equivalent to specifying an alkane group type.

[c] Other types of radicals react rapidly, so should not be lumped.

[d] This should be specified as bonded to groups without hydrogen, e.g. ">C< -N[.]- >C<", since tertiary amino radicals with adjacent groups with H atoms will rapidly react with O_2.

- The "and" keyword is optionally included between structural group specifications to indicate that the molecule must include not only the group or series of groups before the "and" but also the ones after that, though they do not need to be next go each other in the molecule.

- Likewise, the "or" keyword is optionally included between structural group specifications to indicate that the match is successful if the molecule contains either the group or series of groups before or after the "or", but not necessarily both.

- The "when" keyword is optionally included to indicate that all subsequent keywords indicate characteristics of the molecule that must be met (or also met) if the molecule is to be assigned the model species. If this is not given, only the groups in the molecule are used to determine if there is a match. In the following discussion, the input before the "when" keyword (or all the input if there is no "when") is referred to as the "group" specification, while that afterwords is referred as to the "conditions". Both must be matched if this keyword is given. However, if there is no group input before the "when" keyword, then the "when" is the first keyword, and only the conditions

input is used to determine if there is a match, and groups in the molecule are not considered (other than as needed to by the MechGen software to determine if the specified condition is met.). Note that the "when" keyword has no effect if there are no conditions specified after that on the input line.

- The conditions keywords that can be used following the "when" keyword are listed in Table 26. In most cases these are associated with a value, which is indicated by a "=" following the keyword, with no intervening spaces. More than one such keyword and value set can be used, separated by spaces.

- The special keyword "all" is used to indicate that the compound is to be assigned this model species regardless of its groups and conditions. All other keywords are ignored in this case. This must be the last specification in the assignment input because subsequent input will be ignored because the match is unconditional. This is generally used for unreactive model species, because all reactive compounds should have been assigned model species by previous assignment input.

Note that the software that determines lumping for compounds searches for full structure matches before matches based on groups or conditions, so the ordering of assignment input lines does not matter for assignments based on matching full structures for the compounds. However, the order does matter when group or conditions matching is used, since the first assignment line that gives a match for the compound is the one that is used.

Examples of model species assignment input can be seen in the "input-rules" input for SAPRC22 mechanisms, which can be viewed using the MechGen web system as discussed in Section 4.6.2.

12. CREATING MECHANISMS FOR MIXTURES

Developing lumped mechanisms for airshed models require not only a means to derive lumped mechanisms for individual compounds as discussed above, but also mechanisms for the lumped model species used to represent reactions of complex mixtures. Hundreds of types of organic compounds are emitted into the atmosphere, and representing each separately is generally not practical in most airshed modeling applications. Because of composition uncertainties, use of large mechanisms requiring guesses of detailed compositions of emissions involving hundreds of compounds is not necessarily more inaccurate than using a mechanisms with a much more limited number lumped species to represent complex mixtures if the model species appropriately represent the reactions of the types of compounds they are intended to represent. While there are uncertainties in using lumped species, they may not necessarily have greater impact uncertainties in compositions of emissions. This is why almost all mechanisms used for airshed model application use lumped model species to represent reactions of compounds assumed to be chemically similar.

Earlier lumped mechanisms generally chose either an individual compounds or an idealized generic compound to be representative of all compounds of the same type, such as using propene to represent all monoalkenes, or acetaldehyde or propionaldehyde to represent all aldehydes. However, SAPRC mechanisms use mixtures of compounds considered representative of those represented by the lumped model species to derive mechanisms for the lumped species based on those derived for the individual compounds in the mixture. MechGen has tools and procedures that can be used for this purpose while deriving complete lumped mechanisms. This involves the following process, where the types of MechGen objects involved are underlined:

1. Estimate detailed composition of organic compounds to be emitted in atmospheres to be modeled, from both anthropogenic and biogenic sources. These compositions are then input into <u>mixture database</u> objects within MechGen. This is referred to as the ambient emissions mixture.

2. Use the <u>lumping method</u> associated with the mechanism to determine which model species represents each of the compounds in the mixture database.

3. Create a <u>reactant container</u> object that will hold all the reactants whose mechanisms need to be generated for this mechanism. These are necessary for the creation of <u>reactant mixture</u> objects used to represent the mixtures used to derive mechanism for lumped model species. It also allows reactions of all the many reactions required for complete mechanism development to be generated with a single command.

4. Create all the reactants that are to be represented explicitly in the mechanism and move them to this reactant container object.

5. Derive relative compositions of model species used to represent primary organic mixtures based on the relative compositions of compounds in the mixture databases that are represented by each model species. By default, compounds used are chosen to represent at least 90% of the moles in the mixture of compounds for each lumped model species, or 15 compounds, whichever is less. Each mixture is represented by reactant mixture objects that is created in the reaction container object, along with reactant objects representing each of the compounds in the mixture. Note that compounds in the database that are represented explicitly or treated as inert in the mechanism are not considered in this analysis.

6. Fully react each of the reactants in the reactant container and process the results using the lumping method employed. This involves reacting many reactants (almost 200 for SAPRC-22) but only requires giving a single command. Note that the results processing also involves

deriving lumped mechanisms for the mixtures based on the mechanisms derived for the components.

7. Based on the results of the reactions of the compounds in the reactant container and the compositions of the compounds in the mixture representing emissions, determine the compositions of the products that are formed when these react under the conditions of a~~standard environment~~ (see Section 6) for a set amount of time, which is 6 hours for SAPRC mechanisms. This is referred to as the primary products mixture.

8. Determine which model species represents each of the products, then derive mixtures to use to represent each model species that is used for oxygenated products, similar to the procedures used in Steps 2 and 5 for model species used to represent primary emissions.

9. Create reactant objects representing each of the compounds in the model species used for lumped products, and add these to the reactant container, along with reactant objects representing their components, similar to the procedure used in Step 5.

10. Fully react the reactants added to the container as part of the previous steps (around 150 in the case of SAPRC-22), and process the results for lumping, including deriving mechanisms for the new mixtures. This is similar to the procedure used in Step 6.

11. If there are lumped model species that represent secondary or other subsequent generation products (e.g., the catechol model species in SAPRC mechanisms), repeat steps 7 through 10 for compounds represented by these model species.

12. Output the lumped mechanism for the lumped model species to the mechanism developer (user), along with the lumped mechanisms for the explicitly represented compounds.

Note that the creation of reacant container or mixture database objects can only be carried out by authorized users employing the Telnet interface.

The lumped mechanisms that are output can then be added to the manually-derived base mechanism for the inorganics and for the organic compounds not currently handled by MechGen, The latter include elementary compounds like formaldehyde, or those with unknown mechanisms like nitrophenols and naphthalenes. The result is a complete mechanism for airshed models.

The process discussed above involves working with three types of MechGen objects that have not been discussed previously, specifically mixture databases, reactant containers, and reactant mixture objects. Table 28 gives a summary of all terminal commands used to create and manage these objects and obtain output concerning mechanisms derived for multiple compounds and mixtures. These objects and their associated commands are discussed further in the following sections. Note that only authorized users can work with these objects.

12.1. Mixture Databases

Mixture database objects consist of lists of reactants and optionally their mole fractions in a mixture. Mixture databases that include mole fractions define compositions of emissions mixtures and mixtures of products formed, while those that do not have mole fractions define lists of compounds that can be used for various purposes. These are required when creating mixtures for to derive mechanisms for lumped product model species, and also can be used to fill reactant containers without having to list all the individual compounds, or indicate which compounds cannot be used to derive mechanisms for mixtures.

Table 28. Summary of commands related to creation and use of reactant containers and mixtures.

Command	Description
Creation and managements of mixture databases	
Create-mixdb <mix db name> as <mix db description> <structure or name 1> [<moles 1>] <structure or name 2> [<moles 2>] … .	Creates a mixture database object and gives the lists of compounds and optionally their molar concentrations in the mixture. If given, the molar amounts are normalized to mole fractions. The composition input is required, and is terminated by a "." line. This is required to define mixtures used to derive mechanisms for lumped model species primarily representing emissions.
Create-mixdb <new mix db name> for @<envcond> <existing mix db name> <container>	Creates or updates a mixture database object to include the compositions of products formed from the reactions of all reactants in an existing mixture database object. The new mixture database contains the list of products weighted by the molar yields when they react under the conditions of the standard environment named <envcond> and by the mole fractions of the reactants in the existing mixture database. All the components of the existing mixture database must be in the container named <container> and have been fully reacted or the command will fail. This is required to define mixtures used to derive mechanisms for lumped model species primarily representing organic reaction products.
Lump-mixdb <mix db name>	Updates the lumping assignments in the mixture database if the lumping assignment for the reactor is changed or if the lumping object has been updated since assignments previously made. [a]
Delete <mix db name>	Deletes the mixture database
Creation and management of reactant containers	
Create-container <container>	Creates a new reactant container named <container> and places it in the reactor.
Put <reactant> in <container>	Puts a reactant in the container, where < reactant> is the name or a valid structure of a reactant. It is moved from the reactor to the container if exists, or it is created if needed.
Put <mix db> in <container>	Creates all the reactants listed in a mixture database and puts them in the container.
Fill <container>	Moves all reactants in the reactor into the container.
Empty <container>	Moves all the reactants in the container into the reactor where the container is located
Get <reactant name> from <container>	Moves a named reactant from the container to the reactor
Zap-reactants in <container>	Deletes all the reactants in the container

Table 28 (continued)

Command	Description
Fullreact in <container>	Fully reacts all the reactants in the container that have not been fully reacted previously. Reactants that fail to react are moved from the container to the reactor.
Process in <container>	Re-derive the lumped mechanisms for all the previously reacted compounds in the chamber, and re-derives lumped mechanisms for mixtures. Not normally needed since this processing is automatically done at the end of "fullreact in <container>" command, but may be appropriate if lumping changes made.
Erase in <container>	Deletes the reaction results for all reactants in the container, but does not delete the reactants.
Delete <container>	Deletes the reactant container and any reactant objects (compounds or mixtures) it contains.
Creation and management of reactant mixture objects	
Create-mixture <mixname> in <container> <reactant 1> <moles 1> <reactant 2> <moles 2> … .	Creates a mixture object named <mixname> in the reactant container and the relevant composition in moles. Moles are normalized to mole fraction. The composition input is required and is terminated by a "." line. Component reactants that are not already in the container are created and moved to the container.
Create-mixture <mixname> <reactant> in <container>	Creates a mixture object named <mixname> that consists of only a single reactant. The reactant is created in the container if it is not already there. This is useful for naming model species that represent compounds using the "lumped molecule" method where multiple compounds are representing using the mechanism of a representative single compound.
Prepare-ms-mixes <mix db> in <container> <msname 1> [<msname 2> …] or Prepare-ms-mixes <mix db> in <container> <msname 1> <msname 2> … .	Creates one or more reactant mixture objects named <msname> in the reactant container linked with the mixture database named <mix db>. The "link <container> to <mix db>" command must be given first. The mixture object compositions are derived based on the mixture of compounds in the mixture database that are represented by the lumped model species named <msname> using the lumping method assigned to the reactor. One reactant mixture object is created for each listed model species listed on the command line or, if not given there, in separate lines following the command, terminated by a "." line. All reactants used in the new reactant mixtures are created and placed in the container if they are not already there.

Table 28 (continued)

Command	Description
Process in <container>	Derives or re-derives mechanisms for mixtures in the container based on mechanisms generated for their components. Also re-lumps mechanisms for all reactants in case minor changes were made to lumping options. Only reactants that are fully reacted or mixtures with fully reacted components are processed. Note that this is carried out automatically after a "fullreact in <container>" command, so this is usually only needed when mixtures are added or modified following "fullreact in <container>" operations.
Obtaining lists of reactants not to be used to derive model species mechanisms	
Add-nouse to <lumping> <reactant 1> <reactant 2> … .	Inputs a list of reactants *not* to be used in mixtures for deriving mechanisms of lumped model species, where <reactant> is either the name or MechGen structure string for compounds not to be used, and <lumping> is the name of the lumping method assigned to the reactor. List is terminated by a line with "."
Obtaining information about mixture databases and contents of reactant containers where "<outcmd>" can be either "read", "@ftpout", or "fileout" (see Table 6)	
<outcmd> <mixdb>	Lists compounds, compositions (if applicable) and lumped assignments in mixture databases.
<outcmd> lumpinfo on <mix db>	List compounds, compositions, and lumping assignments for compounds in mixture database, organized by model species. [b]
<outcmd> MSinfo on <mix db>	Lists total amounts of model species assigned to compounds in this mixture database. [b]
<outcmd> list in <container>	Outputs a list of reactants or mixtures in the container, giving their name, structure, SMILES string, description, and what they reacted with (if reacted).
<outcmd> summary in <container>	Outputs the same information as "list" but also gives lumping used to generate the reactions and the numbers of explicit and lumped reactions and species if reactions were generated.
<outcmd> <item> in <container>	Outputs a file or lines to the terminal containing results of "<outcmd> <item> in <reactant>" for each reactant in the container, giving selected results of their full reactions. "<item>" could be "reactions", "rxns", "tabrxns", "reactions", "products", as described on Table 7. Output also includes results for mixtures except for <item>="reactions". No useful output if reactants not reacted.
<outcmd> mixtures in <container>	Outputs compositions of all mixtures in the container, and indicates whether their mechanisms have been derived.

Table 28 (continued)

Command	Description
<outcmd> k<rct> in <container>	Outputs the kinetic parameters for the reactions of each reactant in the container with <rct>, where <rct> can be OH, O3, NO3, O3P, or Cl, if such reactions were generated. The reference is given for the rate constant if it is assigned. Note that these are not given if reactions of a reactant with <rct> has not been generated, even if it has been assigned or can be estimated. No useful output if reactants not reacted.
<outcmd> rxninfo in <container>	Outputs information on all lumped species and reactions of the reactants or mixtures in the container in the format that can be used by the master spreadsheet file used to compile SAPRC mechanisms. No useful output if reactants not reacted.
<center>Obtaining results for complete mechanism development (as used for SAPRC-22 … see Table 29)</center>	
<fileout> rxninfo on <container>	Outputs information on all lumped species and reactions of the mixtures and the explicitly represented reactants in the container <container>. The output is in the format that can be used by the master spreadsheet file used to compile SAPRC mechanisms. All reactants must have been reacted and all mixtures processed using this lumping method.
Basemix <container> is <mixdb>	Determines compounds whose mechanisms are to be included in the "rxninfo" output (see above), along with the mechanisms for the mixtures, where <mixdb> is a mixture database containing a list included compounds (relative compositions ignored), and <container> is the reactant container containing all the needed reactants. Note that reactants needed only for mixtures and not listed in <mixdb> are not included in the rxninfo output.

[a] This usually not necessary since most mixture database operations involving lumping automatically check lumping and update if needed.

[b] No output if explicit lumping. Relative compositions of each compound output as 1.0 for mixture databases that are lists of compounds. Updates lumping if lumping updated or changed in the reactor.

Mixture databases are created using the "create-mixdb" command, as indicated on Table 28. The command can be used in three ways, as follows:

- The database is created as a list of compounds if the compounds are input without molar amounts. This is referred to as a reactant list database. The format of commands creating on this type of database is shown on the first row of Table 28, where the molar amounts are not included in the inputs.

- The database is created as a mixture of specified compounds when the names or structures of the compounds are input with molar amounts. This is referred to as a reactant mixture database. The format of commands creating on this type of database is shown on the first row of Table 28, where the molar amounts *are* included in the inputs.

- The database is created as a mixture of product compounds formed when a mixture of compounds in a separate reactant mixture database is reacted under the conditions of a standard environment for a specified amount of time, where the reaction time is included as a property of the standard environment. The mixture of reacting compounds, the reactant container containing reacted reacting objects representing them and a standard environment in the command creating this type of database, as shown on the second row of Table 28. This is referred as a product mixture database, but the format is the same as reactant mixture databases, with the only difference being the process used to create it.

If the reactor has been assigned a non-explicit lumping method, the compounds in the mixture database are assigned model species according to the lumping method, and this is stored in the mixture database. The "lump-mixdb" command (Table 28) can be used to update the lumping assignments if the lumping assignment for the reactor has changed, or if the lumping object has been modified by using "input-rules" (Section 11) input since the lumping assignments were made for the mixture. However, most mixture database operations that use model species assignments (such as the "create-mixdb" command that creates product mixture databases) automatically update the model species assignments if changes were made to the reactor lumping.

Table 28 also includes commands to obtain information about the mixture database and, if applicable, its lumping assignments. Note that the "lumpinfo" and "MSinfo" output commands automatically update the model species assignments if needed, but "read" output command does not.

12.2.   Reactant Containers

Reactant container objects are used to contain multiple reactant objects and to carry out operations with them. These are required to create mechanisms for mixtures, and can also be used to fully react or otherwise manage multiple reactants in a batch mode and obtain the results without having to give commands for each individual reactant.

The commands to create and manage reactant container objects are included in Table 28. As indicated there, objects can be created in the chamber individually, and previously created objects in the reactor can be moved from the chamber to the reactor. All objects listed in a mixture database can also be created in the chamber using a single command, which is convenient when developing complete mechanisms. The "create-mixdb" command that creates product mixture databases also creates reactant objects in the container that are used to define the mixture if they are not already in the container. One or more reactants in the container can also be moved from the container to the reactor, as indicated on Table 28.

The "fullreact in <container>" command will react all contents of the container that have not been previously reacted, and will process the results for the lumping method assigned to the reactor, if applicable. This command can take a relatively long time if there are many reactants in the chamber. If new reactants are subsequently added to the chamber, the "fullreact" needs to be given again for the container to react the newly added reactants. The "erase in <container>" command deletes the results of these reactions but not the reactant objects themselves. This should be used if any changes are made to the lumping assigned to the reactor. The "fullreact" command then needs to be given again to react the reactants in thecontainer.

The "delete <container>" command deletes the container and also any reactant or reactant mixture objects it may contain.

12.3. Reactant Mixtures

Reactant mixture objects are special types of reactant objects that refer to mixtures of compounds rather than single compounds. They normally exist only in reactant containers along with reactant objects for each of their components, and need to be re-created if any of the reactant objects are deleted. These can be created using "create-mixture" commands giving the name of the container and the components of mixture as indicated on Table 28. Note that the "create-mixture" command will fail if the reactants in the mixture are not already in the container. However, the reactants to not have to have been reacted for the mixture object to be created.

Reactant mixture objects are also created using "prepare-ms-mixes" commands which create reactant mixture objects for each model species listed with the command, based on relative amounts of compounds in reactant or product mixture databases. In this case, it is not necessary that all compounds in the mixture be already in the container, since the command creates the compounds in the container as needed. In some cases the mixtures used to derive their mechanisms can consist of large numbers of compounds with relatively small contributions to the total. The lumping property "MixParms" (Table 24) is used to limit the number of compounds used eliminate the relatively unimportant compounds from these mixtures. This property specifies "SumOK", which is the total mole fraction of the most important compound considered to be sufficient for mechanism derivation, and "MaxNcomp" which gives the maximum number of components that can be used. The default values for SumOK and MaxNcomp, which were used when deriving SAPRC mechanisms, are 90% and 15, respectively.

In some cases, there are compounds that are represented by a lumped model species whose mechanisms are considered atypical of other compounds lumped with them, or whose mechanisms cannot be derived using MechGen. Although their contributions to total emissions may be low, they may not be completely negligible relative to emitted compounds represented by the model species, and might be included in mixtures used to derive the model species mechanisms. These can be excluded by this purpose by listing the atypical compounds in the "NoUse" property of the lumping object. The "add-nouse to <lumping>" command (Table 28) is used to input the list of such compounds, resulting in their being excluded from the mixtures used to derive model species mechanisms.

The lumped mechanisms for the mixture objects are derived as part of the lumping processing for all reactants in the chamber, which is carried out automatically as part of a "fullreact in" command or manually using a "process in" command, as indicated on Table 28. The algorithms used to derive lumped mechanisms for mixtures depends on the lumping method. In the case of lumping methods using the "SAPRC07" method of lumping peroxy reactions, where the reactions of compounds with OH and other oxidants are merged into a single reaction for each, the mixture mechanism is derived by using weighted averages of the rate constants and the yields of all the products. In the case of the methods using the SAPRC22 lumping approaches, where each oxidant reaction is represented using an initial reaction followed in many cases by reactions of intermediate radicals or operators, the initial processed reactions for the mixtures are replaced by weighted averages of the rate constants and product yields for the initial processed reactants of the components, and all the processed reactions for the intermediates or operators formed are added, with duplicates removed, and processed using the same procedures as used for individual compounds in order to obtain a lumped mechanism. Note that only lumped mechanisms are derived for mixtures.

Mixture objects are not used when working with explicit lumping. Explicit mechanisms for mixtures can be constructed by placing all the compounds in the mixture in a previously empty container, reacting the contents when explicit lumping is in effect, then using the "<outcmd> reactions on

<container>" command to get the explicit mechanisms for all the compounds (with duplicate reactions removed), or "<outcmd> rxns on <container> to get the minimally processed mechanism for the mixture.

12.4. Process Used to Derive SAPRC-22 Mechanisms

An example of how MechGen could be used in the development of complete mechanisms is shown on Table 29, which gives the MechGen commands used in the development of the SAPRC-22 mechanisms (Carter, 2023a). Note that the detailed compositions of the mixture databases employed are not included in this table, but can also be viewed or output using the web interface as discussed in Section 4.6.2.

. The final command is "@ftpout rxninfo on SAPRC22" (or on SAPRC22F) to output all the information needed from MechGen to develop the mechanisms. This information is then input to the master spreadsheet used for developing SAPRC-22, which merges this information with manually assigned base mechanism to prepare the files used by the SAPRC modeling software to prepare the mechanism and run simulations with it (Carter, 2023b).

Note that the "user mechanism" feature discussed in Section 7.3, which is available to any user, is sufficient if all that is desired to add additional explicit emitted species to an existing mechanism where a base mechanism database object has been created, which is currently only standard SAPRC-22. However, if it is desired to change lumping for VOC reaction products, then the lumping object will be modified as summarized in Section 10 and the steps that depend on mechanism generation results will need to be repeated. These include at a minimum re-reacting the reactants in the VOC reaction container, re-creating the mixtures representing lumped model species, and recreating the product mixture databases. Changing the mixture databases representing ambient mixtures used for reactant weightings when deriving mechanisms for lumped species would also require re-running most of the steps discussed above.

Table 29.   MechGen commands used in the derivations of the SAPRC22 mechanisms.

MechGen Command	Discussion
lumping SAPRC22 or lumping SAPRC22F	Assigns the lumping method for the reactor, which will be used when processing all reactions. The method could be SAPRC22 for standard SAPRC-22 or SAPRC22F for the full version of the mechanism. This is the only command that is different for the two versions SAPRC-22 version.
create-mixdb BaseMix <reactant 1> … .	Creates a mixture database listing all the compounds that are represented explicitly whose mechanisms are to be generated. [a]
create-mixdb ARBmix-22 <reactant 1> … .	Creates a mixture database giving the composition of California total anthropogenic emissions for 2018, excluding biogenics and fires. This is used to derive compositions of lumped model species representing anthropogenic emissions. [a]
create-mixdb ARBbio-22 <reactant 1> … .	Creates a mixture database giving the compositions of California biogenic emissions for 2022 This is used to derive compositions of lumped model species representing biogenic emissions. [a]
create-mixdb ARBemit-22 <reactant 1> … .	Creating a mixture database giving the compositions of equal mass fractions of ARBmix-22 and ARBbio--22 to be used for product weighting.
create-container AllDMS	ALLdms is the reaction container used for all the reactants and mixtures required for the mechanism.
basemix AllDMS is BaseMix	Specifies that compounds listed in the BaseMix mixture database are to be included in the output when the process is completed.
Add-nouse to AllDMS <reactant 1> … .	Gives the list of compounds that are not to be used when deriving mechanisms for mixtures representing lumped model species. [a]
delete-reactants build MACO3 as CH2=C(CH3)-CO[OO.] build R2CO3 as CH3-CH2-CH2-CO[OO.] fill alldms	Create radical reactants that are to be represented explicitly whose reactions are to be generated by MechGen and put them in AllDMS. Any reactants that may previously exist in the reactor are deleted first so they will not go into AllDMS with the radicals.
put BaseMix in AllDMS	Creates all the reactants listed in the BaseMix mixture database and puts them in AllDMS.

Table 29 (continued)

MechGen Command	Discussion
prepare-ms-mixes ARBmix-22 for alldms OLE1 [b] … .	Creates mixtures to represent all the lumped model species used to represent anthropogenic emissions. Their compositions are based on the relative amounts of compounds in the ARBmix-22 mixture that are represented by the various model species. [c]
prepare-ms-mixes ARBbio-22 for alldms TERP	Creates the TERP mixture to represent terpenes, and derive its compositions using the compositions of terpenes in the ARBbio-22 mixture. [c]
create-mixture STYRS STYRENE in AllDMS create-mixture SESQ B-CARYOP in AllDMS create-mixture FURNS FURAN in ALLDMS create-mixture BENX BENZENE in AllDMS create-mixture ETCHO PROPALD in AllDMS create-mixture MGLY MEGLYOX in AllDMS create-mixture TAMNS TBU-AMIN in AllDMS create-mixture APANS MAPAN in AllDMS create-mixture PAN2 PBN in AllDMS create-mixture BACL BIACETYL in AllDMS create-mixture MGLY MEGLYOX in AllDMS	Creates the model species used to represent multiple compounds based on the mechanism for a single compound ("lumped molecule" representation). This is needed for cases where the model species name is different than the name of the compound used to derive the mechanism. [c]
fullreact in AllDMS	Reacts all compounds in the AllDMS container. This can take several hours, depending on the speed of the computer.
create-mixdb EmitProds for @stdenv ARBemit-22 AllDMS	Creates a mixture database named EmitProds that contains all the products formed when reacting the compounds in the ARBemit-22 mixture database, with relative compositions derived from the fractions of the reactants in ARBemit-22 and the yields of the products when the reactants are reacted under the "stdenv" standard environmental conditions (see Table 9).
prepare-ms-mixes EmitProds for AllDMS CRES [d] … .	Creates mixtures to represent all the lumped model species used to represent reaction products. Their compositions are based on the relative amounts of compounds in the EmitProds mixture that are represented by the various model species. [c]
create-mixture APANS MAPAN in AllDMS create-mixture PACID PAA in AllDMS	Creates the model species used to represent multiple product compounds based on the mechanism for a single compound. [c]
fullreact in AllDMS	Reacts the compounds that were added to represent lumped model species for products. This can take several hours depending on the speed of the computer.

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Table 29 (continued)

MechGen Command	Discussion
create-mixdb EmitProds2 for @stdenv EmitProds AllDMS	
	Creates a mixture database named EmitProds2 that contains all the secondary products formed when reacting the compounds in the EmitProds mixture database, with relative compositions derived from the fractions of the reactants in EmitProds and the yields of the products when the reactants are reacted under the "stdenv" standard environmental conditions (see Table 9).
prepare-ms-mixes EmitProds2 for AllDMS CATL	Creates mixture used to represent the catechol model speices based on the relative amounts formed when the cresols react in the "envcond" standard environment [c]
fullreact in AllDMS	This reacts the three catechols added to AllDMS by the previous command.
fileout base rxninfo on AllDMS	Sends the list of lumped reactions and model species derived for radicals, mixtures, and all the explicitly represent compounds to a file on the host computer that is input into the master spreadsheet used to prepare this version of the SAPRC-22 mechanism,[e]

[a] The list of compounds or compositions of these mixtures can be viewed by selecting the " Show information used by MechGen to derive the SAPRC-22 mechanism" link in the main menu of the web interface, then selecting the mixture name in the " Mixture databases used" section.

[b] The model species listed are OLE1, OLE2, OLE3, OLE4, AMINS, ARO1, ARO2, ALK1, ALK2, ALK3, ALK4, ALK5, and ALK6.

[c] This also creates any reactants needed to derive the mechanisms of the mixtures in AllDMS.

[d] The model species listed are CRES, XYNL, RCHO, KET2, LVKS, OLEA1, OLEA2, OLEP, RCNO3, RHNO3, RANO3, RPNO3, RDNO3, R1NO3, R2NO3, RUOOH, RAOOH, HPCRB, ROOH, AFG1, AFG2A, AFG2B, AFG3, and OACID.

[e] "@ftpout" could also be used instead of "fileout" if the user is set up for FTP access.

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