Basic Operations for MechGen Web Users

MechGen 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 the author, William P. L. Carter: carter@cert.ucr.edu.

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 a user-specific "reactor" system. Once created, the username and password are necessary to login back to your own reactor system in the future.

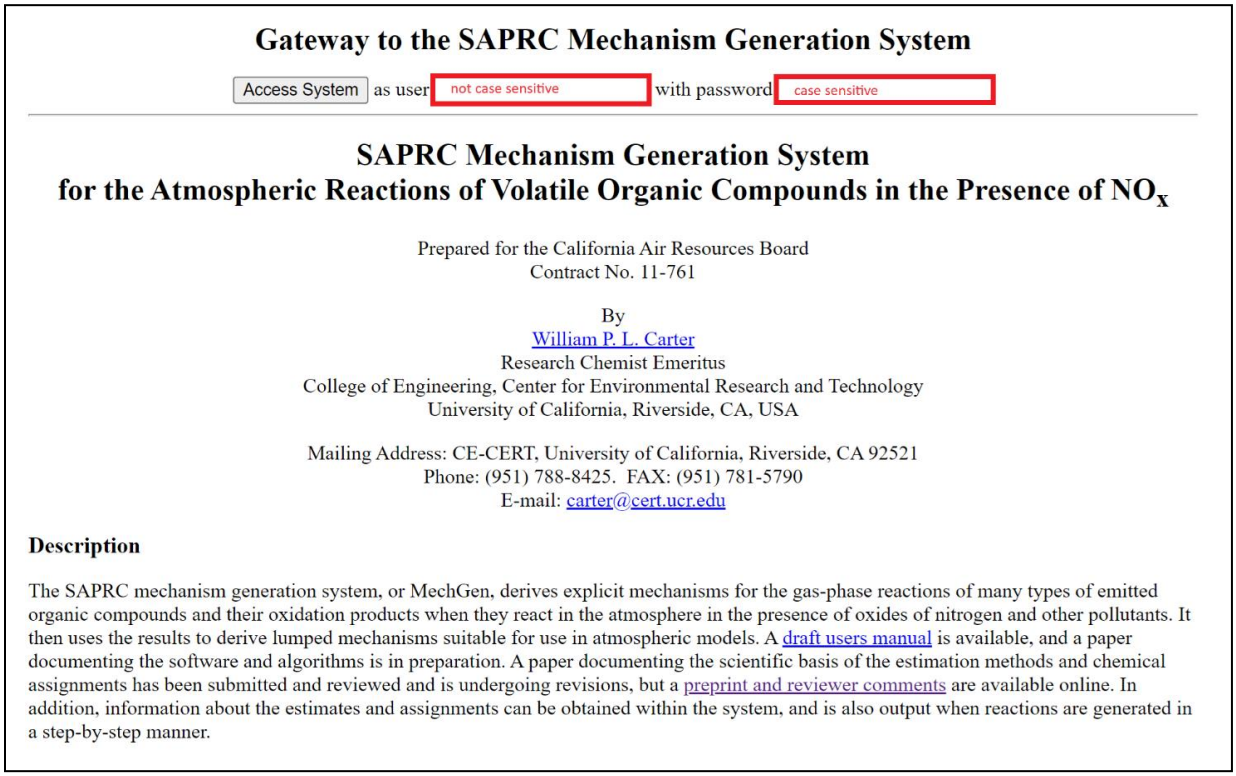


Figure 1. Screen shot of the MechGen login page.

Main Menu

When first logged into the system, the user is presented with a web page with a reactor with the default settings when a new user reactor is created. In Figure 2, three reactants have been created, with one fully reacted for illustration. These sections of the web page in Figure 2 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. You can input SMILES directly, or use MechGen structure notation (similar to SMILES but displays all atoms). Click the links on the website for detailed explanations of "structure" and "assigned name".

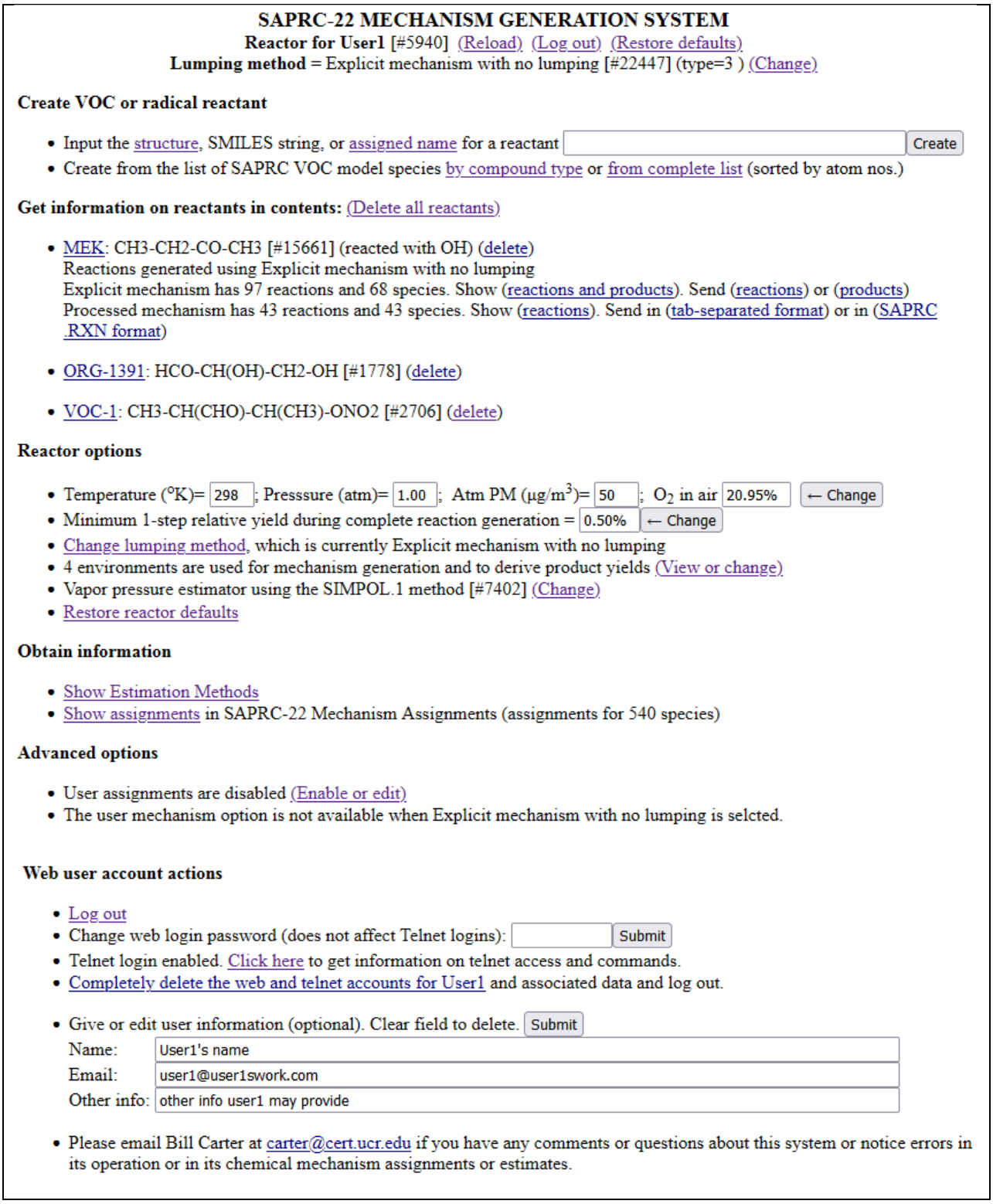


Figure 2. Screen shot of the main menu for the web interface with default settings.

- Get information on reactants in contents. This lists reactants that previously created by the user. It has links to go to the "Reactant Information" page for the reactant (discussed later). If a reactant has been fully reacted, there are links to access the reaction results. Note that radical reactants are not displayed in this list unless they have been completely reacted.
- 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 SAPRC.
- Advanced options. Users can employ "user assignments" to add to or override the default mechanism assignments. This might be useful for advanced users for the purpose of developing new mechanisms consistent with new data or theories, or modeling experimental data that appear to be inconsistent with default MechGen predictions. This section is not covered in this quick startup guide; please read the complete user manual on MechGen website for further details.
- 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.

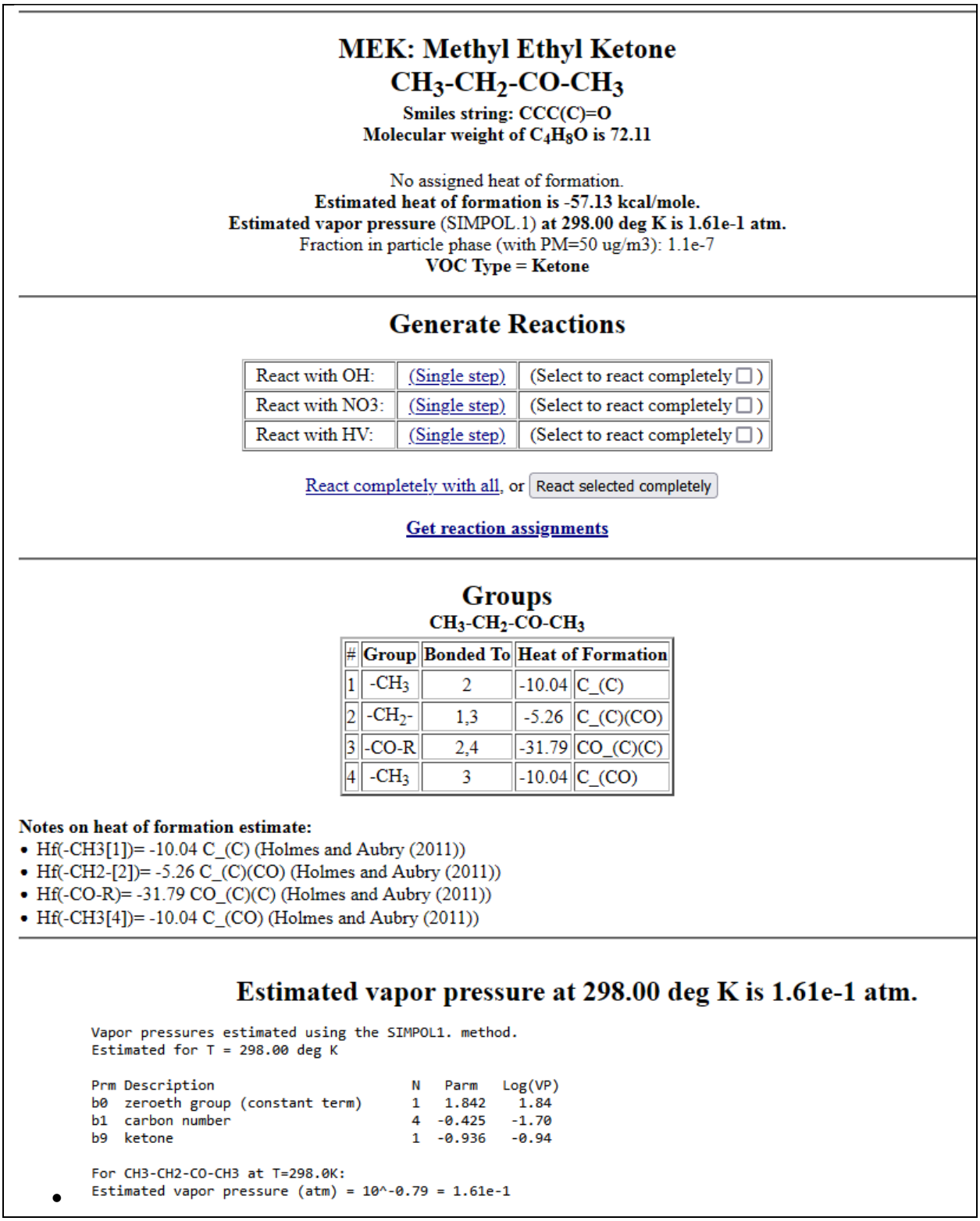
Reactant Information Pages

Reactant information pages are shown when new reactants are created, or existing reactions are selected from the main menu. The content of these pages varies depending on whether the reactant is a stable compound or an intermediate, and whether the reactant has undergone a "react completely" operation. Figure 3 and Figure 4 illustrate examples of a stable reactant "MEK" and a radical reactant "RAD-4". The contents of these pages are as follows:

- 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.

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

  In the case of reactant pages for intermediates, this section gives the results of a single step reaction of this radical, and a link to react this radical completely.
- Groups. This section lists MechGen groups in the molecule and how they were used to estimate the heat of formation.
- Estimated vapor pressure (stable reactants only). Information about how the vapor pressure is estimated.



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

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-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.

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

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*)
			14.02	O*_(C)

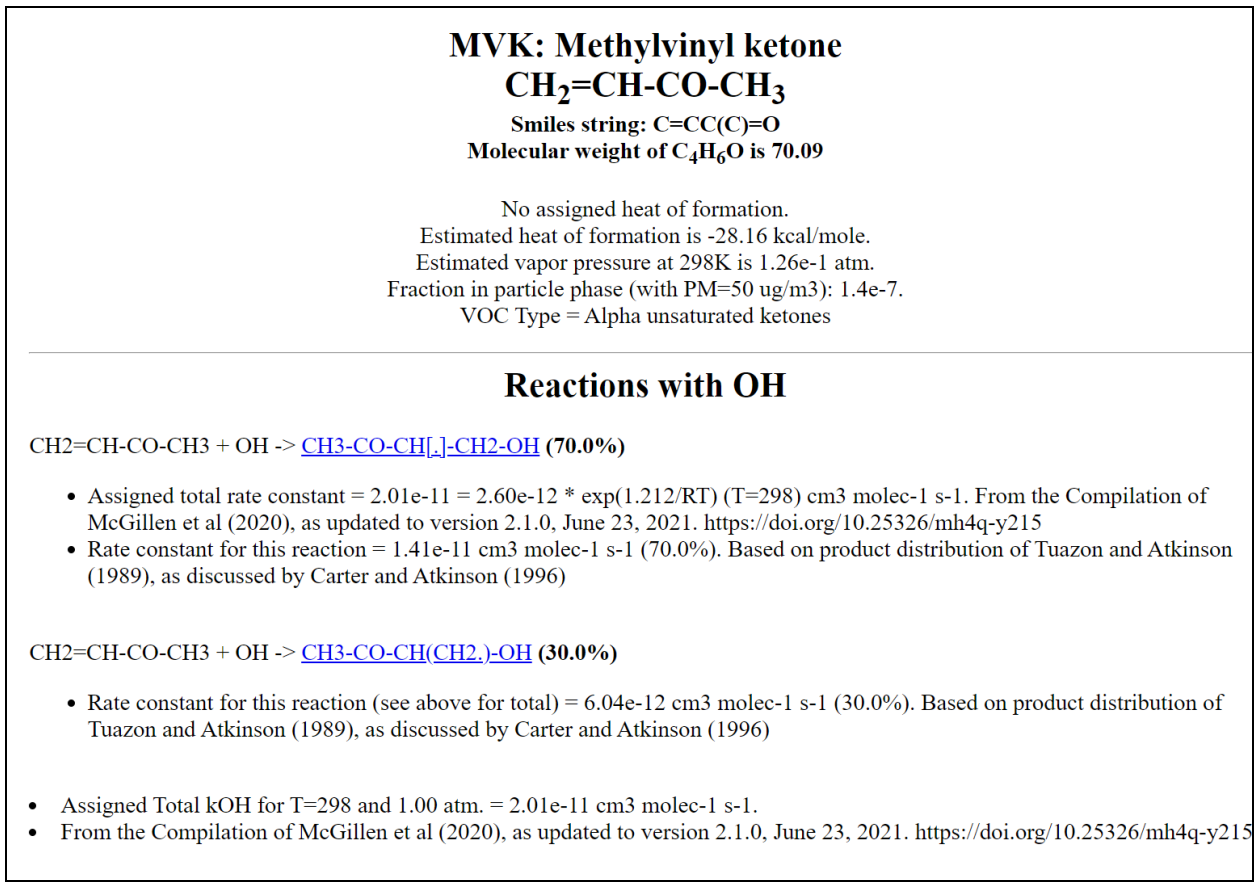
Notes on heat of formation estimate:
- Hf(-CH3[1])= -10.04 C_(CO) (Holmes and Aubry (2011))
- Hf(-CO-R)= -31.79 CO_(C)(C) (Holmes and Aubry (2011))
- Hf(-CH2-[3])= -5.26 C_(C)(CO) (Holmes and Aubry (2011))
- Hf(-CH2O.)= -7.89 C_(C)(O*) (Assume no beta substituent effect on BDE's. Set to [C_(C)(O)])

Figure 4. Screen shot of the reactant page for a newly created radical reactant with default reactor settings, using one of the radicals formed in the initial reactions of OH with MEK as the example.

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. Once a single step reaction is generated, an associated single step reaction results page will be displayed.

These consist of lists of reactions and estimation methods, or mechanism assignments used. Example of single step reaction output for intermediates is shown in Figure 5.



MVK: Methylvinyl ketone

CH_2=CH-CO-CH_3

Smiles string: C=CC(C)=O

Molecular weight of C_4H_6O is 70.09

No assigned heat of formation.
Estimated heat of formation is -28.16 kcal/mole.
Estimated vapor pressure at 298K is 1.26e-1 atm.
Fraction in particle phase (with PM=50 ug/m3): 1.4e-7.
VOC Type = Alpha unsaturated ketones

Reactions with OH

CH2=CH-CO-CH3 + OH -> CH3-CO-CH[.]-CH2-OH **(70.0%)**

- Assigned total rate constant = 2.01e-11 = 2.60e-12 * exp(1.212/RT) (T=298) 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
- Rate constant for this reaction = 1.41e-11 cm3 molec-1 s-1 (70.0%). Based on product distribution of Tuazon and Atkinson (1989), as discussed by Carter and Atkinson (1996)

CH2=CH-CO-CH3 + OH -> CH3-CO-CH(CH2.)-OH **(30.0%)**

- Rate constant for this reaction (see above for total) = 6.04e-12 cm3 molec-1 s-1 (30.0%). Based on product distribution of Tuazon and Atkinson (1989), as discussed by Carter and Atkinson (1996)

- Assigned Total kOH for T=298 and 1.00 atm. = 2.01e-11 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 MVK with OH radicals.

Mechanism generated using Explicit mechanism with no lumping
Full mechanism has 39 reactions and 35 species. Download tab-separated files with (reactions) or (products)
Processed mechanism has 16 reactions and 20 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%	71.6%	CH3-CH[OO.]-CH3 + NO3 -> CH3-CH[O.]-CH3 + NO2 + O2
7	9.92e-12	100%	71.6%	CH3-CH[OO.]-CH3 + HO2 -> CH3-CH(CH3)-O-OH + O2
8	7.80e-15	50%	35.8%	CH3-CH[OO.]-CH3 + RO2 -> CH3-CH[O.]-CH3 + O2 + RO.
9	3.90e-15	25%	17.9%	CH3-CH[OO.]-CH3 + RO2 -> CH3-CH(CH3)-OH + O2 + RO-alpha-H
10	3.90e-15	25%	17.9%	CH3-CH[OO.]-CH3 + RO2 -> CH3-CO-CH3 + O2 + ROH
11	1.28e-11	80%	57.3%	CH3-CH[OO.]-CH3 + RCO3 -> CH3-CH[O.]-CH3 + O2 + RCO2.
12	3.20e-12	20%	14.3%	CH3-CH[OO.]-CH3 + RCO3 -> CH3-CO-CH3 + O2 + RCO-OH
13	3.63e+2	1%	2.4%	CH3-CH[O.]-CH3 -> CH3-CHO + CH3.
14	3.56e+4	99%	230.9%	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%	28.4%	CH3-CH2-CH2OO. + NO3 -> CH3-CH2-CH2O. + NO2 + O2

(not all reactions shown)

37	1.22e-11	90%	2.1%	CH3OO. + RCO3 -> CH3O. + O2 + RCO2.
38	1.35e-12	10%	0.2%	CH3OO. + RCO3 -> HCHO + O2 + RCO-OH
39	8.21e+3	100%	7.5%	CH3O. + O2 -> HCHO + HO2.

* SAPRC-22 photolysis rates (sec-1) for Z=0, calculated using actinic fluxes used by the Carter (1994) reactivity sce

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
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
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%

Figure 6. Portions of the web page displaying following a full reaction of propane with OH showing the explicit mechanism generated with the default (explicit) lumping approach

Full Mechanism Generation

The full mechanism generation process involves reacting all radicals formed in the initial reactions, then reacting the intermediates formed that need to be reacted, until only stable or species or basic species that do not need to be reacted remain. This can take a significant amount of time for larger molecules.

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.

Once the full reaction generation is completed, 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 is shown as Figure 6.

In Figure 6, the top part of the page 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:

Full mechanism (reactions): Reactions, rate constant parameters, and branching ratios in tab-separated format. Columns in this spreadsheet include reaction number, A, Ea, and B parameters for calculating temperature dependences where $k(T)=A*\exp(-Ea/T)*(T/300)^B$, 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.

Full mechanism (Products): List of products and their estimated yields for the standard environmental conditions.

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

Processed mechanism in (SAPRC .RXN format): This gives the processed mechanism in the format that can be used with SAPRC base mechanism.

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 1, 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. Note that changing the lumping method or creating or deleting user mechanisms will delete any previous full reaction results that may have been generated.

Table 1. 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
O2 in air	20.95%	Mole fraction of O2 in the reaction environment
H2O	Present	Used to determine of some intermediates (e.g., Criegee intermediates) react with water
Atm PM	50 ug/m3	Atmospheric particle levels used to estimate fractions of reactants in the particle phase if their vapor pressures can be estimated
Minimum 1-step yield	0.5%	The minimum yield for a competing process in a single step reaction for it to be considered non-negligible during full mechanism generations
Lumping method	Explicit	Lumping method used when generating full reactions and processing results. Currently available options are "Explicit" or SAPRC-11 or versions of SAPRC-22.
Environmental Conditions		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.
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)[a] or EVAPORATION (Compernolle et al. 2011) [b]. SIMPOL.1 is the default because it can be used with a larger variety of compounds,
		Advanced options
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.
User mechanisms	No user mechanisms	Users who select a SAPRC lumping method can optionally add versions of the SAPRC mechanism with selected reactant and product compounds being represented explicitly.

[a] Pankow, J. F. 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. https://doi.org/10.5194/acp-8-2773-2008.

[b] Compernolle, S., K. Ceulemans, and J.-F. Muller (2011): "EVAPORATION: A new vapor pressure estimation method for organic molecules including non-additivity and intramolecular interactions," Atmos. Chem. Phys., 11, 9431-9450. https://doi.org/10.5194/acp-11-9431-2011.