USERS MANUAL FOR THE SAPRC ATMOSPHERIC CHEMICAL MECHANISM GENERATION SYSTEM

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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 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), with a paper on the algorithms and test cases currently 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 an online computer program to derive fully explicit mechanisms for the reactions of various 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 (Carter, 2024), 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 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 version is 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. It also describes how advanced users can install their own versions and use additional capabilities. A quick start guide for the web interface is also available on the MechGen webpage (Jiang and Carter, 2024; Carter, 2024).

MechGen can 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 formed under atmospheric conditions. The system 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/low-pressure systems. Reactions can be generated in either "single step" mode to view predictions and documentation for a single reaction, or in "react completely" mode to obtain a complete mechanism leading to stable products (The intermediates formed are also reacted.). 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), as both can estimate and generate atmospheric chemical mechanisms for organic compounds, and both are available online (Gecko-A 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. 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 serves as a detailed user guide for researchers interested in using MechGen. It includes that basic information, but also gives a more complete discussion of the system, available access methods, and basic and advanced capabilities. It also describes how users can download and configure their own copies of the system and how to use the additional capabilities that are not available to users of the online system. New or casual users may wish to first examine the quick start guide before consulting this document for details or more information.

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 primary 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 provides web access, offering a subset of its capabilities to general users. However, some advanced capabilities of MechGen require that users run their own copies of the system, which may require authorization from system administrators. 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 to use MechGen, a general knowledge of key 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 otherwise specified, this document refers 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 99.3). Each user is assigned a different reactor, which is the programming object that processes the commands and manages the reactants created by that user.

An Authorized User is a user with access to the full capabilities of the MechGen system, including resource-intensive operations that are not available to regular users, such as generating multi-generation mechanisms as discussed in Section 10, creating or modifying lumping methods as discussed

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 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 refers to the MechGen Telnet login used to program and update the MechGen system and to utilize all the advanced and resource-intensive features of the system (see Section 9). This requires that users run their own copy of MechGen to configure and access it as either the primary MechGen user or a MechGen administrator.
MechGen Administrator	As discussed in Section 9.1, MechGen is implemented in a MOO system that requires at least one MOO user with complete system administration capabilities to configure and maintain the system (referred to as "wizards" in MOO parlance). Note that the primary MechGen user cannot have administrative access because of how MOO systems handle user permissions. Access to this login also requires that users run their own copy of MechGen.
Authorized MechGen User	This refers to a Telnet user with additional capabilities not available to regular users, as discussed in Sections 9 through 12. The primary MechGen user is already authorized, but other users with Telnet logins can be authorized by the MechGen Administrator user, as indicated in Section 9.39.3.
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, referred to as the user's "primary reactor". 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 for controlling 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.
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 is assigned a name, either a SAPRC VOC name or a system-generated name.

Table 1 (continued)

Terms	Description
Group	This refers to the portions of reactant molecules that are treated as single units within MechGen for the purpose of generating mechanisms. Groups, each containing no more than one carbon or nitrogen atom but possibly variable numbers of hydrogen or oxygens atoms, are listed in Table 2.
Reactant structure	This is a string used by MechGen to specify the structure of a 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, and are described in Section 3.1
Reactant name / Standard name / ORG- names / RAD- names	Each reactant must have a 2-8 character string to serve as their name. Compounds in the detailed SAPRC mechanisms, and whose reactivities are included in SAPRC reactivity scales (Carter, 1990, 1994, 2000, 2010a,b, 2023a), have been assigned "standard" names, available via the web system or in the SAPRC-22 documentation (Carter, 2023a). For reactants without standard names, the system assigns either ORG-nnnn or RAD-nnnn names when permanent names are 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 / 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 / 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 mechanisms for a compound, and the results are saved for subsequent processing or output.
Multi-generation reacting	This is the process of generating complete reactions of a selected reactant and all 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.
Chemical Estimates	The term "estimates" is used to refer to methods used to derive 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.

Table 1 (continued)

Terms	Description
Chemical Assignments	The term "assignments" refers to assignments of rate constants or branching ratios for reactions of specific compounds based on laboratory, theoretical data, or estimates applicable to only that compound. A list of these is included in the supplementary materials for Carter et al (2024) and available via web interface as discussed 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 initially produced by MechGen. It consists of the elementary reactions 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 also 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. Users can select currently available lumping options for each reactor, including "explicit" or minimal lumping, SAPRC-22 (Carter, 2023a), or 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 produces only minimally reduced processed mechanisms. 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 than 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.
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.
Lumped Mechanism	This is a further reduced or lumped mechanism that is derived if a non-explicit lumping method is selected. SAPRC-22 lumped mechanisms can be incorporated directly into SAPRC-22 mechanisms because all products formed are given as model species. Lumped mechanisms for non-aromatic compounds 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.

Table 1 (continued)

Terms	Description
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 default environmental conditions used to determine product yields and 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.

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, either through a website (the "web interface") or a command-based Telnet interface (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. Stable reactants represent close-shell compounds that might react with OH, O_3, NO_3, O^3P, by photolysis, or in some cases unimolecular reactions, and require an initial reaction mode (e.g., with OH or photolysis) to generate their 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.

Reactor refers to an object assigned to each user for the purpose of managing reactants and changing options affecting how they react and how the results are processed. Each user has its own reactor, allowing independent operations in this multi-user system. 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" in the Telnet interface.

Single-step reaction is the process of generating the reactions of only one reactant, without reacting the products or intermediates formed. This option allows users to select a single step reaction in order to view documentation on how 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 include reactions of 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 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 is 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 all 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 with the species they form in those reactions. This results in mechanisms with approximately 2½ times fewer species and almost 10 times 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 to apply the steady-state approximation for radical intermediates. However, the final stable products, which can number in the hundreds for larger molecules, and the peroxy radical intermediates, which can be numerous, 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 to 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 number of products formed is reduced by representing most with lumped model species, and the number of reactive intermediates is 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 mechanisms.

The lumping method is a user-selectable option that controls whether a lumped mechanism is derived and, if so, specifies the lumping approach employed. The default lumping method is "explicit

lumping", which results in deriving only explicit and minimally reduced 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 after 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 to explicitly represent additional compounds explicitly (see Section 0). 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, including temperature, pressure, O_2 concentration, and the presence of water. Standard Environments refer to sets of concentrations of reactive atmospheric species (e.g., OH, HO_2, NO_x, etc.) that affect competitions involving bimolecular reactions. They 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 via the web interface at http://mechgen.cert.ucr.edu. Although Telnet access is needed to exploit the full capability of the system, the web interface allows general users to generate mechanisms for compounds of interest and access documentation. Users can view explanations of how MechGen generated reactions, estimate rate constants, and get lists of generated reactions and products when compounds are reacted completely. The web system also provides information on various estimation methods and assigned reactions. However, users cannot make or change any of its basic assignments via the web interface; these tasks require authorization, as described in Sections 9 through 12.

When accessing the MechGen website, users are prompted to log in with a username and a password. Passwords are case-sensitive, while usernames are not. A user account is required to ensure each user has a unique reactor that allows independent option customization and session-saving. Account creation is free and requires no personal information, though users may optionally provide an email for updates or collaboration. Once logged in, users can create new reactants, access saved results, change mechanism generation options, view documentation, and provide optional personal information through the "main menu".

2.2. Telnet Access

MechGen also supports a terminal or command-based interface via Telnet. 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 operations that are not possible or practical via the web interface, such as programming and maintaining the system or performing resource-intensive operations by authorized users. Although MechGen inherits multi-user capabilities from MOO-based systems, it is not currently being used for multi-user interaction beyond the brief description in Section 9.1. The following user accounts are relevant to the MechGen system:

MechGen users: Anyone can create a username and password via the web interface, which also allows Telnet access. These users can carry out the mechanism generation operations, including but not limited to most operations available through the web system, with exception of viewing some help or information pages.

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 account has the capability of programming and modifying the MechGen system, including changing chemistry assignments and estimates. The primary user also has all

the privileges of non-administrative users. Users must install MechGen on their own system, as described in Section 9 to be able to become an administrator.

Authorized Users: These consist of the primary user and any others granted permission by a MechGen administrator to perform resource-intensive operations discussed in Sections 10 - 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, and is not used for programming or updating the MechGen capabilities. There is only a single MechGen administrator for any running installation of MechGen, which is currently the primary author (Carter) for the online version at http://mechgen.cert.ucr.edu. However, as discussed in Section 9, users can install their own copy of MechGen on their own computer that will allow them to use administrator accounts.

After logging into the MechGen website, users can enable their Telnet login from the main menu. Then, by entering "telnet mechgen.cert.ucr.edu 8888" in a terminal, they can access the online version of MechGen via Telnet. Upon successful connection, the program will prompt for the username and password used on the web interface. Refer to Section 5 for more details on Telnet operations.

2.3. Obtaining and Installing MechGen for Single User Access

The online version of MechGen is suitable for occasional users, but it is shared with other users and is not appropriate for projects requiring significant resources. For this purpose, it is more appropriate that users set up their own copy of the MechGen core database, where users can become the primary MechGen user and administrator, and make collaborators authorized users. This is discussed in Sections 9.

3. SPECIFICATIONS OF REACTANTS

To use MechGen for generating reactions or mechanisms, it is necessary to specify the structure of the reactant to be reacted. Reactants can represent either stable compounds or radicals. You can create any reactant by giving its structure as discussed here. A large number of stable reactants can be specified using standard names assigned to them.

3.1. Specification by Structure

In MechGen, reactants are specified using portions of molecules treated as single units or "groups", which are listed in Table 2, Table 3a and Table 3b. Each group represents no more than one carbon, nitrogen, or halogen atom, along with a variable number of hydrogens or oxygens. Oxygens bonded to a carbon or nitrogen by double or dative bonds are considered 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 represents H atoms as an elementary radical group (Table 3b). Groups with radical centers are treated as separate radical groups.

Reactants are typically 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 using SMILES strings, but not all SMILES are currently accepted. In any case, MechGen converts SMILES input to MechGen format for subsequent processing. Examples of reactants in terms of MechGen structures are given in Table 4, which also shows corresponding SMILES strings. Note that there can be more than one valid structure specification, and MechGen uses an algorithm to produce a unique standard structure designation string for each compound, regardless of how it is input. This unique string is essential for the system to determine whether reactants created or generated refer to the same or different compounds. 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 "-" (single bonds), "=" (double bonds), or "#" (triple bonds).
- Branched structures uses parentheses "()"'s to denote additional groups bonded to a central group with more than two neighbors, similar to SMILES. 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 use "*" symbols to indicate groups bonded to other groups with single bonds. The "*" can be placed before or after the group name during input, but the standard format is after the name. Bi- and polycyclic structures uses "*1", "*2", etc., to indicate bonded groups, always 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. The standard designation uses groups with the prefix "a" or "p" as indicated on Table 1, with the aromatic or allylic bonds treated as single bonds.
- 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.

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		Excited Criegee 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. 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}" at the end of the compound identification indicates the excitation level 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, as they have established mechanisms or are unreactive. Complete mechanisms 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 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 in lumped mechanisms.

- 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 uses "^" 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 input structures do not have to follow the standard format for MechGen, but they will be converted to the standard form during subsequent processing. The original input string (whether SMILES or MechGen format) is not retained if different.

Reactants containing a single group and other elementary species are listed in Table 3. These can be formed in reactions unless noted otherwise or can indicate how a stable compound reacts. Reactions can be generated for the radical species listed in the second column, while others are treated as stable products.

3.2. Specification by Name

VOC compounds with detailed mechanisms derived for SAPRC mechanisms can also be specified by their 2-8 character standard SAPRC names. These names can be obtained via the web interface by clicking on the links to create reactants by "compound type" "from complete list" in the "Create VOC or radical reactant" section of the main menu (see Figure 1). They can also be obtained from the "DMS" column in Table B-4 of the SAPRC-22 documentation (Carter, 2023a). These names are also shown in outputs when compounds are created by specifying their structures.

Not all stable compounds have standard names, though many are assigned permanent "ORG-nnnn" names, where "nnnn" is a four-digit number used for deriving mechanisms for mixtures (Section 12). These names are displayed when such reactants are listed, but are generally not convenient for input specification because they lack relevance to the nature of the compounds.

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 *syn* CH_3-	(not supported by MechGen)	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.

4. BASIC OPERATIONS FOR WEB USERS

This section discusses basic operations for creating reactants, carrying out reactions, and obtaining information using the web interface. A more concise guide can be found in a separate "quick start" manual (Carter and Jiang, 2024), but this section provides more details on operations and options.

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 in Figure 1. This figure shows the page with a reactor with the default settings after three reactants have been created and one fully reacted. Notations such as "[#nnnn]" refer to internal MOO object numbers, which can normally be disregarded. The main menu includes the following sections:

- 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 by its structure or standard name (a 2-8 character name for VOC species in SAPRC detailed mechanisms). The names used can be determined by using one of the links in this section.
- Reactant Section. Lists previously created reactants, with links to the reactant information page (Section 4.2) and, for fully reacted compounds, links to the reaction results. 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 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 general information about the chemical estimation methods, mechanism assignments, the derivation of SAPRC-22 mechanisms, and the user manual, as discussed in section 4.6.
- Advanced Options. This contains links to user assignments as discussed in Section 8 or derivations of modified SAPRC mechanisms as discussed in Section 7.2.2.
- Files for Download (not shown on Figure 1): This contains file objects that contain data that the user can download. These files are created using "fileout" commands during Telnet sessions, and are stored on the host computer in a subfolder assigned to the user. If no files exist, this section is
- 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 login, 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 from the main menu, and also when reaction products are selected on reaction results pages as

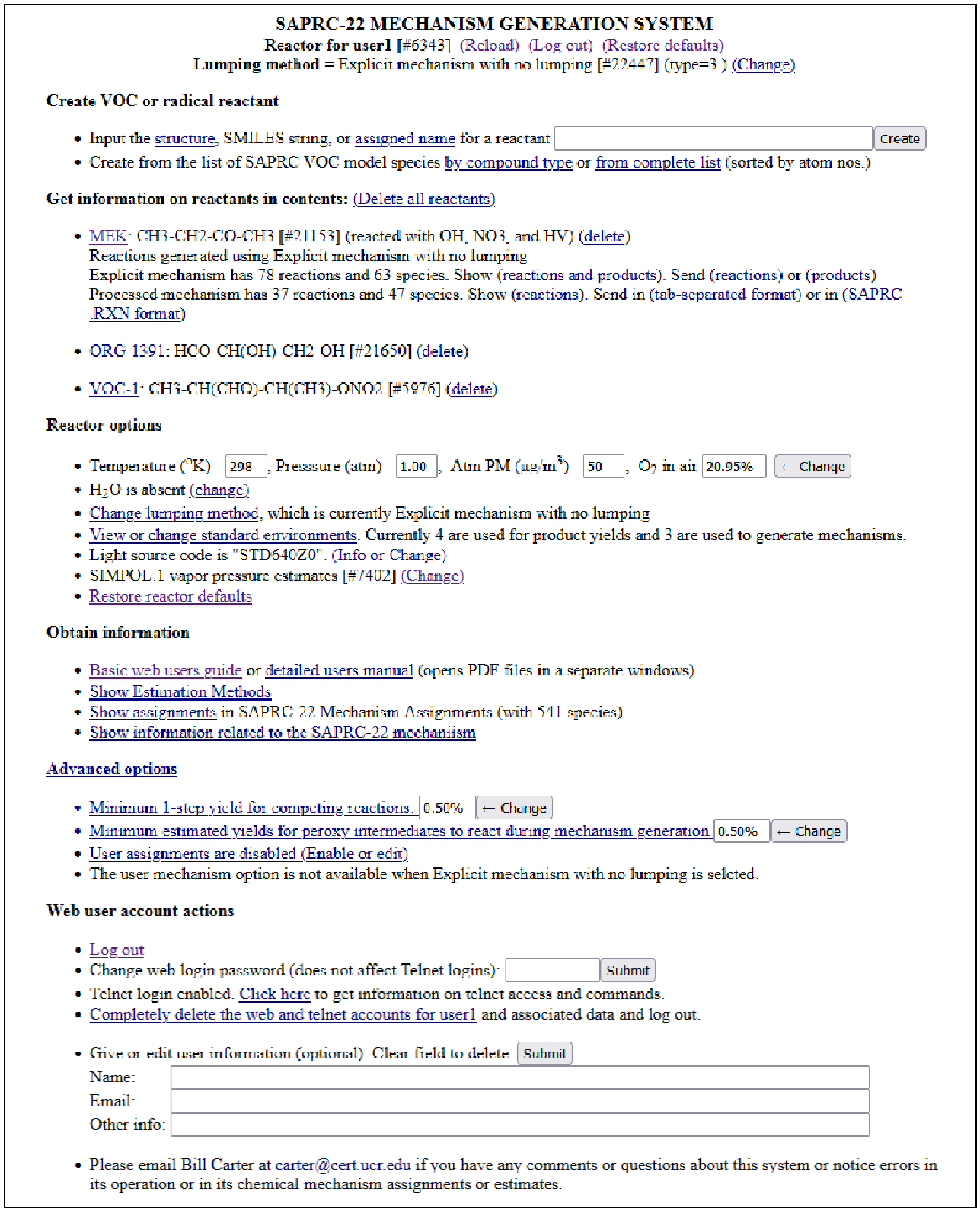


Figure 1. Screenshot of the main menu for the web interface with default settings but after three reactants were created and one was reacted, and after optional user information provided. Arrows show lines with links that are discussed in the text.

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 and Figure 3 show examples for a stable reactant and a radical, respectively, which have not been reacted. Note that Figure 3 is also the 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 methyl ethyl ketone (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 includes information about how the vapor pressure is estimated, if applicable for this type of compound based on the estimation method used. Vapor pressure estimates are made for stable compounds not 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 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 in Figure 3 and **Error! Reference source not found.**, and an example of a selected type of single step reaction of a stable compound is shown on **Error! Reference source not found.**.

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.

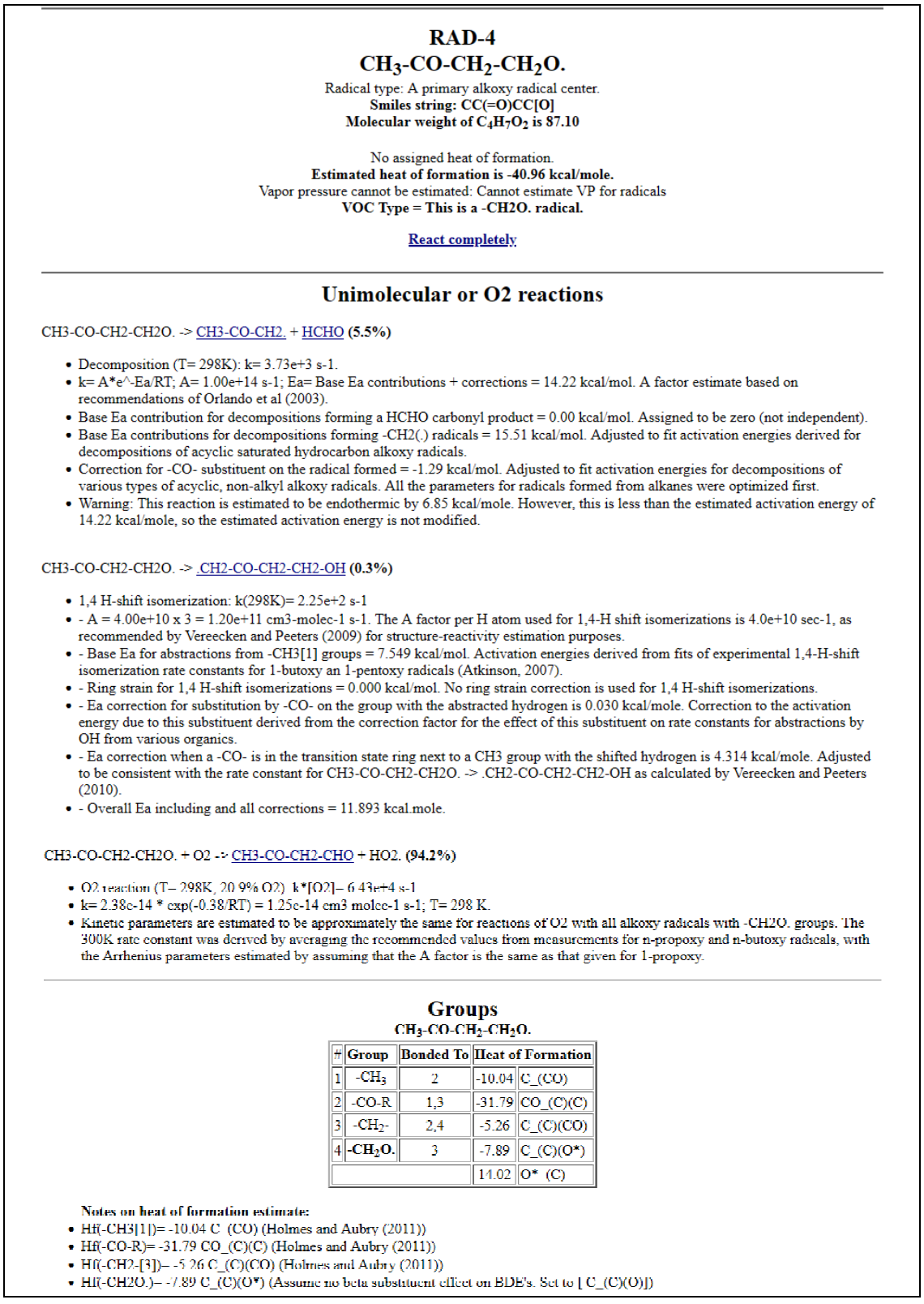
```
Vapor pressures estimated using the SIMPOL1. method.
Estimated for T = 298.00 deg K

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. Screenshot 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-CO-CH_2-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-CO-CH_2-CH_2O.

#	Group	Bonded To	Heat of Formation	
1	-CH_3	2	-10.04	C_(CO)
2	-CO-R	1,3	-31.79	CO_(C)(C)
3	-CH_2-	2,4	-5.26	C_(C)(CO)
4	**-CH_2O.**	3	-7.89	C_(C)(O*)
			11.02	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. Screenshot 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.

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)].

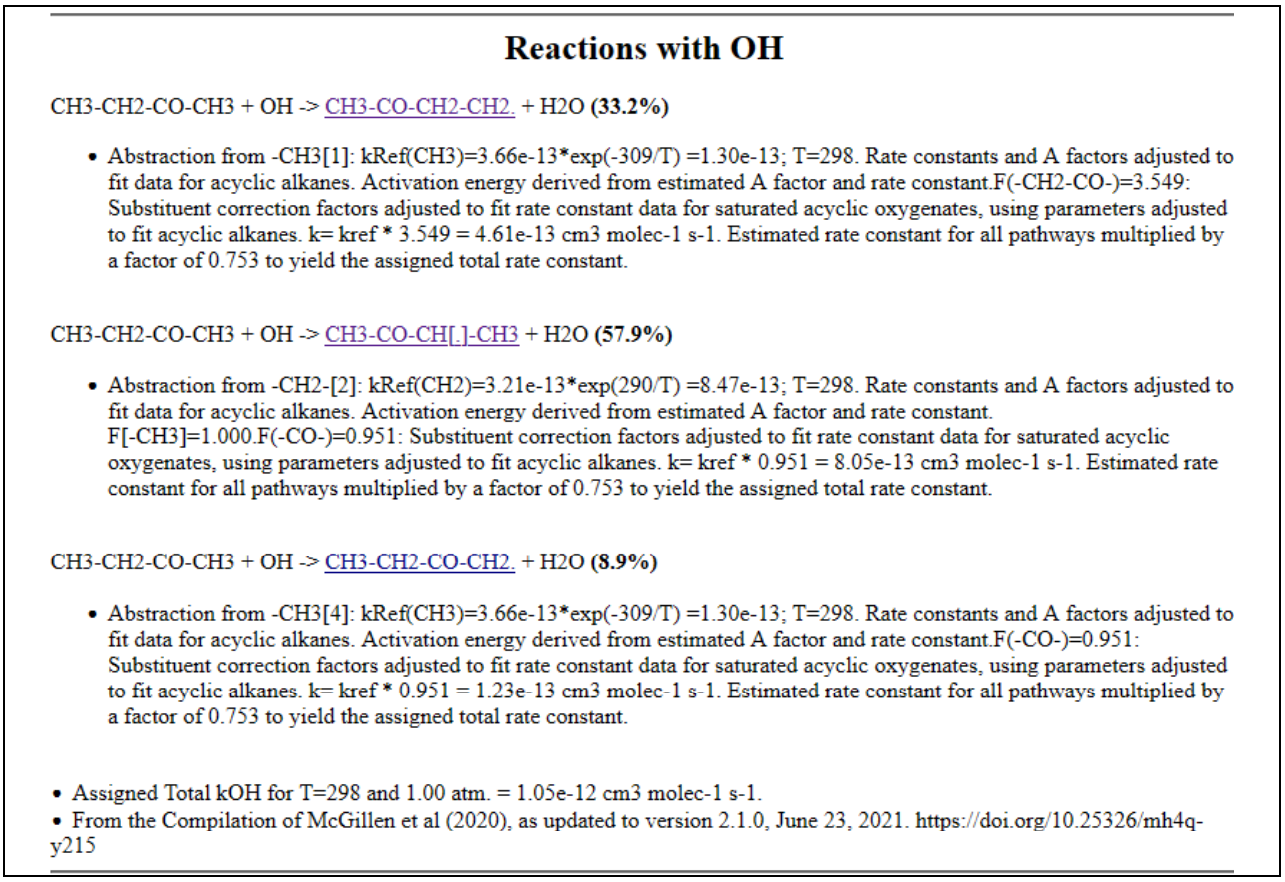
Reactions with RO2

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.



Reactions with OH

CH3-CH2-CO-CH3 + OH -> CH3-CO-CH2-CH2. + H2O **(33.2%)**

- 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(-CH2-CO-)=3.549: Substituent correction factors adjusted to fit rate constant data for saturated acyclic oxygenates, using parameters adjusted to fit acyclic alkanes. k= kref * 3.549 = 4.61e-13 cm3 molec-1 s-1. Estimated rate constant for all pathways multiplied by a factor of 0.753 to yield the assigned total rate constant.

CH3-CH2-CO-CH3 + OH -> CH3-CO-CH[.]-CH3 + H2O **(57.9%)**

- Abstraction from -CH2-[2]: kRef(CH2)=3.21e-13*exp(290/T) =8.47e-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.F(-CO-)=0.951: Substituent correction factors adjusted to fit rate constant data for saturated acyclic oxygenates, using parameters adjusted to fit acyclic alkanes. k= kref * 0.951 = 8.05e-13 cm3 molec-1 s-1. Estimated rate constant for all pathways multiplied by a factor of 0.753 to yield the assigned total rate constant.

CH3-CH2-CO-CH3 + OH -> CH3-CH2-CO-CH2. + H2O **(8.9%)**

- Abstraction from -CH3[4]: 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(-CO-)=0.951: Substituent correction factors adjusted to fit rate constant data for saturated acyclic oxygenates, using parameters adjusted to fit acyclic alkanes. k= kref * 0.951 = 1.23e-13 cm3 molec-1 s-1. Estimated rate constant for all pathways multiplied by a factor of 0.753 to yield the assigned total rate constant.

- Assigned Total kOH for T=298 and 1.00 atm. = 1.05e-12 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

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

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, in Figure 3. Other types of bimolecular reactions are output in separate subsections of the reaction results section, such as shown, for example, in **Error! Reference source not found.**. The percentages shown for each reaction are relative to other reactions with the same reactants, not the total reaction of the radical that includes bimolecular reactions, which depends on environmental conditions.

Single step output shows all the reactions that are generated for a particular radical, regardless of whether they are estimated to be negligible compared to competing processes. Therefore, single step mechanism generation can provide information about minor processes or other processes that are not included during full mechanism generation. However, it should be noted that MechGen will not generate reactions estimated to be unimportant under realistic environmental conditions, such as highly endothermic reactions, reactions involving highly strained transition states, or reactions involving groups that are estimated to be unreactive for the given 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 in Figure 3 or **Error! Reference source not found.**, while selecting a stable product will result in a reactant information page such as shown in 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.

On the other hand, stable reactants are not deleted once complete 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. The reactant will need to be deleted manually using the main menu if it is no longer needed – failure to do so will result in unnecessary clutter on the main menu if many reactants remain after the system has been used for a while.

4.4. Full Mechanism Generation

The full or complete 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, O_3, and NO_3 at the current MechGen site takes around 4 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 larger 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 generation is 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 an intermediate reactant is created or selected, as shown for example in 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, along 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 containing the reaction or product lists that can be imported into spreadsheets or used as inputs for model simulations. Examples of such a page are shown in Figure 6 and Figure 7. Figure 6 includes a list of all the explicit reactions in an abbreviated form, including 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 (see Section 6). 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 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 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 the portion of the output shown in 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 in 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

Mechanism generated using Explicit mechanism with no lumping
Explicit mechanism has 39 reactions and 35 species. Download tab-separated files with (reactions) or (products)
Processed mechanism has 16 reactions and 22 species. Show (reactions). Send in (tab-separated format) or in (SAPRC .RXN format)

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%	15.7%	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

(portions not shown)

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 "STDG40Z0" 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

(see Figure 7)

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.

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 shown in Figure 7, except that lines longer than 80 characters are continued on the following line. Note that selecting the "show (reactions)" link will display the output as a web page, but does not download it.

If a non-explicit (e.g., SAPRC-22) lumping method 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 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 produced during the single-step reaction process due to the large numbers of reactions typically involved. The reactant will be included in the

reactant listing portion of the main menu with a "(Reacted with …)" link that, if selected, will re-display 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 in 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 for users to 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 0 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.

4.6. Obtaining Information

The "Obtain Information" section of the main page includes links to various types of information regarding MechGen and the SAPRC-22 mechanism, including PDFs of this and the basic users manuals. This includes information regarding estimation methods, assignments, and details on the SAPRC-22 mechanism and how MechGen was used to derive it. These outputs are only available using the web interface. The various types of information outputs are summarized below.

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 in 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 and the 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 differ if the user has 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 in 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 a user or (more likely) in the process of deriving the SAPRC-22 mechanism (Carter, 2023a).

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
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
O_2 in air	20.95%	Mole fraction of O_2 in the reaction environment
H_2O	Present	Used to determine if reactions of some intermediates (e.g., Criegee intermediates) with water are to be generated.
Lumping method	Explicit	Lumping method used when generating full reactions and processing results. Currently available options are "Explicit" or SAPRC-22 or SAPRC-11. 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
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 generation.
Minimum yield to react	0.5%	The minimum estimated yield for a peroxy radical intermediate to be reacted during full mechanism generation.
User mechanisms	No user mechanisms	Users who select a SAPRC-22 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.

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.

SAPRC-22 Mechanism Assignments (with 541 species) [#6218]

Chemical mechanism assignments used for for the current version of the SAPRC-22 mechanism.

Show assignments

- Show assignment data for all 541 compounds (this can take around 10 seconds)
- List all 541 compounds and intermediates with assignments (this can take around 10 seconds)
- List assigned parameters used during mechasnsm generations for some types of reactions
- Show assignments for selected species:
  [ ] go
- Show all rate constant assignments: (uni) (OH) (O3) (NO3) (O3P) (Cl) (HV)
- View assignments used when generating mechanisms for selected individual VOC species
  - select from list by type of compound
  - select from full list of compounds with assignments
- Show other assignments (not associated with any particular SAPRC VOC species)

Download data:

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

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 - 5.12e-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 constrant 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 constrant 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.

The output shown in Figure 8 - 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 during full mechanism generation.

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 in 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 and compositions of mixtures used for various purposes, but these are not shown on the user-installed versions (Section 9) because of the amount of data required. All versions include lists of explicitly represented compounds and the model species in the SAPRC-22 mechanism, and the derivation of lumping methods and the input defining these mechanisms are discussed in Section 11. 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.

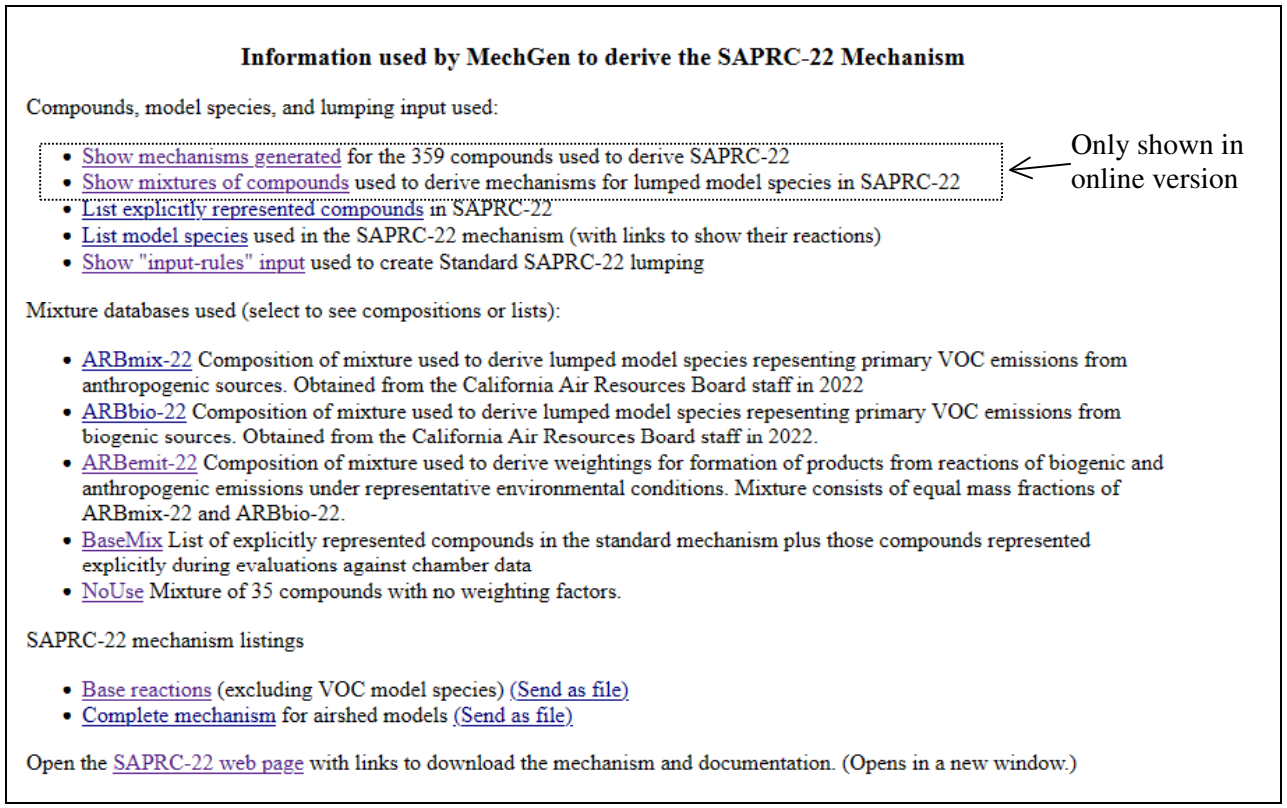


Figure 11. Screenshot of page giving links to information related to the SAPRC-22 mechanisms. Note that the "Show mechanisms generated" and the "Show mixtures of compounds" links appear on the online version of MechGen but not in user-installed versions as discussed in Section 9 because of the amount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

5. BASIC OPERATIONS FOR TELNET USERS

The Telnet 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, as discussed in Section 9.

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* and *userpass* are the user's name and password provided when creating the 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 and the web passwords can be separately changed and do not have to be the same. 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 a Telnet session, and this will not change the web password.

Terminal input and output when the user first connects to the MechGen interface is shown in Figure 12. Figure 12a shows the message displayed when the user first connects to the web system, 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 the "look" command when the user is in the reactor. Note that the user and reactor and its contents are exactly the same as shown in Figure 1, which shows the display if the same user were connected using the web system.

The reactor that the user enters upon logging in is the only virtual location in the system where s non-authorized user can carry out the MechGen operations discussed in this document. 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 users can create additional reactors where they can assign different options and carry out mechanism generation operations separately.

Terminal commands available to MechGen users via Telnet are listed and briefly described in Table 6, with Table 7 describing the types of information that can be output. These commands are only a subset of commands available to Telnet users, and do not include additional commands involving lumping, creating user assignments, or advanced mechanism development, as discussed in Sections 7 to 9, respectively. General MOO commands, for which information can be obtained using the MOO's "help" command, are not generally needed for MechGen users, except for certain 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. Table 6 summarizes basic commands that can be used to manage reactants in the reactor.

```
HTTP/1.0 200
X-moo: This is the SAPRC atmospheric chemical mechanism generation system.
 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.
```

(a)

```
connect User1 user1pass
*** Connected ***
```

(b)

```
Interior of user1's chamber (#6343)
This is a reaction chamber for generating mechanisms for chemical reactions in
 the atmosphere.
Exit:  [out] to The First Room

Options for user1's chamber:
  Lumping Procedure (lumping) .... Explicit mechanism with no lumping
  Minimum 1-step yield (MinYld) .. 0.005
  Minimum RO2 yield (RminYld) .... 0.005
  Vapor pressure estimates (VP) .. SIMPOL.1 vapor pressure estimates

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

Stable reactants: 3
Last connected Tue Mar 19 14:20:38 2024 PDT from CarterHome3
  MEK: CH3-CH2-CO-CH3 (reacted with OH, NO3, HV) [#21153]
  ORG-1391: HCO-CH(OH)-CH2-OH [#21650]
  VOC-1: CH3-CH(CHO)-CH(CH3)-ONO2 [#5976]
```

(c)

Figure 12. Input and output shown when a user ("user1") 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.

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 (or "l")	Generate the display summarizing the environmental conditions and listing reactants in the reactor as shown in Figure 12c.
Options	Output summary of current reactor options.
Reactants (or "r")	List the reactants in the reactor
Delete-reactants / zap-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 clear (delete temporary group properties) in remaining reactants with such properties.
Reset-options	Reset reactor options to defaults, including deleting user mechanisms and user assignments if they were created.
Delete <object>	Delete a reactant, user-created environments, or other user-created objects such as discussed in sections below.
	General reactant maintenance
Delete <reactant> / zap <reactant>	Delete an existing reactant in the reactor, where <reactant> is the name or structure of a previously created reactant in the reactor.
Erase <reactant>	Delete results of a previous "fullreact" operation (see below) for the reactant. Does not clear temporary group properties.
Look <reactant>	Display the name and structure of a previously created reactant in the reactor and indicate 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.
	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>	Create a VOC reactant that has been assigned a standard SAPRC detailed model species (DMS) name.
	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", HV, etc), which must be specified when reacting a stable compound, but not radicals. See Section 5.2.

Table 6 (continued)

Command [a]	Function
React1 <reactant>	Similar to "React" but only generates a single-step unimolecular reaction. 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. If "with <what>" is not given, all supported reactions of the compound 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>	Output results of "fullreact" operations on a reactant to the terminal. The types of results that can be output are listed and briefly described in Table 7.
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 using the "Files for download" section of the main menu in the web interface.
@ftpout <item> on <reactant> / @ftpout <item> on usermech / @ftpout userasns	Same as "read" or "fileout", 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.
Read <item> on usermech Read userasns	Used to obtain information about a user mechanism (usermech) as discussed in section 0, or about user assignments (userasns), as discussed in Section 8.
	Modifying reactor options
Option <item> is <value>	Change reactor options, where <item> indicates which option, and <value> refers to the new option to be used, which could be a number or a MOO object. These options are listed in Table 8.
Option <item> is default	Set the select option to reactor defaults, as given in Table 8. If <item>=all, then all options listed there are set to their defaults.
Reset-options / Option all is default	Restore all options to their defaults, and delete any user mechanisms or assignments that may have been created.
Stdenvts [options]	List or specify the standard environment(s) 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 options.
Lumping [<lumpname>]	Change the lumping to the named lumping method, if available. If <lumpname> is not given, it shows the current lumping method and lists the available lumping methods, offering users to select a different method. See Sections 7 and 11.
Lumpings	List current and available lumping methods and give the user a selection to choose one.

Table 6 (continued)

Command [a]	Function
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, either in addition to or to supersede the MechGen assignments. Additional commands are available to create or delete the assignments. See Section 8.
Basic user commands	
@quit	End 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>]	Change your Telnet login password. It does not affect the web password. You will be prompted to give the old then new password if they are not entered on the command line.
Home	Go back to your reactor. If you find you are getting "I don't understand that" output when giving MechGen commands, it may be because your player object exited your reactor.
Help	Give 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> … .	Provide 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. Afterward, the user is unable to log in again. The user can use the web system to create a new account if desired.

[a] Commands 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 item 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
Tabreactions	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 the 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.

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 commands 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. For example, the input command "Build <structure>" is the same as "Build CH3-CH3" if "CH3-CH3" is the structure. Optional input is indicated using brackets. For example, "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:

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

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 to many VOCs represented by SAPRC detailed mechanisms (see Section 3.2), and <your-choice-of-name> is any name that the user may assign. The name 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 message 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 a temporary name, depending on whether the reactant has a radical group, as specified in Table 2, with "n" being a sequence number used to distinguish it from other generated names. Temporary names are no longer used for the compound once it is deleted.

An example of terminal output following the execution of the "build" command using the Telnet interface is shown in Figure 13. This example shows the same compound as shown in Figure 2 after it was created using the web system. Note that this example 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 an example.

5.2. Generating Single Step Reactions

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

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

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. The "with <reaction>" can be specified when reacting a stable compound, but should not be specified when reacting radicals. 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 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 in unimolecular reactions, the "react1 <name or structure>" command, which generates only unimolecular reactions, should be used instead.

The output of the "react" or "react1" commands is the same as the single-step reaction output using the web system, as shown in 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 in 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 are 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 to the "react" command discussed above, i.e.,

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

where <name or structure> and <reaction> indicate 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, with all types of possible reactions being generated

```
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.

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 is to be generated, the types can be listed following the "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 in 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;

```
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.

"ToGo" -- number of reactants in queue to be processed; "Working on" -- intermediate currently being processed. This continuous output allows users to know if the process is proceeding properly, 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 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, after which 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, 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 except for the reactant itself. 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 generation are not automatically output when the process has successfully completed, other than the summary output as shown in Figure 15. Instead, the results can be output 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 in 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 run your own copy of MechGen (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:

Option <option> is <value>

or Option <option> is default

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 in Table 8. In addition to options listed in Table 8, advanced users can enable "user mechanisms" and "user assignments", which are discussed in Sections 0 and 8. The commands:

Reset-options

or Option all is default

restores the values of all options listed in Table 8 to their defaults, and also deletes any user mechanisms or user assignments that may have been created. The "reset-options" command also restores standard environments (see Section 6) to their defaults. The "options" command does not affect standard environments.

Note that none of these commands affect the reactant objects in the reactor, except for deleting the results of previous "fullreact" operations if 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 $\mu g/m^3$	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.
RMinYld	0.005	The minimum estimated yield for a peroxy radical intermediate to be reacted during full mechanism generation. Peroxy intermediates with lower estimated yields are replaced by HO_2 + "LostMoles" to avoid generation of even lower yield intermediates. Must be greater than 0 and less than 0.05.
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" and "SAPRC22", but others may be available in future 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) and "vpevap" for EVAPORATION (Compernolle et al. 2011), but others may be available in future versions of MechGen.
All	see above	Reset all options to default. Also delete any user mechanisms (Section 0) and user assignments (Section 8.3) that may have been created.

6. STANDARD ENVIRONMENTS AND RELATIVE YIELDS

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

- 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 the "read products on <reactant>" terminal command.
- 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 in Table 5 or Table 8, such as temperature, O_2 content, or parameters that determine which reactions or species are to be treated as negligible.

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 specified environments. This is useful to observe how product yields change with environmental conditions. Only a single standard environment is used when deriving multi-generation mechanisms (see Section 10).

6.1. Determination of Relative Yields After Full Mechanism Generation

Relative yields are defined as yields of stable products formed when a reactant is fully reacted. They depend on environmental conditions because they are affected by competition between unimolecular, bimolecular and photolysis reactions, which depend on concentrations of atmospheric species such as O_2, NO, HO_2, etc., and (if applicable) the light intensity and spectrum. The parameters that affect values of rate constants such as temperature and lighting conditions are specified as reactor options, and the concentrations of the atmospheric species and the total light intensity as a fraction of the maximum are specified for each standard environment. Once these are specified, the relative yields for these options and environmental conditions can be uniquely determined.

Relative yields are determined by (1) assigning a relative yield of 1 to the initial reactant; (2) assigning a weighting factor for each reaction based on the relative yield of the reactant and the rate constants and (if applicable) concentrations of the co-reactant; (3) assigning relative yields for products and radicals based on the sum of weighting factors for reactants forming them. This process is not always straightforward and care must be taken that reactions are generated in the proper order to minimize generation of intermediates that have already been reacted. This is not possible in all cases, and if necessary, a matrix inversion process on the steady state equations is used to determine ratios of steady-state concentrations and therefore relative weights of reacting intermediates. More information about the algorithm employed is given by Carter et al., (2024).

6.2. Estimation of Negligible Processes During Full Mechanism Generation

Mechanisms generated for larger compounds can be much larger than necessary and dominated by reactions of negligible importance if steps are not taken to identify and eliminate such negligible reactions. As mentioned above and discussed in more detail by Carter et al. (2024), two reactor options are used for this purpose, one ("MinYld") being used to determine which competing reactions can be neglected during single-step reaction operations, and the other ("RMinYld") is used to determine which radical intermediates can be represented by HO_2 + "lost moles" during the full mechanism generation process. The latter test is needed when generating mechanisms for larger molecules because sequences of reactions with branching ratios just above the "MinYld" cutoff can result in formation of very low-yield intermediates that can form even lower-yield intermediates when they react. Having low-yield intermediates form HO_2 + "Lost moles" preserves radical balance but does not conserve mass. Because of this, the "lost mole" yields are used to calculate lost carbon and other atoms during subsequent processing, and these results are included in the product yield output. On the other hand, use of the one-step "MinYld" test does not lose mass or radicals because the competing reactions are re-normalized to account for 100% reaction if any competing reactions are eliminated. Effects of varying these parameters on generated mechanisms are discussed by Carter et al. (2024).

Standard environments are used for determining negligible processes if (1) "explicit" or no lumping is in effect, and (2) the option to use at least one standard environment for mechanism generated is selected as a reactor option, as discussed below. Otherwise, the "MinYld" test is only applied to reactions with the same oxidant (or to unimolecular + O_2 reactions), and it is assumed that different types of competing bimolecular and unimolecular are equally likely when estimating upper-limit yields for the purpose of applying the "RMinYld" test. If more than one standard environment is used, the tests are applied using the maximum relative rates among the environments used. Standard environments are not used when determining relative importances of different types of bimolecular reactions when mechanisms are generated using SAPRC lumping, because the way stable compounds are lumped determines which bimolecular reactions they undergo, and because low-yield intermediates are not explicitly represented in lumped SAPRC mechanisms (see Section 11).

6.3. 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 ("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.

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 by Carter et al. (2024).

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

Name	Description of conditions [a]	Default use [b]	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] "MIR", "MOIR", and "EBIR" refer to NO_x conditions as they affect VOC reactivity. See Carter (1994).

[b] 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 6.4.

6.4. 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 in 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-defined environments are created using the Telnet system, as discussed in Section 6.5, 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 reappear 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 in Table 10. 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 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 in 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 in Figure 16c. There may be additional environments on

(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".
Click here to restore defaults, or **click here 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.
```

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

Table 10. 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 in Table 9, are used for product yields, with the last three used for mechanism generation.
Stdenvts list	Lists and briefly describes all the available standards 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 and prompts the user for lines of input creating or modifying the targeted environment. <envtname> is a short namefor the environment and must not be recognized for any other object in the reactor. <label> is optional and is a short label used for output (<envname> is used for this purpose if not given). 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.

the list if the user created any, as discussed below in Section 6.5. 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, use the command:

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

where the <envname> refers 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* 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 in Table 10.

6.5. Creating New Standard Environments

Although only the primary MechGen user is able to 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 modify. 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> (optional) is used to identify the environment in outputs such as shown in Figure 16a and b. If <label> is not provided, <envtname> will be used instead in outputs. Note that <envtname> cannot also be an identifier or name for any other object in the reactor, 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. Both <envtname> and <label> can be used to modify the existing standard environment they refer to.

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 in Figure 16.
Optional lines:	Additional information about the environment that is displayed using the "look" command.
Blank line:	A blank line is required to separate the description and optional information from the remaining 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), "HV"relative light intensity), and "Hours" (reaction hours for multi-generation mechanisms, see Section 10). No other species or option names are allowed.

Termination: A single "." is used to indicate that this is the end of the input.

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

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. This option must be given with a nonzero value to represent non-dark conditions.
- The "Hours" input is used to indicate reaction hours when results of multi-generation mechanisms are processed. The derivation of multi-generation mechanisms is discussed in Section 10). The "hours" input does not affect product yields 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 those shown in 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. These can be deleted using the "delete" command (), 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 in Table 9.

7. GENERATING LUMPED MECHANISMS

Detailed explicit mechanisms, such as those produced using "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 the formation of ozone and other secondary pollutants, and the 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 is 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 with 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), which was derived using the chemical estimation methods and assignments documented by Carter et al. (2024) and the MechGen system 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.

The lumping methods currently supported by MechGen are summarized in Table 11. These include "explicit" or no lumping, which is the default, and lumping for the SAPRC-11 and SAPRC-22 mechanisms. 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 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 in Table 7. The choice of the lumping method also affects which reactions are generated during "react completely" or "fullreact" operations. For example, reactions of radicals represented using lumped model species (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 may cause problems with the mechanism reduction algorithms employed. For that reason, users who are primarily interested in complete explicit mechanism generations should employ the "explicit" lumping option. However, the choice of lumping method does not affect single-step mechanism generation.

Table 11. 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.
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.

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 change the method used. This information and link are also given in the "Reactor options" section of the main menu. Selecting this link will give a page listing the available lumping methods, indicating which is currently selected, and providing links to allow you to select a different one. Note that changing the lumping method will erase all previous "react completely" results in the reactor. This is because these results may not be valid for the new lumping method.

Telnet Interface. Both the "option" and "lumping" commands can be used to change the lumping method, as indicated in Table 8, and the "lumping" command can also be used to change the lumping. The syntax of the commands is:

Option lumping is <lumping>

or Lumping <lumping>

Where <lumping> must exactly match (case insensitive) the short name of a lumping method as shown in Table 11. 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. If the "lumping" command is given by itself, it will indicate which lumping method is currently in effect. Finally, the "lumpings" command will give the user a list of numbered available lumping methods, and then ask the

user to select a number to choose 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 is therefore most appropriate if complete explicit mechanisms are the primary interest of the user.

If explicit lumping is in effect, the "react completely" and "fullreact" operations will not produce lumped mechanism output other than 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 provides options to derive lumped mechanisms that are compatible with two versions of the SAPRC mechanism. As indicated in Table 11, these include the SAPRC-22 mechanism, which is the most recent SAPRC mechanism derived using MechGen, as documented by Carter et al. (2023a). 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). Although lumped mechanisms derived using MechGen using "SAPRC11" are compatible with the SAPRC-11 mechanism 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 from those in SAPRC-11 because of updates to MechGen since SAPRC-11 was developed. However, mechanisms derived by MechGen using "SAPRC-11" lumping can still be added to models using SAPRC-11 or, in most cases, to SAPRC-07 if it is desired to represent additional species explicitly in those models.

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-07 or SAPRC-11.

All the lumped SAPRC mechanisms 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 "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, all types of phenoxy radicals, i.e., all radicals that 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. 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 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. These can also be obtained using "tabrxns" or "rxns" output as indicated in 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, the generated lumped reactions, and their rate constants.

"RXN" outputs using propene as the example compound are shown for the three SAPRC lumping methods in Figure 17. Note that propene is represented explicitly in 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-nnnn" name (see Section 3.2), the name "VOC-n" is used, where n is a number that depends on how many 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.

(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) 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.

Lumped SAPRC-22 mechanisms may require the 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 in 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 regardless of 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.

7.3. User Modified SAPRC-22 Mechanisms

MechGen provides the capability to modify the SAPRC22 lumping method to 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, as they are already represented explicitly in the output. However, it becomes necessary if it is desired to have important products formed from the selected compound(s) to also be represented explicitly. Users can then output the mechanisms generated for the selected compounds and their explicitly-represented products, either with or without the rest of the reactions in the base SAPRC-22 mechanism. 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 for the standard SAPRC22 lumping. This process is referred to as preparing a "user mechanism" that consists of providing a list of compounds to be represented explicitly. The process of preparing user mechanisms [ZW11]involves the following steps:

- Select "SAPRC22" as the lumping method (if not already selected). The web system will have no link to create user mechanisms, and the "usermech" terminal command will fail, if SAPRC22 has not been selected.
- Use the web interface or terminal commands to create the user mechanism by providing the list of explicitly represented compounds. 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 compounds are referred to as the "user mechanism compounds".
- 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 user 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 user mechanism species lists and reactions in RXN files usable by the SAPRC modeling software.

As indicated above, each compound in the user 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 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 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 user 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 user mechanism species. An example of such output is shown in Figure 18, which shows a user mechanism with n-butane and selected major products created as shown in 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 user 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 represented explicitly, the additional compounds(s) will need to be included in the user mechanism.

When a user mechanism has been created, the lumping method changes in the following way:

1. When compounds in the mechanism react completely and form user mechanism species as products, they are represented explicitly in the mechanism.

2. Instead of being lumped together with other similar species under a general, lumped model species (as it would be in the default lumping method), the user mechanism species is represented explicitly by its associated model species name.

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 a different lumping method is selected. Selecting a different lumping method deletes the user mechanism, and it will not be available even if the lumping method is restored to its previous value.

```
! 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.

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. The following sections explain how to work with user mechanisms using the web or Telnet interfaces.

7.3.1. Managing User Mechanisms using the Web Interface

The main menu indicates the current lumping method, and provides links to change it. These 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 user mechanism" link in the "Advanced options" section. It will also indicate the number of user mechanism compounds included, which initially will be zero.

Examples of web pages displayed when selecting the "Manage your user mechanism" link are shown in Figure 19. Figure 19a shows the display if there are no compounds in the mechanism. To add a compound, give its name or structure 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. There is no need to give a model species name if the compound has a standard name, as the standard name will be used even if a different name is entered. Model species names will 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 none is specified, the compound is added to the user mechanism, but a name must be provided before the mechanism is complete. 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 user mechanism, it is created in the reactor and the user mechanism page will be updated to show the new compound. An example of an incomplete user mechanism for n-butane and its major products, where a name is needed for a user mechanism compound, is shown on Figure 19b. Note that there is an input box to give the name for the user mechanism compound that does not have a standard name. After the name is input, the page is updated to show the name with the structure of the compound, and links to react all the compounds.

Note that the user can 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 user mechanism is complete, and has no effect on the actual mechanisms.

After adding all desired compounds, 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 user mechanism products are represented explicitly using their assigned model species names. Once completed, the user mechanism display will resemble as 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 recreate this user mechanism in case it is deleted. However, user mechanisms created using the web system will also be available to the user when logged into the Telnet system, and vise-versa.

7.3.2. Managing User Mechanisms using the Telnet Interface

The commands to create, delete, react, and output results for user mechanisms using the Telnet interface are listed and summarized in Table 12.

As indicated in Table 12, the "usermech create" command is used to provide a list of compounds to be explicitly in the user mechanism, and the model species name to use in the lumped mechanism, if

(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 user 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 user mechanism for reactions of n-butane and its major products. This is the same mechanism as shown on Figure 18.

Table 12. Commands used to work with user mechanisms using the Telnet interface

Command	Description
Usermech create <reactant1> [<name1>] <reactant2> [<name2>] .	Creates a new user 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 in Figure 20
Usermech react	Reacts all reactants in the user mechanism. This is necessary before any output can be generated.
Usermech	Lists compounds and model species names in the user mechanism, indicating 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 for all compounds in this user mechanism, optionally including portions of or the entire base SAPRC-22 mechanism needed for complete mechanism preparation.The "read" command results in outputs going to the terminal, while "@ftpout" sends results to the MechGen FTP site for authorized users. The available options are as follows:
<option> = rxns	Output only species and reactions of user mechanism compounds and any intermediate model species not part of the base mechanism.
<option> = needrxns	Also include the base mechanism for inorganics and C_1 species and reactions needed to represent reactions of all the products. 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 include 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	Output the "usermech create" input that can be used to recreate this user mechanism in case it is deleted. This may be useful for large user mechanisms.

needed. The compound is specified either by its MechGen structure (see Section 3.1) or by its standard SAPRC name (see Section 3.2). If the compound does not have a standard SAPRC name, the model species name must also be on the input line, separated from the compound structure 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 are not needed to be specified if the compound already has a standard SAPRC name, and if a different name is given for such compounds, a warning message will indicate 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 allow deleting or adding compounds to an existing user mechanism. 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 user mechanism with n-butane and selected major products it forms. This is the same user mechanism shown as Figure 19 for the web system and whose output is shown in 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

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

(b) Input using names where applicable.

```
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 in Figure 18.

8. USER ASSIGNMENTS

Whenever MechGen derives reactions of a given reactant, it first examines available assignments and if applicable uses these to derive the reactions rather than using the general estimation methods (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, and is also useful in specifying mechanisms for unique compounds where general estimation methods are not useful. Although MechGen provides for the possibility of having alternative mechanism assignment databases, the current system uses only the SAPRC-22 mechanism assignments as described by Carter et al (2023a), viewable through the web interface as described in Section 4.6.

Although only the primary MechGen user can modify the default mechanism assignments, other users can employ "user assignments" to add to or override the default SAPRC-22 assignments if desired. This might be useful for advanced users who wish to incorporate new data or address inconsistencies with default MechGen predictions. User assignments are disabled by default, but can be enabled using either the web or telnet system.

Once enabled, MechGen will use user assignments if available; otherwise, it only uses the default assignments. If user assignments are enabled but have no assignments, MechGen will operate as if no user assignments exist. User assignments are referenced and retrieved giving a reactant structure, so if user 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 assignments include rate constants for reactions with OH, O_3, and NO_3, and a user assignment specifies a 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 ensure any 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 removes user assignments permanently, requiring re-entry 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 commands, described on Table 13, 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. regardless of whether the web or telnet access is used 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).

Several representative examples of the various assignment commands summarized on Table 13 are indicated below. Note that these examples are not necessarily current SAPRC-22 assignments, but are sufficient for illustrative purposes.

Table 13. 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).

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 14 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:

- 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.

Table 14. 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.

- 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 is 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 to be considered 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 for 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 illustrates 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.
- 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. 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 to test user assignments 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 multiple 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 via the telnet interface or selecting the "(delete)" link on the web interface. However, you cannot delete individual assignments for particular reactant, though assignments of individual rate constants or branching ratios can be modified. Assignments of total rate constants can be modified by giving a new k-assign-(ox) command, 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, if the reactions or products are to be changed, all existing assignments for the compound must be deleted before entering new assignments. In such cased, it will also be necessary to re-input all assignments for the compound that are to be retained.

The telnet interface is recommended if large numbers of assignments are to be made, as it allows batch input of multiple assignments, unlike the web interface, which requires one command 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.

Note that the primary MechGen user (named "MechGen") should be careful when creating or managing user assignments, because if user assignments are not in effect, then assignment commands (discussed in the following section) given by this user will change the default assignments that apply to all users. If the user logged in as "MechGen" thinks user assignments are enabled but they are not, the assignment commands may change the default assignment rather than user assignments. Use of the web system to make user assignments eliminates this possibility because the web system cannot be used to change default assignments regardless of the status of the user.

Although the mechanism assignment commands are the same regardless of which interface is used, the procedures for enabling, disabling, listing, or deleting assignments vary by 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 "Advanced options" section will display 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 for entering a single user assignment command, as discussed in the previous section and shown on Table 13, along with instructions detailed 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.

(a) Output if no assignments exist

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)

(b) Output if one assignment exists

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

(same as above)

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

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 "Advanced options" section of the main menu will also show a line indicating that user assignments are enabled, 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 13. 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 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 or MOO implementation issues that the authors do not understand, it is not possible to input multiple lines of assignment commands without losing data, so assignments must 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 15. User assignments are disabled by default, but are enabled whenever the user enters an assignment command such as is listed in Table 13 in the user's reactor, or gives the "userasns enable" command as indicated on Table 15. 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 assignment command 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 15, 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

Table 15. 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	Creates user assignments (if not created previously) and enable them. Note that enabling user assignments 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>	Displays user assignments for a selected reactant if user assignments are enabled. The default assignment for the reactant is shown if user assignments are not enabled.
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 13
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 13, 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-asn-cmds [<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-asn-cmds" 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.

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 available for web users.

9. INSTALLING MECHGEN FOR ADDITIONAL CAPABILITIES

The previous sections discuss how anyone can access MechGen online, use it to generate explicit and lumped mechanisms for small to moderate sized compounds, and obtain results in various formats. MechGen also offers additional capabilities such as generating mechanisms for larger compounds, generating multi-generation mechanisms, and creating new complete lumped mechanisms for airshed models. However, due to software limitations, the current web system does not operate properly when Telnet users are running highly resource operations, such as generating mechanisms for large numbers of compounds in batch mode. For this reason, unauthorized users are not given the capability of doing such operations when logged into the online MechGen system.

Therefore, users who want to access MechGen's full capabilities should obtain their own copy of the system, which allows them to access the system as authorized users. They could also configure their systems for web access, though it should not be relied upon to be always functional when Telnet users are carrying out resource-intensive operations. The files and software required to run stand-alone copies of MechGen are available for download as discussed below. This section also provides details on how to install and maintain the system, obtain and configure the software, and authorize users to access 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). The MOO object-oriented programming language is similar to Python, so theoretically, the MechGen software could be converted to Python or other supported platforms. However, this would be a major effort that has not yet started, so use of MOO software remains 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. MOO servers must have accessd the network, and users normally access the system using the Telnet virtual terminal protocol. The MOO database is a file that contains all the programs and data structures contained in a MOO. 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 data used by MechGen are contained in the MechGen MOO database, along with programs and objects used in the MOO for virtual reality or user interaction experiences, most of which are unused in MechGen systems. 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.

Users considering installing MechGen are encouraged to familiarize themselves with the MOO systems. The LamdaMOO website at https://www.moo.mud.org provides links to a MOO FAQ, a MOO programmer's manual, and the Unix version of the MOO server software. Although the site focused on MOOs for multi-user interactions rather than hosting systems like MechGen, the information regarding

the server, MOO databases, and MOO programming is still relevant and should be read by those considering installing MechGen.

A complete discussion on programming MechGen and updating its data and algorithms in a MOO system is beyond the MOO server and scope of this document. Those who are interested in further development of MechGen, or reprogramming it into a more widely used programming language, are encouraged to contact the authors concerning potential collaborations.

9.2. Obtaining, Installing and Configuring MechGen Software

MOO server software is available for both Unix/Linux and Windows systems. While MechGen was initially developed on a Unix server, it is now primarily maintained on a Windows-based server, so either type of server software can be used. MechGen uses the File Utility Package (FUP) extension to send result files to users (via the "fileout" command, discussed elsewhere), so it is recommended to install the MOO server with this extension. Although most MechGen functions work without FUP, error messages may appear due to references to FUP functions. [ZW13]

9.2.1. Installing and Running MechGen on Windows Systems

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.

To set up MechGen on a Windows system, extract all contents of the zip file into an empty folder. This should create a subdirectory called "files" with an empty subdirectory named "users," which is necessary for files created or accessed using FUP. 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 file named MechGen.db.

The batch file "MechGen.bat", shown on Table 16, 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 shut down the server without saving changes made since the database saved. Typing control-C with the window selected will save the current database and then shut down the server.

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 the server is shut down properly and the appropriate batch or command file is used, the last output database will be used as the input when the server is re-run.

9.2.2. Installing and Running MechGen on Unix or Linux Systems

A guide on how to install and run a copy of MechGen on Unix/Linux system is available at https://github.com/SAPRC/MechGen/wiki/Install-and-Run-MechGen-on-Unix-or-Linux-Systems. To run MechGen, users need to first install the MOO server and its FUP extension. The LamdaMOO Server that runs on Unix or Linux systems is available from Sourceforge[1] or Github[2]. These sources include a

[1] https://sourceforge.net/projects/lambdamoo
[2] https://github.com/verement/lambdamoo

Table 16. 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.

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. Note that installing FUP is optional and does not affect the core functionality of MechGen. However, without FUP, the "fileout" command will not function, and error messages may appear due to references to FUP-related functions. The FUP extension also includes a README file with installation instructions for integrating it with the MOO server.

After installing the MOO server, users can download the MechGen database file for Unix/Linux from our GitHub page at https://github.com/SAPRC/MechGen. MechGen can be run with the following command:

./[path_to_moo]/moo mechgen_unix.db > out.db &

Where "./[path_to_moo]/moo" is the executable of the MOO server, "mechgen_unix.db" is the MechGen database file, "out.db" (or any name) is the output database. The ">" symbol redirects the output to the specified file (out.db). The "&" symbol is optional, allowing MechGen to run in the background. This is recommended, as MechGen needs to remain active while being accessed via the web or Telnet interface.

If the command above runs successfully, follow the instructions in Section 9.2.3 to configure MechGen for enabling web and/or Telnet access on the assigned port. For example, if the configuration is successful and the port number 7777 is assigned, users can access MechGen via a web interface at https/localhost:7777. If the Telnet protocol is installed, users can also access MechGen using the command:

telnet localhost 7777

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 port used to access the MOO systems with the Telnet interface should be specified when the server is run (e.g., see the last row on Table 16), but if not 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. 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.

When first connecting to the server, the system will have a blank password for the "owner" wizard, allowing initial Terminal (Telnet) access with the command "connect owner" without 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/programmer named "MechGen".

The system will then ask the user to provide configuration input summarized in Table 17, 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 programs that are not part of the MechGen system, or managing users. Most programs and non-user objects in MechGen are controlled by the primary user "MechGen", who initially has the same password as "MGadmin", though passwords can be changed. 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 18 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 17. 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 the only 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 be 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 be optionally changed.

9.3. Creating and Authorizing Users and Authorized User Capabilities

As indicated on Table 18, the MGadmin login can be used to create and authorize users. 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. 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 users created by non-MechGen programs within the system. 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 command:

authorize-user <name>

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 have one. MGadmin can revoke the authorization by giving the command:

unauthorized-user <name>

Table 18. 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 or new user and <password> is the password for both web and Telnet logins
Deletes a MechGen 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. Can only be done for non-system web users or users created by the "User" command, above.
Control whether a user is authorized for additional capabilities	Authorize-user <user> Unauthorize-user <user>		<user> is the name of an existing MechGen 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 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
Enable telnet access using another port	;listen(#0, <port>)		

Table 18 (continued)

Action	Command	Discussion
Disable web or telnet access using a port	;unlisten (<port>)	<port> is an active port number that can be viewed using the ";listeners()" command, below.
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.

Note that the "unauthorized" operation does not delete the user or its Telnet login. MGadmin can delete users and both their web and telnet accounts using the command

Delete-user <name>

If a user is logged in to the Telnet interface when deleted, 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. Note that deleted users can re-create their accounts as discussed in Section 2.1 and 2.2, using the same or different name and any password they chose. However, any reactor configurations or reactants created previously would be lost.

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 MechGen operations. 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 in the room 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, nor in any other users' reactors. The user can enter the new reactor by giving the command: enter <reactor name>", 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. However, the web system only uses the users' primary reactor.

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

In addition, 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. 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 above.

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. Although the MechGen login can perform all operations, it is recommended to avoid using it for this purpose, since there is always the chance that this login could make errors that could modify the system in unintended ways. For example, mistakenly giving an assignment command intended for user assignments, while user assignments are disabled, could result altering 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 is similar to Python. 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. 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, will need a deep understanding of the software and are encouraged to contact the authors 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. The MechGen login can use the same assignment commands as those discussed in Section 8.1 to modify the default assignments, as long as user assignments are disabled. 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 a "Userasns-disable" or "Userasns-delete" command to disable user assignments. (3) 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 15 in that section are applicable except for those referencing "userasns. (4) 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. It is also a good idea to test the assignments by generating reactions that may be affected in single step model. Although the MechGen primary user login can also make user assignments, it is recommended it not be used this way to avoid accidentally changing default assignments for all users.

9.5. Creating New Standard Names for Reactants

As discussed in Section 3.2, most 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 19 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 19. Commands that the primary MechGen user can use to create and manage standard names for compounds

Command	Discussion
DMS <name> is <structure> [<option1> <option2> …]	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:
Type=<compound type>	Compound type (e.g., "Normal alkanes").
Desc=<description>	Common name used for the compound (e.g., "Propane")
Name2=<shortname>	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, which 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 authorized for these capabilities. In practice, this means that users who desire the full capability of MechGen should 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. If 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, it may require more time and computer resources than are available. Therefore, mechanisms 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, be in a reactor that has the lumping option set to "explicit" (see Section 7), and have at least one standard environment selected for mechanism generation (see Section 6.4). Note that 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, the first on the list is used for deriving multi-generation mechanisms.

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 will 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 in Section 9.5, or create and name the reactant using the "build" command (see Section 5.1) before giving the "create-MGmech" command.

In either case, the result is the creation of a "MG-<name>" object within the reactor. This MGmech object is a type of "reactant container" object (see Section 12) that contain reactant objects, allowing operations 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, and also by the minimum yield ("MinYld"), reaction hours ("Rxnhours"), and minimum vapor pressure ("Minvp") options of the MGmech object. The minimum yield option, which is 0.0001 (0.01%) by default, is the threshold for including a product to be a non-negligible reactant in the mechanism. The reaction hours option, which is 6 hours by default, estimates the relative yields of the products. The default minimum vapor pressure is 10^{-13} atmospheres,

and compounds with vapor pressures less than this are treated as unreactive products. These options can be changed after the MGmech object is created by giving the commands

Minyld MG-<name> is <yield>
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, 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 when single step or single generation reactions are generated.

The next step involves reacting the initial reactant and all the non-negligible products formed in subsequent generations, using the command:

Allreact MG-<name>

This operation can take a very long time because even moderately sized reactants can produce very large numbers of non-negligible multi-generation products unless a large minimum yield 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 been reacted, which usually takes around 5 or 6 generations.

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, given by:

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

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, the command:

Look MG-<reactant>

will indicate whether this process is completed. If not, the command:

Reset MG-<reactant>

will delete the processing results but retain the results of the reactions of the individual reactants. Rerunning the "allreact" command will result in the results being processed again, but already reacted reactants will not have to be re-reacted.

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

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

where <item> is optional, indicating the type of output as listed in Table 20. As indicated in 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.

Table 20. Lists of types of output that can be obtained from the results of a multi-generation mechanism generation.

Item	Description
	Information Output
(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 this output after being loaded into a spreadsheet for MG-PROPANE.
Summary Cmpdinfo	Outputs information about reactants in contents. Same as "summary" or "cmpdinfo" output for reactant containers (see Section 12.2).
	Processed Mechanism Output
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 (Carter, 2023b) to conduct model simulations of the reactions of the initial reactants and its reactive products and intermediates. 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. These must be included with the reactions in the base mechanism, available with the SAPRC software and files (Carter, 2023b) to give a complete mechanism for model simulations. The output has 3 parts. The first part summarizes the parameters used, the second lists the reactants and products that are not in the base mechanism and gives their structures or descriptions, and the third part gives the reactions, with lines wrapped to be no more than 80 characters to be compatible with SAPRC modeling software. Figure 23 and Figure 24 show the rxnfile and rxnfile1 results, respectively, for MG-ETHANE.

Table 20 (continued)

Pseudo-Unimolecular Reaction Mechanism Output	
Unirxns	Outputs pseudo-unimolecular reactions for all the reactions of the reacting species for the conditions of the first environment used for mechanism generation. This output is also in the format that can be used by the SAPRC modeling software (Carter, 2023b), and is similar to rxnfile or rxnfile1 output except for the reactions. Figure 25 shows an example of this type of output for MG-ETHANE.

MG-PROPANE	1	7/5/24	Generation options: T=298; P=1.0; O2=0.2095; MinYld=0.0050; RminYld=0.0050; Lumping = explicit; Lumptype=3; Environ:										
EnvCond	StdEnv		Mid NOx standard urban conditions (near EBIR)										
Reacted	37	MGminYld	0.0001										
Reactions	330	Min VP	0.0000										
Radicals	47	R MinYld	0.0050										
Low reactivity	1	MinYld	0.0050										
Low Yield	59												
Failed reactants	0												
Reactants (37)	Gen	Moles	Carbons	VP	C	H	O	N	Name	Rct'd	kUni	Obj	Formed from	(Truncated ->)
CH3-CH2-CH3	0	1.0000	3.0000	3.7033	3	8	-	-	PROPANE	2	1.23e-5	#14277		
CH3-CO-CH3	1	0.6799	2.0396	0.4287	3	6	1	-	ACETONE	3	3.14e-6	#6571	CH3-CH2-CH3	
CH3-CH2-CHO	1	0.2699	0.8098	0.1774	3	6	1	-	PROPALD	3	2.79e-4	#6210	CH3-CH2-CH3	
CH3-CHO	1	0.2557	0.5113	0.4715	2	4	1	-	ACETALD	3	1.73e-4	#6803	CH3-CH2-CH3	
CH3-CH(CH3)-ONO2	1	0.0283	0.0849	0.0242	3	7	3	1	IC3-ONO2	3	7.09e-6	#9533	CH3-CH2-CH3	
CH3-CH(CH3)-O-OH	1	0.0280	0.0840	0.0134	3	8	2	-	ORG-0125	3	9.62e-5	#14659	CH3-CH2-CH3	
CH3-CH2-CH2-ONO2	1	0.0112	0.0337	0.0242	3	7	3	1	ORG-0050	3	1.09e-5	#7795	CH3-CH2-CH3	
CH3-CH2-CH2-O-OH	1	0.0111	0.0333	0.0134	3	8	2	-	ORG-0129	3	9.61e-5	#12665	CH3-CH2-CH3	
CH3-O-OH	1	0.0041	0.0041	0.0949	1	4	2	-	MEOOH	3	1.18e-4	#2646	CH3-CH2-CH3	
CH3-CH2-CO-O-ONO2	2	0.1285	0.3855	0.0175	3	5	5	1	PPN	3	3.48e-4	#4771	CH3-CH2-CHO	CH3-CH2-CH3
CH3-CO-O-ONO2	2	0.1050	0.2099	0.0465	2	3	5	1	PAN	2	3.40e-4	#12681	CH3-CHO	CH3-CH2-CH3
HCO-CO-O-OH	2	0.0075	0.0150	0.0018	2	2	4	-	GLYACID	3	4.10e-4	#20389	CH3-CHO	CH3-CH2-CH3
CH3-CH2-O-OH	2	0.0071	0.0142	0.0357	2	6	2	-	ETOOH	3	7.32e-5	#4437	CH3-CH2-CHO	CH3-CH2-CH3
CH3-CH2-CO-O-OH	2	0.0026	0.0078	0.0138	3	6	3	-	ORG-2561	3	8.31e-6	#20841	CH3-CH2-CHO	CH3-CH2-CH3
HCO-CH2-CO-O-OH	2	0.0019	0.0057	0.0007	3	4	4	-	ORG-0541	3	3.01e-4	#14800	CH3-CH2-CHO	CH3-CH2-CH3
CH3-CO-CH2-ONO2	2	0.0016	0.0048	0.0028	3	5	4	1	ORG-0106	3	5.31e-5	#20893	CH3-CH2-CH2-ONO2	CH3-CH2-CH3
CH3-CO-CH2-O-OH	2	0.0010	0.0029	0.0016	3	6	3	-	ORG-0473	3	8.82e-5	#6306	CH3-CO-CH3	CH3-CH2-CH3
CH3-CH2-CO-OH	2	0.0009	0.0028	0.0011	3	6	2	-	PROPACID	2	1.33e-5	#11134	CH3-CH2-CHO	CH3-CH2-CH3
CH3-CO-OH	2	0.0008	0.0015	0.0030	2	4	2	-	ACETACID	1	8.30e-6	#21263	CH3-CHO	CH3-CH2-CH3
CH3-CH(CHO)-ONO2	2	0.0005	0.0016	0.0012	3	5	4	1	ORG-0318	3	3.93e-4	#11551	CH3-CH2-CHO	CH3-CH2-CH3
HO-O-CH2-CO-O-OH	2	0.0004	0.0009	0.0001	2	4	5	-	ORG-0549	3	6.98e-5	#10200	CH3-CHO	CH3-CH2-CH3
HCO-CH2-CH2-ONO2	2	0.0004	0.0011	0.0012	3	5	4	1	ORG-0266	3	3.03e-4	#18813	CH3-CH2-CH2-ONO2	CH3-CH2-CH3
CH3-CH(CHO)-O-OH	2	0.0002	0.0006	0.0006	3	6	3	-	ORG-0486	3	4.75e-4	#5210	CH3-CH2-CHO	CH3-CH2-CH3
HCO-CH2-CH2-O-OH	2	0.0002	0.0005	0.0006	3	6	3	-	ORG-0502	3	3.86e-4	#6170	CH3-CH2-CH2-O-OH	CH3-CH2-CH3
CH3-CH(CO-O-OH)-O-OH	2	0.0001	0.0004	0.0001	3	6	5	-	ORG-0536	3	7.82e-5	#12503	CH3-CH2-CHO	CH3-CH2-CH3
CH3-CH(CH2-O-OH)-O-OH	2	0.0001	0.0003	0.0000	3	8	4	-	ORG-1166	3	1.75e-4	#4801	CH3-CH(CH3)-O-OH	CH3-CH2-CH3
HCO-CH2-CO-O-ONO2	3	0.0065	0.0195	0.0008	3	3	6	1	PRD-8	4	6.39e-4	#2336	CH3-CH2-CO-O-ONO2	CH3-CH2-CHO
HO-O-CO-CH2-CO-O-ONO2	3	0.0024	0.0072	0.0001	3	3	8	1	PRD-17	2	3.43e-4	#17128	HCO-CH2-CO-O-OH	CH3-CH2-CHO
HO-O-CO-CO-O-ONO2	3	0.0010	0.0029	0.0002	2	1	8	1	PRD-31	2	7.83e-4	#7053	HCO-CO-O-OH	CH3-CHO
HCO-CH2-ONO2	3	0.0006	0.0011	0.0031	2	3	4	1	ORG-0107	3	3.00e-4	#9737	HCO-CH2-CH2-ONO2	CH3-CH2-CH2-ONO
O2NO-CH2-CH2-CO-O-ONO2	3	0.0005	0.0014	0.0001	3	4	8	2	PRD-9	3	3.56e-4	#8880	CH3-CH2-CO-O-ONO2	CH3-CH2-CHO
CH3-CH(ONO2)-CO-O-ONO2	3	0.0003	0.0009	0.0001	3	4	8	2	PRD-6	2	3.50e-4	#17920	CH3-CH(CHO)-ONO2	CH3-CH2-CHO
HO-O-CH2-CH2-CO-O-ONO2	3	0.0003	0.0009	0.0001	3	5	7	1	PRD-10	4	4.31e-4	#16224	CH3-CH2-CO-O-ONO2	CH3-CH2-CHO
CH3-CO-CHO	3	0.0002	0.0005	0.0205	3	4	2	-	MEGLYOX	3	4.12e-4	#20915	CH3-CO-CH2-O-OH	CH3-CO-CH3
HO-O-CH2-CH2-CO-O-OH	3	0.0001	0.0004	0.0001	3	6	5	-	ORG-0534	3	9.24e-5	#6005	HCO-CH2-CH2-O-OH	CH3-CH2-CH2-O-O
O2NO-O-CO-CH2-CO-O-ONO2	4	0.0018	0.0055	0.0001	3	2	10	2	PRD-37	2	3.50e-4	#9482	HCO-CH2-CO-O-ONO2	CH3-CH2-CO-O-ON
O2NO-CH2-CO-O-ONO2	4	0.0003	0.0006	0.0003	2	2	8	2	PAN-N	2	3.50e-4	#15594	HCO-CH2-ONO2	HCO-CH2-CH2-ON
Low reactivity or volatility produ	1													
CH3-CO-O-OH	2	0.0022	0.0044	0.0366	2	4	3	-	PAA		1.33e-6		CH3-CHO	CH3-CH2-CH3
Low yield reactants	59	Not listed												
Multi-generation mechanism complete, with 330 reactions generated.														

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

```
! Full mechanism in MG-ETHANE as of 07/05/24
! Minimum estimated yield to react = 0.010%
! Reaction days to calculate amounts reacted = 0.25
! Minimum volatility to react = 1.0e-13 atm.
! Reacted for environment(s) Mid NOx
!
! Initial reactant(s) (1)
.ACT
ETHANE    ! CH3-CH3
!
! Reacting products (7)
ACETALD   ! CH3-CHO
ETOOH     ! CH3-CH2-O-OH
PAN       ! CH3-CO-O-ONO2
MEOOH     ! CH3-O-OH
GLYACID   ! HCO-CO-O-OH
ORG-0549  ! HO-O-CH2-CO-O-OH
PRD-2     ! HO-O-CO-CO-O-ONO2
!
! Counter species used for the 3 low-yield products that were not reacted
NegC    ! Total Carbons in low-yield products
NegO    ! Total Oxygens
NegN    ! Total Nitrogen
NegH    ! Total Hydrogen
.
!
! Reacting intermediates (7)
.STS
RAD-1     ! CH3-CH2OO.
RAD-2     ! CH3-CO[OO.]
RAD-3     ! HCO-CH2OO.
RAD-4     ! CH3OO.
RAD-5     ! .OOCH2-CO-O-OH
RAD-6     ! .OOCH2-CH2-O-OH
RAD-7     ! CO[OO.]-CO-O-OH
!
! Reactions (37)
.RXN
R) 1.51e-12 1.059 1.92   ;ETHANE + OH = RAD-1 + H2O
R) 2.55e-12 -0.755       ;RAD-1 + NO = ACETALD + HO2 + NO2
R) 7.44e-12              ;RAD-1 + HO2 = ETOOH + O2
R) 1.60e-11              ;RAD-1 + RCO3 = ACETALD + HO2 + O2
R) 2.40e-12 -1.085 0.77  ;ACETALD + OH = H2O + #0.95 RAD-2 + #0.05 RAD-3
R) PF=CCHOR-13           ;ACETALD + HV = #0.9 CO + HO2 + #0.9 RAD-4 +
                          #0.1 RAD-2
R) 6.70e-12 -0.676       ;RAD-2 + NO = RAD-4 + CO2 + NO2
R) 7.70e-12              ;RAD-2 + NO2 = PAN
R) 3.14e-12 -1.153       ;RAD-2 + HO2 = RAD-4 + CO2 + O2 + OH
R) 1.60e-11              ;RAD-2 + RO2 = RAD-4 + CO2 + O2
R) 6.02e+7 10.052        ;RAD-3 = RAD-5
R) 2.55e-12 -0.755       ;RAD-3 + NO = #0.935 HCHO + #0.935 CO +
                          #0.065 GLYOXAL + HO2 + NO2
R) 2.55e-12 -0.755       ;RAD-5 + NO = #0.251 CO2 + #0.251 HCHO +
                          #0.749 GLYACID + #0.749 HO2 + #0.251 OH + NO2
R) 1.27e-11              ;RAD-5 + HO2 = #0.85 ORG-0549 + O2 + #0.038 CO2 +
                          #0.038 HCHO + #0.112 GLYACID + #0.112 HO2 +
                          #0.188 OH
R) 1.60e-11              ;RAD-5 + RCO3 = #0.251 CO2 + #0.251 HCHO +
                          #0.749 GLYACID + #0.749 HO2 + #0.251 OH + O2
R) 2.30e-12 -0.715       ;RAD-4 + NO = HCHO + HO2 + NO2
R) 3.80e-13 -1.550       ;RAD-4 + HO2 = MEOOH + O2
R) 1.35e-11              ;RAD-4 + RCO3 = HCHO + HO2 + O2
R) 6.00e-12              ;ETOOH + OH = #0.025 RAD-6 + H2O + #0.156 ACETALD +
                          #0.156 OH + #0.819 RAD-1
R) PF=COOH               ;ETOOH + HV = ACETALD + HO2 + OH
```

(Truncated. Full set of reactions is in Figure 24)

Figure 23. Example of output of a "read rxnfile on MG-ETHANE" command

```
! Full mechanism in MG-ETHANE as of 07/05/24
! Minimum estimated yield to react = 0.010%
! Reaction days to calculate amounts reacted = 0.25
! Minimum volatility to react = 1.0e-13 atm.
! Reacted for environment(s) Mid NOx
! Thermal rate constants for T = 298.0 deg K
! Z=0 solar spectrum used for Carter (1994) reactivity scales scenarios. Summer ...
```

(Reactant list is the same as in Figure 23)

```
! Reactions (37)
.RXN
R) 2.493e-13  ;ETHANE + OH = RAD-1 + H2O
R) 9.125e-12  ;RAD-1 + NO = ACETALD + HO2 + NO2
R) 7.440e-12  ;RAD-1 + HO2 = ETOOH + O2
R) 1.600e-11  ;RAD-1 + RCO3 = ACETALD + HO2 + O2
R) 1.492e-11  ;ACETALD + OH = H2O + #0.95 RAD-2 + #0.05 RAD-3
R) 7.73e-6    ;ACETALD = #0.9 CO + HO2 + #0.9 RAD-4 + #0.1 RAD-2
R) 2.098e-11  ;RAD-2 + NO = RAD-4 + CO2 + NO2
R) 7.700e-12  ;RAD-2 + NO2 = PAN
R) 2.200e-11  ;RAD-2 + HO2 = RAD-4 + CO2 + O2 + OH
R) 1.600e-11  ;RAD-2 + RO2 = RAD-4 + CO2 + O2
R) 2.559e+0   ;RAD-3 = RAD-5
R) 9.125e-12  ;RAD-3 + NO = #0.935 HCHO + #0.935 CO + #0.065 GLYOXAL + HO2 +
               NO2
R) 9.125e-12  ;RAD-5 + NO = #0.251 CO2 + #0.251 HCHO + #0.749 GLYACID +
               #0.749 HO2 + #0.251 OH + NO2
R) 1.273e-11  ;RAD-5 + HO2 = #0.85 ORG-0549 + O2 + #0.038 CO2 + #0.038 HCHO +
               #0.112 GLYACID + #0.112 HO2 + #0.188 OH
R) 1.600e-11  ;RAD-5 + RCO3 = #0.251 CO2 + #0.251 HCHO + #0.749 GLYACID +
               #0.749 HO2 + #0.251 OH + O2
R) 7.693e-12  ;RAD-4 + NO = HCHO + HO2 + NO2
R) 5.206e-12  ;RAD-4 + HO2 = MEOOH + O2
R) 1.350e-11  ;RAD-4 + RCO3 = HCHO + HO2 + O2
R) 6.000e-12  ;ETOOH + OH = #0.025 RAD-6 + H2O + #0.156 ACETALD + #0.156 OH +
               #0.819 RAD-1
R) 6.56e-6    ;ETOOH = ACETALD + HO2 + OH
R) 9.125e-12  ;RAD-6 + NO = #1.922 HCHO + #0.961 OH + #0.078 NegC +
               #0.165 NegH + #0.117 NegO + #0.039 HO2 + #0.671 LostMass + NO2
R) 1.273e-11  ;RAD-6 + HO2 = #2 NegC + #6 NegH + #4 NegO + O2
R) 1.600e-11  ;RAD-6 + RCO3 = #1.922 HCHO + #0.961 OH + #0.078 NegC +
               #0.165 NegH + #0.117 NegO + #0.039 HO2 + #0.671 LostMass + O2
R) 3.387e-4   ;PAN = RAD-2 + NO2
R) 1.02e-6    ;PAN = #0.6 RAD-2 + #0.6 O2 + #0.6 NO2 + #0.4 RAD-4 + #0.4 CO2 +
               #0.4 NO3
R) 1.003e-11  ;MEOOH + OH = #0.028 HCHO + #0.028 OH + H2O + #0.972 RAD-4
R) 6.56e-6    ;MEOOH = HCHO + HO2 + OH
R) 1.175e-11  ;GLYACID + OH = RAD-7 + H2O
R) 2.80e-4    ;GLYACID = CO2 + OH + CO + HO2
R) 2.098e-11  ;RAD-7 + NO = OH + #2 CO2 + NO2
R) 7.700e-12  ;RAD-7 + NO2 = PRD-2
R) 2.200e-11  ;RAD-7 + HO2 = #2 OH + #2 CO2 + O2
R) 1.600e-11  ;RAD-7 + RO2 = OH + #2 CO2 + O2
R) 5.694e-12  ;ORG-0549 + OH = #0.959 RAD-5 + H2O + #0.041 GLYACID +
               #0.041 OH
R) 6.56e-6    ;ORG-0549 = #0.251 CO2 + #0.251 HCHO + #0.749 GLYACID +
               #0.749 HO2 + #1.251 OH
R) 3.387e-4   ;PRD-2 = RAD-7 + NO2
R) 4.44e-4    ;PRD-2 = #2 CO2 + OH + NO3
.
! END
```

Figure 24. Example of output of a "read rxnfile1 on MG-ETHANE" command.

```
! Pseudo-unimolecular mechanism for MG-ETHANE for Mid NOx standard urban ...
! File created 07/05/24
! Minimum estimated yield to react = 0.010%
! Reaction days to calculate amounts reacted = 0.25
! Minimum volatility to react = 1.0e-13 atm.
! Thermal rate constants for T = 298.0 deg K
! Z=0 solar spectrum used for Carter (1994) reactivity scales scenarios. ...
!
! Reactants
.ACT
ETHANE     ! CH3-CH3
ACETALD    ! CH3-CHO
ETOOH      ! CH3-CH2-O-OH
PAN        ! CH3-CO-O-ONO2
GLYACID    ! HCO-CO-O-OH
MEOOH      ! CH3-O-OH
ORG-0549   ! HO-O-CH2-CO-O-OH
PRD-2      ! HO-O-CO-CO-O-ONO2
!
! Lost atom counters
LostO      ! Total lost O due to RMinYld
LostH      ! Total lost H due to RMinYld
!
! Other unreacting products (in base mechanism)
= HO2 + NO2 + CO + CO2 + OH + HCHO + NO3
.
! Reactions
.RXN
0001) 1.660e-4 ;ETHANE = #0.97 ACETALD + #0.03 ETOOH + #0.97 HO2 + #0.963 NO2
0002) 1.040e-2 ;ACETALD = #0.595 PAN + #0.009 MEOOH + #0.032 GLYACID +
                 #0.002 ORG-0549 + #0.043 CO + #0.428 HO2 + #0.328 CO2 +
                 #0.69 NO2 + #0.023 OH + #0.362 HCHO
0003) 4.390e-3 ;ETOOH = #0.955 ACETALD + #0.022 ETOOH + #0.253 OH +
                 #0.814 HO2 + #0.042 HCHO + #0.001 LostO + #0.001 LostH +
                 #0.739 NO2 + #0.004 NegC + #0.01 NegH + #0.007 NegO
0004) 2.038e-2 ;PAN = #0.652 PAN + #0.009 MEOOH + #1.663 NO2 + #0.348 CO2 +
                 #0.001 NO3 + #0.013 OH + #0.34 HCHO + #0.34 HO2
0006) 2.462e-2 ;GLYACID = #0.207 PRD-2 + #0.903 CO2 + #0.797 OH + #0.682 CO +
                 #0.682 HO2 + #0.104 NO2
0005) 7.077e-3 ;MEOOH = #0.023 MEOOH + #0.977 HCHO + #0.082 OH + #0.951 HO2 +
                 #0.888 NO2
0007) 4.186e-3 ;ORG-0549 = #0.731 GLYACID + #0.037 ORG-0549 + #0.37 OH +
                 #0.233 CO2 + #0.233 HCHO + #0.694 HO2 + #0.819 NO2
0008) 4.696e-2 ;PRD-2 = #0.282 PRD-2 + #0.574 NO2 + #1.435 CO2 + #0.723 OH +
                 #0.567 NO3
.
```

Figure 25. Example of output of a "read unirxns on MG-ETHANE" command.

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 their 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 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 create more than one reactor that they can employ, assign different lumping methods or assignment sets, or other options to each, and can choose which reactor to employ by "moving" from one reactor to another.

The commands used to create and manage lumping objects are summarized in Table 21, with additional information concerning options, properties, and model species given in Table 22 through Table 25. The command "create-lumping <lumping name>" creates a lumping method, and makes it available as an object in the user's reactor. 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 and parameters are input using the "input-rules to <lumping name>" command as indicated in the tables.

Table 21. 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(s)> .	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. The user is prompted for one or more description lines, terminated by a line with a single ".".
Delete <name>	Deletes a user-created 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. Lumping methods available to all users cannot be deleted except by the primary MechGen user.
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 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 a line with "end" to indicate end of input of that type or ".", to indicate the end of all input. An example of "Input-rules" input for the standard SAPRC22 mechanism can be viewed using the web system by first selecting "Show information related to the SAPRC-22 mechanism" at the main menu, then selecting "show 'input-rules' link on the resulting page (last link on the top section -- see Figure 11). Options — Specify non-default lumping parameters as indicated in Table 22. Properties — Give values for lumping properties that may differ from the defaults. Properties most likely to be modified are indicated in Table 23. 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 24. See Section 11.3 for more information. Assignments — Give information that indicates how model species are assigned to compounds, based on 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.

Table 22. 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>	Control how peroxy radicals are treated in the lumped mechanisms. 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 for the "full" version of SAPRC-22 as discussed by Carter (2023a). This method is not currently recommended for SAPRC-22 but MechGen includes this as an option for new lumping methods. SAPRC07 — As lumped in SAPRC-07 or SAPRC-11, with the "EffNO" parameter used to handle unimolecular reactions.
kRO2slow <kUni> [a]	Unimolecular rate constant for peroxy radical reactions, below which unimolecular reactions are ignored. 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}.
Applicable only to SAPRC lumping methods	
kRCO3fast <kUni> (Standard, SAPRC07)	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. Applicable to all lumping methods that lump acyl peroxy radicals. Default is 200 sec^{-1}.
EffNO <conc> (SAPRC07)	Effective NO concentration (in ppb) used to determine reaction fractions for competitions between unimolecular and bimolecular reactions of peroxy radicals with SAPRC07 peroxy lumping. See Carter (2023a) for more details. Default is 0.5 ppb.
EffNOmid EffNOhigh (Standard)	Effective NO concentrations (in ppb) used to determine reaction fractions for competitions between unimolecular and bimolecular reactions of peroxy radicals with SAPRC22 peroxy lumping. Two values are used to allow interpolations or extrapolations for different NO concentrations, and give the low and high NO values used for this purpose. Defaults are EffNOmid=5 ppb and EffNOhigh=1000 ppb.
MinYldRO2 (Full)	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.

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

Table 23. Lumping object properties that can be input using the "Properties" section of the "input-rules" input. Note that 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 (e.g., Carter, 2010a, 2023a) 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 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.
Allow_cyclics	Determine whether reactions that might form cyclic radical dependences will be generated. Currently applicable to H-shift reactions between peroxy radicals and hydroperoxy groups and reactions of phenoxy radicals with O_3. Set to 1 to allow generating these reactions and 0 not to allow. The default is 1 to allow these reactions, but this needs to be set to 0 for SAPRC lumping methods.

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

Table 24. 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. 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 after the "=" is the name of the model species used to represent the products formed when the z<name> model species reacts with NO_3 or other peroxy radicals. Not applicable to explicit peroxy 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 after the "=" is the name of the model species used to represent the products formed when the y<name> model species reacts with HO2 or other peroxy radicals. Not applicable to explicit peroxy lumping.
Type=	Code indicating whether this model species 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. The default is "Act", indicating an active species. 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 24 (continued)

Keyword [a]	Property specified and default values
Rad=	Code indicating whether this model species is 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 0. 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 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 the 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.

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 by 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 use. The "get" command moves the lumping object to the possession of the MechGen primary user, who "holds" most MechGen system objects. The "@corify" and "addlump" commands are valid only 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 21 and discussed further below, needs to be given to create this lumped method. This gives all the non-default options and assignments associated with the lumping method, collectively referred to as "rules" input or lumping rules in the subsequent commands.

As shown on Table 21, the "input-rules" command is used to specify the lumping options, properties, list of model species, and model species assignments. This command prompts the user for

Table 25. List and descriptions of conditions keywords that can optionally be included in the "Assignment" 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 the 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 in Table 26.
	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 C*n*H*n*O*n*N*n*Cl*n*, 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 22).
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.

input, which come in four 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 the "Assignments" section, but the other sections can be given in any order. Each section consists of lines of input as indicated in Table 21 and are terminated 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 be 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 similar, with the only difference being that the "Type" option selected in the "Options" section is set to "full" rather than "standard".

11.1. Lumping Options

Table 22 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 22, 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 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 mechanisms, as described in the available SAPRC-07 mechanism documentation (Carter, 2010a,b). In this method, no model species are used to represent individual or lumped peroxy radicals. Instead, chemical "operator" model species are used to represent the effects of peroxy radical reactions. This includes two default operators, called "RO2C" and "RO2XC" that represent the conversion of NO to NO_2 or the consumption of NO caused by the reactions. It also includes up to three operators for product or intermediate model species that can be formed in the overall reactions of the peroxy radicals:

1. 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. The "xProd" operators are also used to approximate the products formed following reactions of peroxy radicals with NO3 and other organic peroxy radicals or acyl peroxy radicals.

2. 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.

3. 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.

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. However, it becomes problematic when two types of reactions are competitive. In order to handle such cases, an "EffNO" parameter (Table 21) 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). Note that the full version of SAPRC-22 is not currently recommended for use in airshed models because the standard version gives significantly smaller mechanisms with similar predictions. Nevertheless, MechGen continues to support this option for new lumping types.

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 in the mechanism, as discussed in Section 6.2. 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 the 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% (Carter, 2023a).

"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, it determines net product yields for three different "EffNO" values: zero, "EffNOmid", and "EffNOhigh" (Table 22) and then adds a separate operator model species is also added, representing effects of unimolecular reactions for each reaction forming such peroxy radicals and determining 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. It is preferred for general use because it gives essentially the same predictions as the "full" method (see Carter, 2023a), while requiring far fewer model species.

11.1.2. Options and that Control the Peroxy 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 in Table 22, 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, since reactions of radicals that are assigned lumped species are not generated.

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. These are applicable regardless of the peroxy lumping approach 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. The "kRCO3fast" parameter is generally lower than "kRO2fas"t 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.

These options only affect the full mechanism generation process and are ignored along with other lumping parameters when generating single-step reactions (see Sections 4.3 and 5.2).

11.2. Specification of Non-Default Lumping Properties

Table 23, above, lists the types of properties that might be modified using the "Properties" section of the rules input. Lumping objects have other 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. Note that both the SAPRC-22 lumping options use the defaults for all the properties listed in Table 23, 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 mechanisms may either ignore or do incorporate all types of VOC reactions, such as reactions with 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 Cl atoms. Although the software and VOC rate constant assignment methods (Carter et al, 2024) support reactions of VOCs with Cl 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 are the default, some model species, such as "NROG" (for unreactive) or "NVOL" (for nonvolatile), are represented using mass units in SAPRC-22. 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 for 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 in lumped mechanisms, and also to determine the order in which they appear on lists of products formed in the reactions. Most input lines consist 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 in 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 in Table 24. These do not need to be included if the default values (also given in the table) are used. These include:

1. Type codes indicating how the model species is to be treated in simulations.

2. The types of reactions it can undergo if it represents non-radical reactants.

3. Whether "x", "y" or "z" operators are to be added forming this model species following peroxy radical reactions and how they react.

4. The numbers of carbon, nitrogen, and molecular weights that can optionally be associated with the model species.

5. Photolysis information if the model species undergoes photolysis reactions.

The “ID=<structure>” keyword is used when the model species represents a compound explicitly, where the structure must be given in the MechGen standard format as discussed in Section 3.1. It should not be used if the model species is being used for a purpose other than explicitly representing a single compound. In those cases, model species assignments are made based on the input in the "Assignments" section discussed below.

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 "Assignments" 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 assigned to a single compound with the "ID=" keyword. Tests are carried out in the order that they appear in the assignments section when MechGen determines how to lump individual compounds. 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 that 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 any applicable associated values cannot contain embedded spaces. The following types of keywords are optionally used 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 that this model species may also be used for different compounds based on 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 can be used to 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", and group designations that can be used in assignments input are given in Table 26. Note that some of the entries in Table 26 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 26, 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).
- The "and" keyword is optionally included between structural group specifications to indicate that the molecule must include both the groups (or series of groups) before and after the "and". However, the groups do not need to be adjacent in the molecule.
- 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.

Table 26. 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 "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. The input before the "when" keyword (or all the input if there is no "when") is referred to as the "group" specification, while that after is referred to as the "conditions". Both must be matched if this keyword is given. 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 25, above. 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 assigned to 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 any subsequent input will be ignored. 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 SAPRC-22 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 many compounds or complex mixtures. Since hundreds of types of organic compounds are emitted into the atmosphere, representing each compound individually is generally impractical 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 accurate than using a mechanism 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 compound 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 steps, where the types of MechGen objects involved are underlined:

1. Estimate detailed composition of organic compounds emitted into the atmosphere from both anthropogenic and biogenic sources. These compositions are then input into mixture database objects in MechGen, referred to as the "ambient emissions mixtures".
2. Use the lumping method associated with the mechanism to determine which model species represents each of the compounds in the mixture database.
3. Create a reactant container object that will hold all the reactants whose mechanisms need to be generated, either because they are represented explicitly or are needed to derive mechanisms for mixtures. These are necessary for the creation of reactant mixture objects used to represent the mixtures used to derive mechanisms for lumped model species. Reactant containers are also used to aid deriving mechanisms for explicitly represented compounds.
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 up to 15 compounds, whichever are fewer. Each mixture is represented by reactant mixture objects created in the reaction container object, along with reactant objects representing each of the compounds in the mixture. Note that compounds 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 requires only 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 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 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 any lumped model species 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, along with the lumped mechanisms for the explicitly represented compounds.

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 inorganics, CO, or formaldehyde, or those with unknown or simplified 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 27 gives a summary of all terminal commands used to create and manage these objects, as well as 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 using the Telnet interface 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 without mole fractions define lists of compounds used for various purposes. These are required when creating mixtures 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.

Mixture databases are created using the "create-mixdb" command, as indicated in Table 27. The command can be used in three ways:

- 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 for creating this type of database is shown on the first row of Table 27, where the molar amounts are not included in the inputs.

Table 27. Summary of commands related to creation and use of reactant containers and mixtures.

Command	Description
Creation and management 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 with a list 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 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 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 a mixture database if there are changes to the lumping assignment. [a]
Delete <mix db name>	Deletes a 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 it 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 27 (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. This can take a long time if there are many unreacted reactants in the container.
Process in <container>	Derives or re-derives mechanisms for mixtures in the container based on mechanisms generated for their components. It also re-lumps mechanisms for all reactants in case minor changes were made to lumping options. Only fully reacted reactants or mixtures are processed. Note that this is carried out automatically after a "fullreact in <container>" command and is only needed when mixtures are added or modified following "fullreact in <container>" operations.
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.
<u>Creation and management of reactant mixture objects</u>	
Create-mixture <mixname> in <container> <reactant 1> <moles 1> <reactant 2> <moles 2> … .	Creates a mixture object named <mixname> in the reactant container with 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 represented 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 mixture compositions are derived from the mixture database for 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, on 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 27 (continued)

Command	Description
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 that are *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 the mixture database, organized by model species. [b]
<outcmd> MSinfo on <mix db>	Lists the 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 details 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 in Table 7. Output also includes results for mixtures, except for <item>="reactions". No useful output if reactants have not reacted.
<outcmd> mixtures in <container>	Outputs compositions of all mixtures in the container, and indicates whether their mechanisms have been derived.
<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. No useful output if reactants have 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 have not reacted.

Table 27 (continued)

Command	Description
Obtaining results for complete mechanism development (as used for SAPRC-22 … see Table 29)	
<fileout> rxninfo on <container>	Outputs information on all lumped species and reactions of the mixtures and 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. <mixdb> is a mixture database containing a list of 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] 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.

- 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 for creating this type of database is shown on the first row of Table 27, 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, and a standard environment are included in the command creating this type of database, as shown in the second row of Table 27. This is referred to 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 information is stored in the mixture database. The "lump-mixdb" command (Table 27) 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 27 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 the "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 manage multiple reactants in a batch mode and obtain the results or obtain information about the compounds without having to give commands for each individual reactant.

The commands to create and manage reactant container objects are included in Table 27. As indicated, objects can be created in the container individually, and previously created objects in the reactor can be moved from the container to the reactor. All objects listed in a mixture database can also be created in the container 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 define the mixture if they are not already in the container. Reactants in the container can also be moved from the container to the reactor, as indicated in Table 27.

The "fullreact in <container>" command will react all the 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 unreacted reactants in the reactor. If new reactants are subsequently added to the reactor, the "fullreact" needs to be given again for the newly added reactants. The "erase in <container>" command deletes the results of previous reactions but not the reactant objects themselves. This should be used if any changes are made to the lumping assigned to the reactor before rerunning the "fullreact" command.

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

In addition to their use in mechanism development as indicated in Table 27, the "read | fileout | @ftpout <info> on <container>" command can be used to obtain information about the reactants in the container and output it to the user. "<Info>" is the keyword indicating the type of information requested, and the output is delimited by tabs, suitable for loading into spreadsheets. The two main options for "<Info>" are:

- Summary. Lists the compounds in the container, including their name and structures in MechGen and SMILES format. If they have been reacted, the types of reactions are listed and numbers of explicit, processed, and (if applicable) lumped reactions and species (including intermediates and base products) are given. No output is shown in the "Lumped" columns if using explicit lumping. For reactant mixtures in the container (see below), the composition is shown in the MechGen ID column, and if its components are reacted then the types of reactions and number of processed and (if applicable) reactions and species are shown. An example of such output once loaded into a formatted spreadsheet is given in Figure 26.
- Cmpdinfo. Lists the compounds in the container, including more detailed information about the properties of reactants in the container, as listed in Table 28. Too many columns of data are output to show specific examples here. Note that reactant mixture objects in the container are not listed in the output, nor is information about results of reactants that may have been reacted. The same information can be obtained by the command "fileout | @ftpout Cmpdinfo on Util", which prompts the user for a list of compounds (provided as standard names or structure strings), terminated by a single "." line. The "read" command is not appropriate for this case because of the amount of data output.

Contents of Example Reactant Container									
				Explicit		Processed		Lumped	
Name	ID	SMILES	Reacted with	Rxns	Spec	Rxns	Spec	Rxns	Spec
N-C6	CH3-CH2-CH2-CH2-CH2-CH3	CCCCCC	OH	161	112	62	74	1	17
1-HEXENE	CH2=CH-CH2-CH2-CH2-CH3	C=CCCCC	OH O3 NO3 O3P	543	373	189	232	4	49
M-XYLENE	CH3-aC*-aCH-aCH-aCH-aC(CH3)-aCH*	Cc1cccc(C)c1	OH	109	96	31	53	1	19
1C4RCHO	CH3-CH2-CH2-CHO	CCCC=O	OH NO3 HV	101	78	41	48	3	27
APAN	CH2=CH-CO-O-ONO2	C=CC(=O)OON(=O)=O	uni OH O3 NO3 HV	92	78	31	41	5	28
OLE4	Mix (2) = #.9 2M-2-BUT + #.1 2M-2-C5E	n/a	OH O3 NO3 O3P			81	102	6	40

Figure 26. Example "Summary" output listing information about the contents of a reactant container. This example container contains a subset of compounds and mixtures used to derive the SAPRC-22 mechanism.

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 recreated 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 in Table 27. Note that the "create-mixture" command will fail if the reactants in the mixture are not already in the container.

Reactant mixture objects can also be created using "prepare-ms-mixes" commands (e.g., see Table 27) 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 for all compounds in the mixture to be already in the container, since the command creates the compounds in the container as needed. In some cases, the mixtures used to derive mechanisms can consist of large numbers of compounds with relatively small contributions to the total. The lumping property "MixParms" (Table 23) is used to limit the number of compounds by eliminating relatively unimportant ones 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 27) 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 mixture objects are derived as part of the lumping processing for all reactants in the reactor, which is carried out automatically as part of a "fullreact in" command or manually using a "process in" command, as indicated in Table 27. The algorithms used to derive lumped mechanisms for mixtures depends on the lumping method, as follows:

1. 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,

Table 28. Types of information about compounds in "Cmpdinfo" output for reactant containers.

Item	Description
	General reactant information
Identity	MechGen structure string
Smiles	SMILES string
DMS	Standard detailed model species (DMS) name
Type	Compound type and type code number
	Structure information
SepDBs	Number of separated double bonds
ConjDBs	Number of sets of conjugated double bonds
CumDBs	Number of sets of cumulated double bonds
Tbonds	Number of triple bonds
NArings	Number of non-aromatic rings
AroRngs	Number of aromatic rings
Subst2	Number of groups in molecule bonded to two or more non-carbon centered groups
OHs	Number of non-acid OH groups
OOHs	Number of hydroperoxy groups
Acids	Number of carboxylic acid groups
Pacid	Number of peroxyacid groups
EtherO	Number of ether oxygens
EsterO	Number of ester groups
OOs	Number of peroxy groups (excluding hydroperoxides or peroxy acids)
CHOs	Number of aldehyde groups
COs	Number of ketone groups (carbonyls not in acid, peroxyacid, or ester groups)
ONO2s	Number of nitrate groups
PANs	Number of acyl peroxy (-CO-O-ONO2) groups
NO2s	Number of nitro groups
ONOs	Number of nitrite groups
OONO2	Number of peroxy nitrate groups (excluding acyl peroxy nitrates)
Amins	Number of amino groups (excluding those in amide groups)
Amids	Number of amide (-CO-NHx) groups
Mwt	Molecular weight
nC, etc.	Numbers of C, H, O, N, S, F, Cl, I, Br, Si, and P atoms
Rad	Indicates if the compound is a radical

the mixture mechanism is derived by using weighted averages of the rate constants and the yields of all the products.

2. 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. 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 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 in Table 29, which gives the commands used in the development of the SAPRC-22 mechanisms (Carter, 2023a). While the detailed compositions of the mixture databases employed are not included in this table, they 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" to output all the information needed from MechGen to develop the mechanism. This information is then input to the master spreadsheet used for developing SAPRC-22, which merges this information with the 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 the goal is 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 listed in Table 29 would need to be repeated.

Table 29. MechGen commands used in the derivations of the SAPRC-22 mechanism.

MechGen Command	Discussion
lumping SAPRC22	Assigns the lumping method for the reactor, which will be used when processing all reactions.
create-mixdb BaseMix <reactants, one per line> .	Creates a mixture database listing all the compounds that are represented explicitly whose mechanisms are to be generated. [a]
create-mixdb ARBmix-22 <reactants, one per line> .	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 <reactants, one per line> .	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 <reactants, one per line> .	Creates 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	Creates the reaction container "AllDMS" used for all the reactants and mixtures required for the mechanism.

Table 29 (continued)

MechGen Command	Discussion
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 <reactants, one per line> .	Gives the list of compounds that should not be used when deriving mechanisms for mixtures representing lumped model species. [a]
delete-reactants	Deletes any reactants previously in the reactor.
build MACO3 as CH2=C(CH3)-CO[OO.] build R2CO3 as CH3-CH2-CH2-CO[OO.]	Creates radical reactants to be represented explicitly in the mechanism.
fill alldms	Put the created radicals in ALLDMS
put BaseMix in AllDMS	Creates all the reactants listed in the BaseMix mixture database and puts them in AllDMS.
prepare-ms-mixes ARBmix-22 for alldms <mixtures, one per line> [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 derives its compositions from 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 from 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 computer's performance.
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. The relative compositions are derived from the fractions of the reactants in "ARBemit-22" and the yields of the products when the reactants are reacted under the "stdenv" environmental conditions.

Table 29 (continued)

MechGen Command	Discussion
prepare-ms-mixes EmitProds for AllDMS <mixtures, one per line> [d] .	Creates mixtures to represent all the lumped model species used for 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 computer performance.
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. The relative compositions are derived from the fractions of the reactants in "EmitProds" and the yields of the products when reacted under the "stdenv" environmental conditions.
prepare-ms-mixes EmitProds2 for AllDMS CATL	
	Creates a mixture used to represent the catechol model species based on the relative amounts formed when the cresols react under the "envcond" standard environment [c]
fullreact in AllDMS	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 explicitly represent compounds to a file on the host computer. This file is then input into the master spreadsheet used to prepare this version of the SAPRC-22 mechanism. [e]

[a] The list of compounds or compositions in 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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