Basic Operations for MechGen Web Users

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MechGen is a system that can be used to generate explicit reactions of organic compounds under atmospheric conditions. It can be accessed using the web interface that is currently available at: http://mechgen.cert.ucr.edu. This quick guide will walk through the basic operations for web users. If you are unable to access this website, please contact William P. L. Carter at carter@cert.ucr.edu. More complete information is available in the full user's guide, available at http://mechgen.cert.ucr.edu or https://intra.engr.ucr.edu/~carter/MechGen/.

When first accessing the MechGen website, the user is presented with a login page with a form to give a username and a password to create or return to a user-specific "reactor" system. The top portion of the page is shown on Figure 1, where your username is entered in location "A", and your password is entered in location "B". The password is case sensitive but the name is not. If you are a new user, an account will be created for you with that name and password, unless the name is already taken. Once created, the username and password are necessary to login back to your own reactor system in the future. No personal information is required.

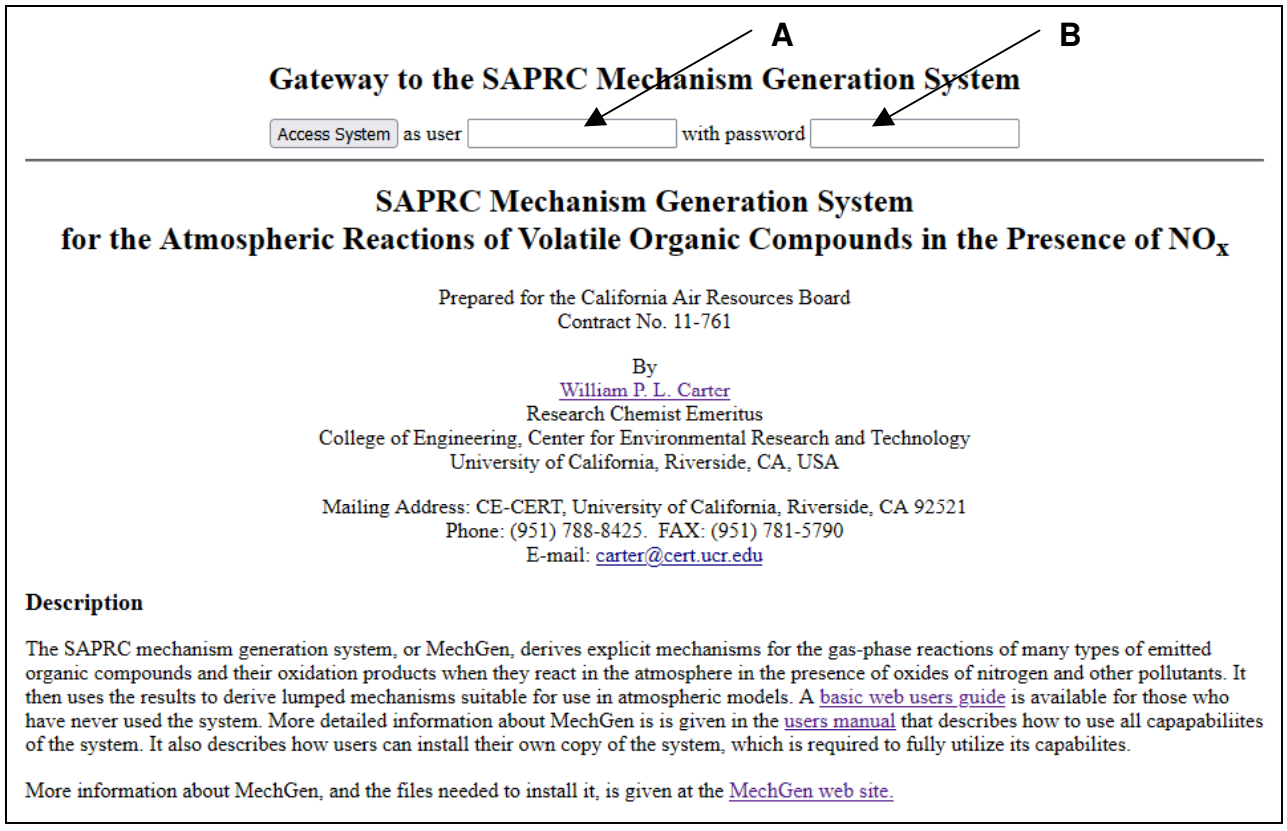


Figure 1. Screen shot of the MechGen login page.

Main Menu

When first logged into the system, a new user reactor is created and the user is presented with a web page showing the reactor with the default settings, as on Figure 2. The sections of the web page are as follows:

- **Header**. Identifies the user and reactor and gives links to reload, log out, or restore reactor defaults. Also indicates the current lumping method that controls how mechanisms are generated and processed.
- **Create VOC or radical reactant**. This section has a form to create a reactant, which you can input at a location marked "C" on the figure. You can input SMILES directly, or use MechGen structure notation (similar to SMILES but displays all atoms). Click the "structure" link (location "D") to get information about MechGen's structure notation.
- **Get information on reactants in contents** (not shown on Figure 2). This only appears if a reactant is created and retained. This portion of the page and managing reactants is discussed later.
- **Reactor options**. This contains links to change options that control mechanism generation and lumping options. Restoring reactor defaults sets all these options to those for a new user.
- **Other information**. This section includes links to obtain general information about MechGen and the SAPRC-22 mechanism. This includes a link to obtain the complete users guide as well one to obtain this quick start guide.
- **Advanced options**. Links to modify or utilize various advanced options are given in this section. These are described in the full users guide and are briefly summarized in the "Other Advanced Features" section near the end of this document.
- **User Account Section**. This section has links to log out, change user password, enable telnet logins, or completely delete this web and (if applicable) telnet account, or provide optional user information. Providing user information is not required, but is recommended if users wish to be notified when MechGen is changed, updated, or moved to a different URL.

Creating Reactants and Reactant Information Pages

A reactant is any organic compound or radical that MechGen can process, which includes most compounds with only C, H, O, N, or halogen atoms. Note, however, that not all halogen-containing compounds can be successfully reacted using the current version of MechGen. New reactants can be created from the main menu by entering its structure or assigned name at location "C", on Figure 2. Reactants can also be created by selecting hyperlinks with the reactant name or structure if they appear on other pages, as discussed later. An error message will be displayed and the main menu will be reloaded if the user inputs an improper structure designation or unrecognized reactant name. Information on structure designations used by MechGen can be obtained by selecting the link at location "D" on Figure 2.

a) Reaction Information Pages for Stable Reactants

Reactants can either be stable (filled-shell) compounds or a radical. If a stable compound is created or selected, a reactant information page such as shown on Figure 3 is displayed (using methyl ethyl ketone as the example). This page contains the following sections.

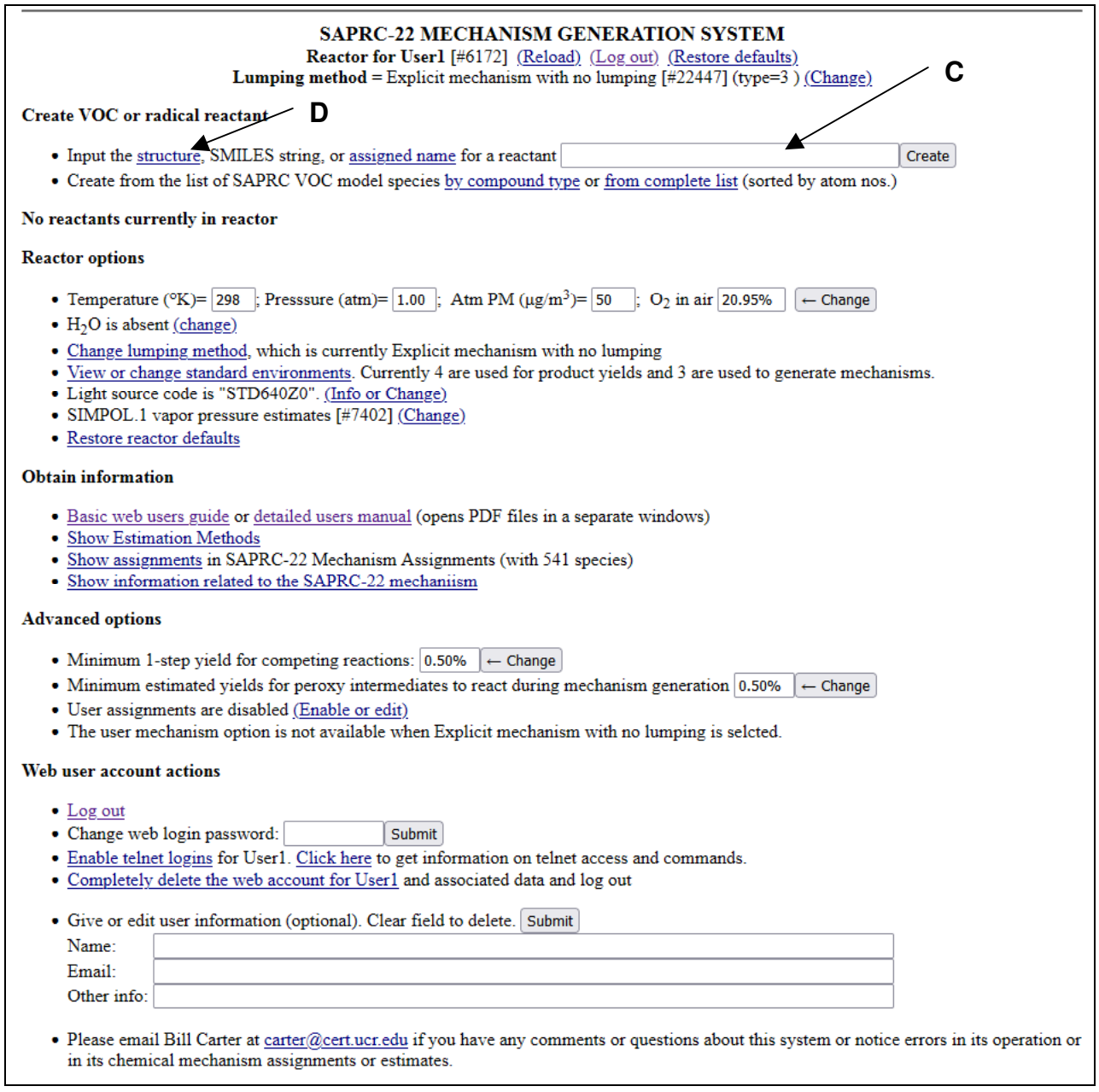


Figure 2. Main menu for a new user or with default options and no reactants.

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 (SIMPOL.1) **at 298.00 deg K is 1.61e-1 atm.**
Fraction in particle phase (with PM=50 ug/m3): 1.1e-7
VOC Type = Ketone

Generate Reactions

E

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 ☐)

F

G

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-R	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-R)= -31.79 CO_(C)(C) (Holmes and Aubry (2011))
- Hf(-CH3[4])= -10.04 C_(CO) (Holmes and Aubry (2011))

Estimated vapor pressure at 298.00 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
```

Figure 3. Screen shot of the reactant menu for a newly created reactant with default reactor settings, using MVK as an example.

- **Header**. The top section gives basic information about the reactant, including its structure in both MechGen and SMILES format, and lumping information if applicable.
- **Generate Reactions**. This section gives links to generate single step or complete reactions of the various type that this reactant can undergo, which is reaction with OH, NO_3, and photolysis in the case of MEK, but can also include unimolecular reactions or reactions with O_3, O^3P, depending on the compound. If reactions of this compound have previously been used in deriving a SAPRC mechanism, the page also includes a "Get Reaction Assignments" link to obtain information about the assignments that were used in previous complete mechanism generations for this compound.
- **Groups**. This section lists MechGen groups in the molecule and how they were used to estimate the heat of formation.
- **Estimated vapor pressure**. This section gives the estimated vapor pressure and information about how it is estimated.

Once created, stable reactants are not deleted, and will show up in a "Get information on reactants in contents" section when the user returns to the main menu. This replaces the "No reactants currently in reactor" line that is shown in Figure 2. The reactants can be deleted by selecting the "(Delete)" link by the reactant name or structure, or by selecting the "(Delete all reactants)" link. Figure 4 shows a screenshot of the portion of the main menu after MEK has been created but not yet fully reacted.

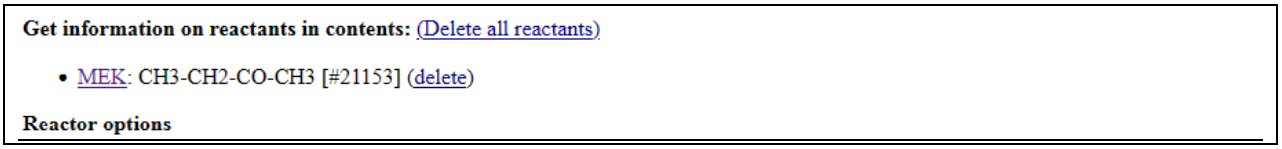


Figure 4. Screen shot of the portion of the main menu that appears when returning to the main menu after the reactant MEK has been created

b) Reaction Information Pages for Radicals

If a radical reactant is created or selected, then single step reactions are automatically generated and the results are shown on the reactant information page that is output, with the reactions displayed in place of the "Generate Reactions" sections. The "Header" and "Groups" sections display the same types of information as for stable reactants, but there is no "Estimated vapor pressure" section because vapor pressures are not estimated for radicals. An example of this output is shown on Figure 5, which shows the results if the radical designated "CH3-CO-CH2-CH2O." (formed in the reactions of MEK with OH) is created or selected.

Generating Single Step Reactions

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 are derived or assigned. Single step reactions are generated automatically when radicals are created or selected, with an example of the results shown on Figure 5, but this is not automatic when stable compounds are created. This is because the type of initial reaction has to be selected.

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.

H → 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*)
			14.02	O*_(C)

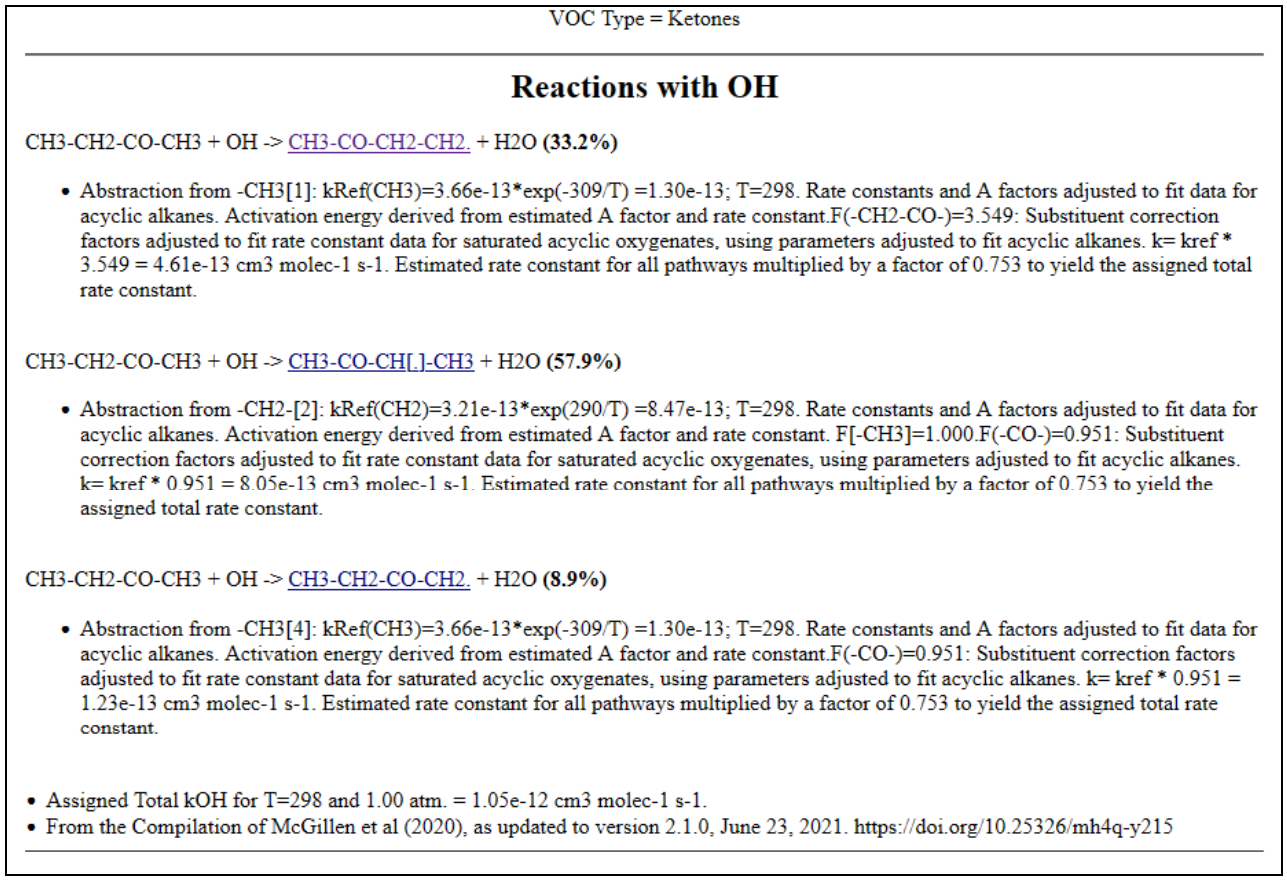
Notes on heat of formation estimate:

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

Figure 5. Screen shot of the reactant information page when the radical with the structure "CH3-CO-CH2-CH2O." is created or selected.

A single step reaction for stable compounds is generated by selecting the "(single step)" link for the desired type of reaction in the "Generate Reactions" section of the reactant information page. For example, to generate the single-step reactions of OH with methyl ethyl ketone, select the link marked "E" on the reactant information page shown on Figure 3.

This produces a page with the same sections and information as the reaction information page, discussed above, except it also has a "Reactions with …" section between the "Header" and "Generate Reactions" sections, similar to the display when a radical is reacted. An example of portions of such a page is shown on Figure 6. The results include all the generated reactions of the selected type, giving the fractions reacting by each reaction, the total rate constant (assigned or estimated), and documentation information. Note that the organic products and radicals formed are hyperlinked, and selecting those links will produce reaction information pages for those reactants, i.e., the same output as would result had it been created by giving its structure on the main menu.



VOC Type = Ketones

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 6. Screen shot of the portion of the reactant information page for methyl ethyl ketone showing the results of its single-step reactions with OH radicals.

Full Mechanism Generation

The full mechanism generation process involves first generating one or more selected initial reactions, then reacting all radicals formed in the those 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. Because of this, the online system will not generate full mechanisms for compounds with more than 9 groups. In such cases, the "Generate Reaction" section will not contain any active links to generate full reactions, but will still have links to generate single step reactions.

In the case of MEK, whose reaction reactant menu is shown on Figure 3, selecting the check-off box and then the control as indicated by "F" on the figure will generate a full mechanism with MEK with OH, and selecting the link "React completely with all ("G") will generate all reactions of this compound that are currently predicted, which in the case of MEK are reactions with OH, NO_3, and by photolysis. Once the full reaction generation is completed (which may take many seconds for larger molecules), a page showing the generated reaction is displayed with links for downloading the reaction or product lists. An example of the portions of such a page resulting from generating all reactions of MEK (e.g., selecting link "G" on Figure 3) is shown on Figure 7. Such pages include the following sections. See the full user's manual for more discussion of the items discussed.

- **Header** (not shown on Figure 7) The top section gives basic information about the reactant, which is shown on reactant menu pages. For MEK this is the same as the header shown on Figure 3, so it is not shown on Figure 7.
- **Links to download results.** This contains links to download various types of results of full mechanism generations, as summarized below.
- **Full Set of Reactions.** This lists the explicit reactions that were generated, giving their rate constants ("k") for the default conditions of the reactor, the relative fraction that each reaction reacts via the reaction shown ("Fac"), the estimated relative importance of the reaction used when generating the mechanism for the purpose of determining pathways that can be neglected ("Weight"), and the reactants and products in the reaction ("Reaction"). There can be hundreds of reactions generated for larger compounds.
- **Products from reacting under standard conditions.** This gives yields of the products when the reactant reacts under representative environmental conditions, and includes a summary of conditions used, relative fractions for the various types of initial reactions (if more than one type of reaction was generated), and yields of the products relative to the amount of reactant reacted.
- **Minimally reduced processed mechanism** (not shown on Figure 7). This is the explicit mechanism that has been simplified by combining reactions of the same reactant with product coefficients based on ratios of rate constants for the default temperature of the reactor, and by eliminating intermediates with only unimolecular or O_2 reactions by using the steady state approximation, and using 8-character model species names for each of the explicitly represented reactants and products. It is given in the format that can be used by the SAPRC box modeling programs (See "Additional Information Available"), and includes lists of model species and what they represent, and then the reactions of the model species.

Mechanism generated using Explicit mechanism with no lumping
Explicit mechanism has 78 reactions and 63 species. Download tab-separated files with (reactions) or (products)
Processed mechanism has 37 reactions and 47 species. Show (reactions). Send in (tab-separated format) or in (SAPRC .RXN format)

Full set of reactions of MEK with OH, NO3, and HV

Full set of reactions of CH3-CH2-CO-CH3 with OH, NO3, and HV

Rxn	k	Fac	Weight	Reaction
1	3.47e-13	33%	33.2%	CH3-CH2-CO-CH3 + OH -> CH3-CO-CH2-CH2. + H2O
2	6.06e-13	58%	57.9%	CH3-CH2-CO-CH3 + OH -> CH3-CO-CH[.]-CH3 + H2O
3	9.29e-14	9%	8.9%	CH3-CH2-CO-CH3 + OH -> CH3-CH2-CO-CH2. + H2O
4	1.53e-17	100%	100.0%	CH3-CH2-CO-CH3 + NO3 -> CH3-CO-CH[.]-CH3 + HNO3
5	2.39e-6 *	85%	85.0%	CH3-CH2-CO-CH3 + HV -> CH3-CH2. + CH3-CO. (PF=MEK-06, QY=1.49e-1)
6	4.22e-7 *	15%	15.0%	CH3-CH2-CO-CH3 + HV -> CH3. + CH3-CH2-CO. (PF=MEK-06, QY=2.63e-2)
7		100%	157.9%	CH3-CO-CH[.]-CH3 + O2 -> CH3-CO-CH[OO.]-CH3
8	8.47e-12	93%	146.5%	CH3-CO-CH[OO.]-CH3 + NO -> CH3-CO-CH[O.]-CH3 + NO2
9	6.59e-13	7%	11.4%	CH3-CO-CH[OO.]-CH3 + NO -> CH3-CO-CH(CH3)-ONO2
10	2.30e-12	100%	157.9%	CH3-CO-CH[OO.]-CH3 + NO3 -> CH3-CO-CH[O.]-CH3 + NO2 + O2
11	1.05e-11	85%	134.3%	CH3-CO-CH[OO.]-CH3 + HO2 -> CH3-CO-CH(CH3)-O-OH + O2
12	1.86e-12	15%	23.7%	CH3-CO-CH[OO.]-CH3 + HO2 -> CH3-CO-CH[O.]-CH3 + OH + O2
13	1.28e-11	80%	126.4%	CH3-CO-CH[OO.]-CH3 + RCO3 -> CH3-CO-CH[O.]-CH3 + O2 + RCO2.
14	3.20e-12	20%	31.6%	CH3-CO-CH[OO.]-CH3 + RCO3 -> CH3-CO-CO-CH3 + O2 + RCO-OH
15	2.25e+8	100%	454.5%	CH3-CO-CH[O.]-CH3 -> CH3-CHO + CH3-CO.
16		100%	33.2%	CH3-CO-CH2-CH2. + O2 -> CH3-CO-CH2-CH2OO.

--- (not all reactions shown) ---

75	5.21e-13	10%	195.4%	CH3OO. + HO2 -> HCHO + O2 + H2O
76	1.22e-11	90%	1758.5%	CH3OO. + RCO3 -> CH3[O.] + O2 + RCO2.
77	1.35e-12	10%	195.4%	CH3OO. + RCO3 -> HCHO + O2 + RCO-OH
78	9.91e+3	100%	5666.1%	CH3[O.] + O2 -> HCHO + HO2.

* Photolysis rates calculated using the "STD640Z0" light source [Z=0 solar spectrum used for Carter (1994) reactivity scales scenarios. Summer conditions, 640 meters, data provided by Jeffries (1993, unpublished results)].

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

Products from reacting under standard conditions

Explicit products formed when MEK CH3-CH2-CO-CH3 reacts with OH, NO3, and HV 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. Yields < 0.05% not shown.

Mid NOx	High NOx	Low NOx	Night	Explicit product or reacted
80.5%	73.6%	57.8%	89.7%	OH reacted
0.0%	0.0%	0.0%	10.3%	NO3 reacted
19.5%	26.4%	42.2%	0.0%	HV reacted
135.49%	162.18%	139.38%	64.86%	NO2
7.34%	-	31.47%	105.48%	O2
80.55%	73.63%	58.21%	89.73%	H2O
63.98%	80.99%	82.47%	23.53%	HO2.
60.62%	66.52%	62.06%	50.11%	CH3-CHO
38.65%	34.56%	29.66%	48.93%	CH3-CO-O-ONO2
31.42%	41.04%	38.98%	10.25%	HCHO
23.37%	33.16%	35.70%	2.08%	CO2
22.29%	21.41%	13.72%	22.93%	CH3-CO-CH2-CHO
-	-	-	10.29%	HNO3
1.92%	-	5.32%	9.90%	CH3-CO-CH(CH3)-O-OH
6.02%	5.45%	4.88%	6.08%	CH3-CH2-CO-O-ONO2
1.29%	-	3.58%	5.56%	CH3-CO-CH2-CH2-O-OH
0.58%	-	4.95%	-	CH3-CH2-O-OH
0.84%	-	3.78%	2.21%	OH
0.52%	-	3.41%	0.23%	CH3-O-OH
3.18%	3.08%	1.91%	-	CH3-CO-CH(CH3)-ONO2

--- (not all products shown) ---

Figure 7. Portions of the web page displaying following a full reaction generation for MEK with default options, showing the explicit mechanism and major products formed in various environments.

The following types of results can be downloaded using the links shown between the header and the section giving the full set of reactions. Details concerning these outputs are given in the user's manual.

- **Full mechanism (reactions).** Reactions, rate constant parameters, and branching ratios in the mechanism in tab-separated format. Details are given in the user's manual.
- **Full mechanism (products).** List of products and their estimated yields for the standard environmental conditions. Standard environmental conditions are discussed in the user's manual.
- **Processed mechanism (reactions & tab-separated format).** List of products and intermediates (steady state species) in the minimally reduced processed mechanism. The "(reactions)" link or the "(SAPRC RXN format)" links give the reactions in the format can be used by the SAPRC modeling programs, and is same as shown on the reaction results page. The "(tab-separated format)" link gives the result in a format similar to that used for the "Full Mechanism" link.

The reactant remains in the reactor after it is fully reacted and is not deleted. This is also the case when radicals are fully reacted as would occur, following selecting the "React Completely" link on single-step reaction results for radicals (for example, by selecting link "H" on Figure 5).

When one returns to the main menu, the entry for the reactant in the portion of the main menu showing the list of reactants also has the links to obtain the results of the full mechanism generation for the reactants that reacted. For example, after reacting MEK, the listing of MEK on main menu shown on Figure 5 changes to that shown on Figure 8. Figure 8a shows the display if there are fewer than five reactants in the reactor, while Figure 8b shows the display if there

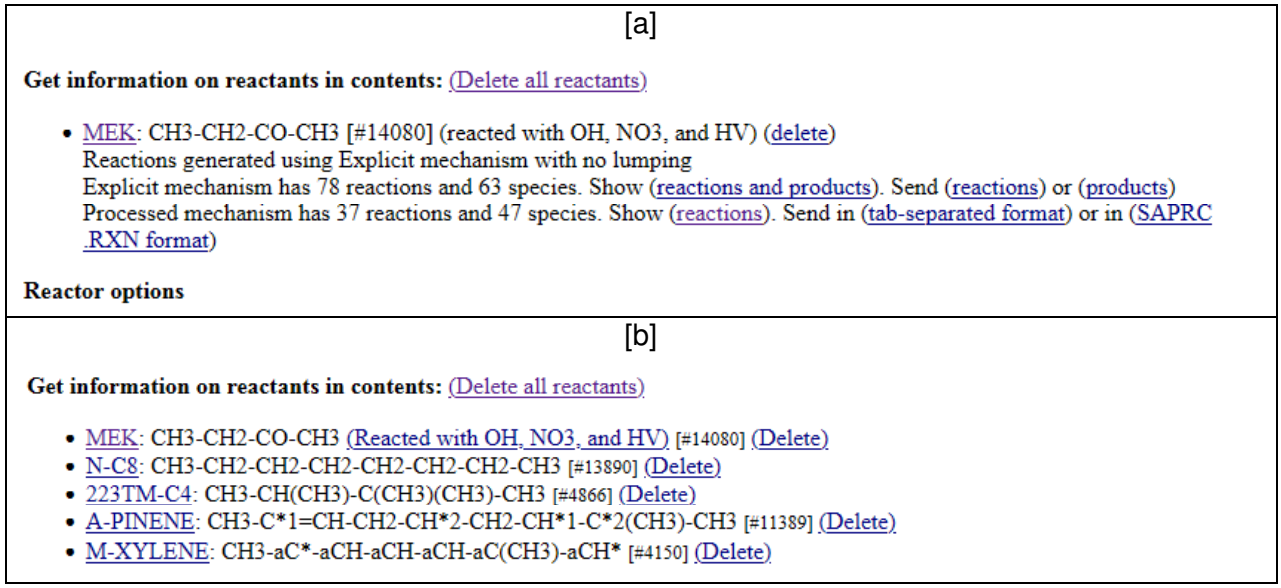


Figure 8. Screen shot of the portion of the main menu that appears when returning to the main menu after fully reacting MEK. [a] Display if there are fewer reactants in reactor. [b] Display if there are five or more reactants.

are more than five. Selecting the "Show (reactants and products)" link on Figure 8a or the "(Reacted with …)" link on Figure 8b will return the user to the reaction results page (e.g. as shown on Figure 7).

These reactants will persist in your reactor even after you have logged out, assuming that your account was not deleted or reset, as may happen from time to time when MechGen is updated. Reactants can be deleted by selecting the appropriate links on the main menu. You can also re-generate reactions of selected types for a reactant that was already reacted, but in that case all the previous results will be over-written.

Modifying Mechanism Generation Options

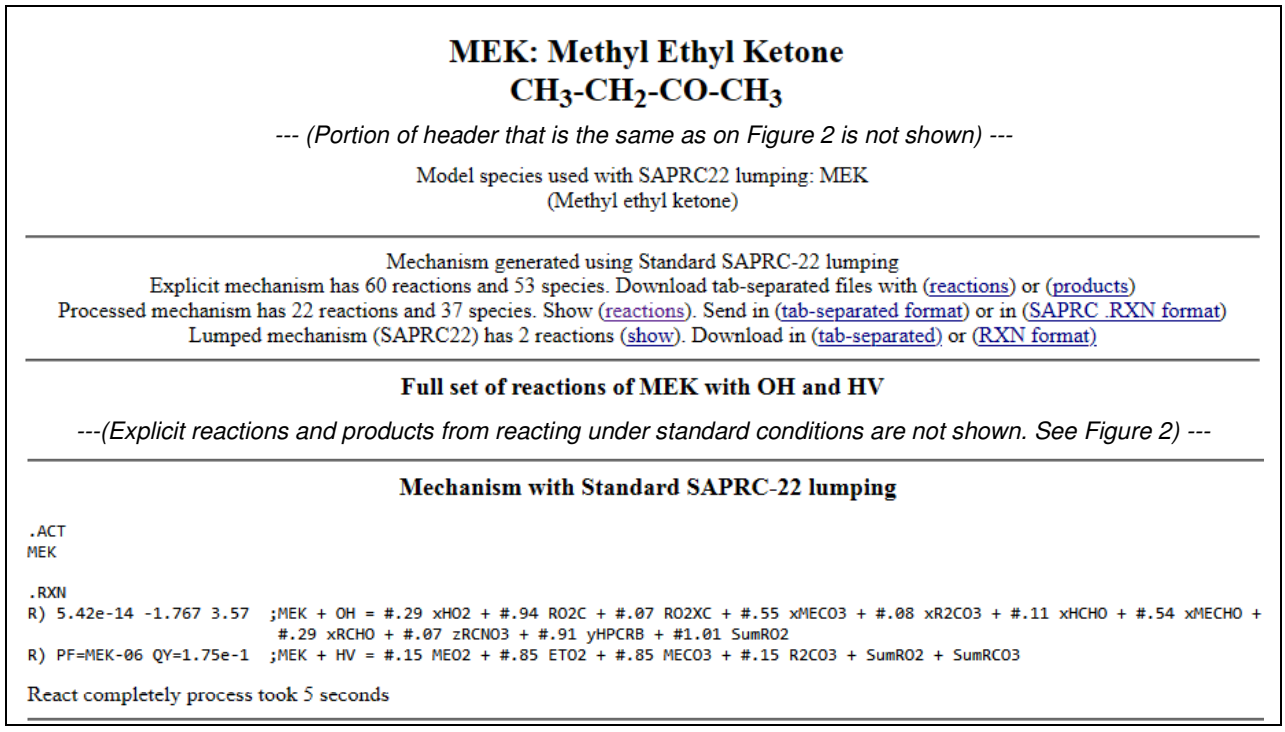
The options that affect mechanism generation and results processing in the reactor that the user can modify are indicated in the "Reactor Options" section of the main menu as on Figure 2. The options are shown as following, and are discussed in more detail in the user's manual.

- **Options affecting generated mechanisms.** These include temperature and pressure, which affect temperature and pressure-dependent rate constants, the presence of water vapor, which affects reactions of slowly reacting Criegee intermediates, and the concentration of O_2 in the air, which affects predicted fates of alkoxy radicals that have both O_2 and unimolecular reactions.
- **Options affecting results displays or processing of generated mechanism.** These include standard environments that are used when displaying product yields, the light source that affects outputs of rates of photolysis reactions, and atmospheric PM levels and method used to estimate vapor pressures, which affect predictions of SOA formation shown in some outputs.
- **Lumping Method.** This affects whether and how the results of full mechanism generations are used to prepare lumped SAPRC mechanisms and also affects mechanism generation in that reactions that are not used when deriving lumped mechanisms are not generated. The default is no lumping. Lumping is discussed further below.

Generating Lumped Mechanisms

MechGen can optionally be used to derive lumped SAPRC mechanisms used in airshed models. Lumping involves representing organic products using a more limited set of explicit and lumped model species, and using various approaches to reduce the numbers of model species representing reactive intermediates. The default is no lumping, but users can chose lumping using versions of the SAPRC mechanism as described in the full user's manual, by using links either in the header or the Reactor Options section of the main menu (see Figure 2).

If non-explicit lumping is selected, the reaction results pages displayed following full mechanism generations include a listing of the lumped rather than the minimally processed mechanism. For example, Figure 9 shows sections of the reaction results page displayed following full mechanism generation for MEK when SAPRC-22 lumping is selected. The header section shows how the selected compound is lumped. Note that the end of the header section gives the model species used to MEK in this mechanism (it is represented explicitly, so in this case the model species also named "MEK"). There are links for downloading both the processed and lumped mechanisms in various formats, and the lumped mechanism is much shorter than the processed mechanism. The sections showing explicit reactions and products



MEK: Methyl Ethyl Ketone
CH_3-CH_2-CO-CH_3

--- (Portion of header that is the same as on Figure 2 is not shown) ---

Model species used with SAPRC22 lumping: MEK
(Methyl ethyl ketone)

Mechanism generated using Standard SAPRC-22 lumping
Explicit mechanism has 60 reactions and 53 species. Download tab-separated files with (reactions) or (products)
Processed mechanism has 22 reactions and 37 species. Show (reactions). Send in (tab-separated format) or in (SAPRC .RXN format)
Lumped mechanism (SAPRC22) has 2 reactions (show). Download in (tab-separated) or (RXN format)

Full set of reactions of MEK with OH and HV

---(Explicit reactions and products from reacting under standard conditions are not shown. See Figure 2) ---

Mechanism with Standard SAPRC-22 lumping

```
.ACT
MEK

.RXN
R) 5.42e-14 -1.767 3.57  ;MEK + OH = #.29 xHO2 + #.94 RO2C + #.07 RO2XC + #.55 xMECO3 + #.08 xR2CO3 + #.11 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
```

React completely process took 5 seconds

Figure 9. Portions of the web page displayed following the full reaction generation for MEK with SAPRC-22 lumping selected. Portions that are nearly the same as those shown when it is reacted without lumping, shown on Figure 7, are not shown.

are essentially the same as those shown on Figure 7, except that acyl peroxy radicals, which are represented explicitly, are treated as unreacting products.

If SAPRC-22 lumping is selected, MechGen provides the ability of users to derive "Users Mechanisms", consisting of the SAPRC-22 mechanism with selected compounds represented explicitly. Links to do so are included in the "Advanced Options" section of the main menu (see Figure 2). This is described in the full user's manual.

Revising Mechanism Assignments

When MechGen is generating mechanisms it first determines if there are any assignments for reactions or rate constants for specific compound and type of reaction being generated, and uses those rather than estimation mechanisms for the reactions that are generated. The mechanism assignments that are used by default can be using the "Show Assignments" link in the "Obtain Information" section of the main menu (Figure 2). MechGen provides users the ability to add or revise mechanism assignments used when generating mechanisms in their reactor, with the link to do so being in the "User Assignments" line in the "Advanced Options" section of the main menu (Figure 2). Instructions on how to do this are given in the full user's manual, and a summary of the input used for assignments are also provided in the pages used to input assignments. These modified assignments do not affect reactions generated by other users.

Other Advanced Features

MechGen has several additional features available to advanced users, but using them requires that the users obtain a login and password for terminal (command line) access to MechGen using a terminal emulator program such at Telnet. Terminal access is also required if users wish to generate mechanisms for compounds with 10 or more structural groups, such as decanes or terpenes. A link to create a "telnet login" is included in the "Web user account actions" section of the main menu.

Some advanced features require that users download, install and configure MechGen to run on their own computers, as described in the full user's manual. This will give knowledgeable users the capability to modify the MechGen programs, defaults, or estimation methods. (However, a programmers' guide to the MechGen software is not yet available).

The following additional features may be of interest to some advanced users. They are described in detail in the full user's manual and are only briefly summarized here.

- **Deriving multi-generation mechanisms.** The full mechanism generation procedure involves reacting radical intermediates but not the stable products predicted to be formed. A "multi-generation" mechanism also includes reactions of all stable products formed in non-negligible yields. In order to determine which products are formed in sufficient yields to include in a multi-generation mechanism, it is necessary for the user to select one or more standard environments for estimating product yields. The results can be downloaded to the users in several formats, as described in the user's manual.
- **Creating or modifying lumping methods.** Authorized users can create or modify lumping methods that they or other users can employ when generating mechanisms. The users manual describes the procedures used to derive the lumping methods for SAPRC. Users can modify how organic compounds or intermediates are lumped, but program changes are required to use methods to represent peroxy intermediates other than those used for SAPRC-11 or 22.
- **Creating complete lumped mechanisms.** MechGen was used for deriving the representation of organics in the most recent versions of the SAPRC mechanisms. The user's manual describes the features and operations used to derive the SAPRC-22 mechanism, and similar procedures can be used to derive other mechanisms using the same peroxy lumping approach.

Additional Information Available

The following additional information is currently available, or expected to be available soon, concerning the current version of the SAPRC MechGen system. Links to obtain the latest available documents are at the MechGen login page at http://mechgen.cert.ucr.edu and at the MechGen information page at https://intra.engr.ucr.edu/~carter/MechGen. Additional information can also be obtained from William Carter at carter@cert.ucr.edu or MechGen GitHub page at https://github.com/SAPRC/MechGen.

- **Full users manual.** This gives details concerning the capabilities and operations in MechGen, and how to download and install it to take advantage of its full capabilities are given in the full user's manual. Although it is not necessary to read this entirely to use this system, users interested in specific features are advised to read the chapters discussing the features they may wish to use.

- **Chemistry documentation.** The scientific basis for the chemical mechanism assignments and estimation methods used when deriving reactions for MechGen is given in the paper titled "Derivation of Atmospheric Reaction Mechanisms for Volatile Organic Compounds by the SAPRC Mechanism Generation System (MechGen), by W. P. L. Carter, J. Jiang, J. J. Orlando, and K. C. Barsanti, that has recently been accepted for publication in Atmospheric Chemistry and Physics[1].
- **System documentation.** A manuscript describing MechGen as a software system and discussing the major algorithms used is nearing completion for submission to Geoscientific Model Development. The full users manual and this basic operations guide will be included among the Supplementary Information with this manuscript. Once it is available, links to obtain it can be obtained from the MechGen web sites listed above. In the meantime, the full users manual provides the best available description of the software.
- **SAPRC mechanism documentation.** Information and links concerning the lumped SAPRC mechanisms for model simulations of gas-phase atmospheric reactions is available at the SAPRC mechanism web page at https://intra.cert.ucr.edu/~carter/SAPRC/. The SAPRC-11 mechanism is documented by W. P. L. Carter and G. Heo "Development of Revised SAPRC Aromatics Mechanisms".[2] The SAPRC-22 mechanism is documented by W. P. L. Carter, "Documentation of the SAPRC-22 Mechanisms".[3] A manuscript describing an updated version of SAPRC-22 is in preparation.
- **SAPRC box modeling programs.** The SAPRC modeling software consist of Fortran programs that can carry out box model simulations that were used to evaluate various mechanism against chamber data and calculate ozone reactivity scales is available for download at https://intra.cert.ucr.edu/%7Ecarter/SAPRC/SAPRCfiles.htm. This includes the Fortran source files, executable files that run in DOS windows in Windows-based computers, and example input and output files. This software can be used to carry out model simulations using mechanisms derived using MechGen, as described in the full user's manual.

[1] Available at https://egusphere.copernicus.org/preprints/2023/egusphere-2023-2343/

[2] Atmos. Environ. 77, 404-414, 2013. DOI: 10.1016/ j.atmosenv.2013.05.021

[3] Report to the California Air Resources Board contract no. 21AQP011, September 9, 2023, available at https://intra.engr.ucr.edu/~carter/SAPRC/22/