

This document contains the 1, 10, and 40 atm rate constant expressions for:

A. Andersen and E. A. Carter, *First-Principles-Derived Kinetics of the Reactions Involved in Low-Temperature Dimethyl Ether Oxidation*, Molecular Physics, 106, 367-396 (2008).

Table I: 1 atm rate expressions in the form of Eq. 4 for primary unimolecular and recombination reactions involved in dimethyl ether oxidation chain propagation. Unimolecular reaction rate coefficients are in s^{-1} and recombination (or association) rate coefficients are in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$. A “-” in front of an equation number indicates the reverse reaction. Activation energies are in kcal/mol.

Reaction (Eq. #)	$k_{1atm}(T)$
<i>primary propagation reactions</i>	
6	$1.99 \times 10^{49} T^{-12.1} e^{-8.1/RT}{}^a$
-6	$8.10 \times 10^{81} T^{-21.3} e^{-52.6/RT}{}^a$
7	$1.00 \times 10^{27} T^{-4.68} e^{-29.2/RT}$
-7	$2.46 \times 10^{28} T^{-5.18} e^{-16.7/RT}$
8	$8.29 \times 10^{21} T^{-3.35} e^{-11.6/RT}$
	$5.39 \times 10^{33} T^{-7.03} e^{-21.2/RT}{}^b$
	$1.00 \times 10^{35} T^{-7.37} e^{-22.8/RT}{}^c$
<i>competing reaction to $\text{CH}_3\text{O}\dot{\text{C}}\text{H}_2 + \text{O}_2$ addition</i>	
9	$8.25 \times 10^{34} T^{-7.01} e^{-27.1/RT}$
<i>alternative $\text{CH}_2\text{OCH}_2\text{OOH}$ dissociation reactions</i>	
10	$2.04 \times 10^{35} T^{-7.08} e^{-30.0/RT}$
11	$2.48 \times 10^{24} T^{-3.33} e^{-56.7/RT}$

^aVRRKM calculation using VARIFLEX.²⁶ Varshni potential adjusted heat of reaction implied by Curran et al.^{4,5} group additivity estimates.

^b E_0 of reaction (see Eq. 2) increased by 6.0 kcal/mol.

^c E_0 of reaction (see Eq. 2) increased by 7.0 kcal/mol.

Table II: 10 atm rate expressions in the form of Eq. 4 for primary unimolecular and recombination reactions involved in dimethyl ether oxidation chain propagation. Unimolecular reaction rate coefficients are in s^{-1} and recombination (or association) rate coefficients are in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$. A “-” in front of an equation number indicates the reverse reaction. Activation energies are in kcal/mol.

Reaction (Eq. #)	$k_{10\text{atm}}(T)$
<i>primary propagation reactions</i>	
6	$4.87 \times 10^{39} T^{-8.78} e^{-6.2/RT}{}^a$
-6	$5.32 \times 10^{78} T^{-20.0} e^{-52.8/RT}{}^a$
7	$7.69 \times 10^{19} T^{-2.39} e^{-27.3/RT}$
-7	$1.89 \times 10^{21} T^{-2.89} e^{-14.7/RT}$
8	$6.91 \times 10^{23} T^{-3.64} e^{-13.2/RT}$
	$2.78 \times 10^{34} T^{-6.93} e^{-22.6/RT}{}^b$
	$4.57 \times 10^{34} T^{-6.96} e^{-23.8/RT}{}^c$
<i>competing reaction to $\text{CH}_3\text{O}\dot{\text{C}}\text{H}_2 + \text{O}_2$ addition</i>	
9	$7.97 \times 10^{33} T^{-6.41} e^{-27.7/RT}$
<i>alternative $\text{CH}_2\text{OCH}_2\text{OOH}$ dissociation reactions</i>	
10	$5.26 \times 10^{29} T^{-5.18} e^{-28.8/RT}$
11	$5.84 \times 10^{17} T^{-1.26} e^{-54.7/RT}$

^aVRRKM calculation using VARIFLEX.²⁶ Varshni potential adjusted heat of reaction implied by Curran et al.^{4,5} group additivity estimates.

^b E_0 of reaction (see Eq. 2) increased by 6.0 kcal/mol.

^c E_0 of reaction (see Eq. 2) increased by 7.0 kcal/mol.

Table III: 40 atm rate expressions in the form of Eq. 4 for primary unimolecular and recombination reactions involved in dimethyl ether oxidation chain propagation. Unimolecular reaction rate coefficients are in s^{-1} and recombination (or association) rate coefficients are in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$. A “-” in front of an equation number indicates the reverse reaction. Activation energies are in kcal/mol.

Reaction (Eq. #)	$k_{40\text{atm}}(T)$
<i>primary propagation reactions</i>	
6	$4.63 \times 10^{32} T^{-6.43} e^{-4.6/RT}{}^a$
-6	$1.43 \times 10^{75} T^{-18.8} e^{-52.2/RT}{}^a$
7	$1.06 \times 10^{16} T^{-1.17} e^{-26.1/RT}$
-7	$2.61 \times 10^{17} T^{-1.67} e^{-13.6/RT}$
8	$2.08 \times 10^{24} T^{-3.62} e^{-13.9/RT}$
	$4.79 \times 10^{32} T^{-6.22} e^{-22.6/RT}{}^b$
	$1.49 \times 10^{33} T^{-6.34} e^{-23.9/RT}{}^c$
<i>competing reaction to $\text{CH}_3\text{O}\dot{\text{C}}\text{H}_2 + \text{O}_2$ addition</i>	
9	$7.53 \times 10^{31} T^{-5.65} e^{-27.5/RT}$
<i>alternative $\text{CH}_2\text{OCH}_2\text{OOH}$ dissociation reactions</i>	
10	$4.00 \times 10^{25} T^{-3.84} e^{-27.7/RT}$
11	$1.20 \times 10^{15} T^{-0.420} e^{-53.8/RT}$

^aVRRKM calculation using VARIFLEX.²⁶ Varshni potential adjusted heat of reaction implied by Curran et al.^{4,5} group additivity estimates.

^b E_0 of reaction (see Eq. 2) increased by 6.0 kcal/mol.

^c E_0 of reaction (see Eq. 2) increased by 7.0 kcal/mol.

Table IV: 1 atm rate expressions in the form of Eq. 4 for primary unimolecular and recombination reactions involved in chain branching. Unimolecular reaction rate coefficients are in s^{-1} and recombination (or association) rate coefficients are in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$. A “-” in front of an equation number indicates the reverse reaction. Activation energies are in kcal/mol.

Reaction (Eq. #)	$k_{1atm}(T)$
<i>primary branching reactions</i>	
12	$8.86 \times 10^{45} T^{-11.0} e^{-7.2/RT}{}^a$
-12	$3.45 \times 10^{52} T^{-11.9} e^{-43.7/RT}{}^a$
13	$2.17 \times 10^{37} T^{-7.63} e^{-30.0/RT}$
15	$1.57 \times 10^{38} T^{-7.43} e^{-51.4/RT}$
16	$1.30 \times 10^{91} T^{-23.6} e^{-66.3/RT}{}^b$
<i>competing HPMF decomposition reactions</i>	
22	$1.57 \times 10^{38} T^{-7.43} e^{-51.4/RT}$
23	$3.89 \times 10^{40} T^{-8.47} e^{-36.5/RT}$
25	$7.04 \times 10^{29} T^{-4.85} e^{-57.4/RT}$
26	$2.12 \times 10^{27} T^{-3.89} e^{-67.6/RT}$
<i>decomposition reactions of short-lived intermediates</i>	
24	$2.81 \times 10^{21} T^{-3.13} e^{-10.9/RT}$
17	$2.27 \times 10^{11} T^{-1.45} e^{-11.1/RT}$
21	$4.91 \times 10^{11} T^{-0.598} e^{-2.4/RT}$
27	$1.64 \times 10^{33} T^{-6.46} e^{-32.5/RT}$
28	$3.32 \times 10^{27} T^{-6.23} e^{-34.9/RT}$
29	$1.25 \times 10^{29} T^{-5.46} e^{-24.7/RT}$
30	$9.31 \times 10^{26} T^{-4.86} e^{-21.5/RT}$
31	$4.91 \times 10^{30} T^{-6.02} e^{-11.1/RT}$
32	$1.34 \times 10^{45} T^{-9.50} e^{-16.7/RT}$
33	$5.71 \times 10^{28} T^{-4.65} e^{-71.9/RT}$
34	$1.28 \times 10^{30} T^{-5.34} e^{-72.0/RT}$

^aVRRKM calculation using VARIFLEX.²⁶ Varshni potential adjusted heat of reaction implied by Curran et al.^{4,5} group additivity estimates.

^bVRRKM calculation using VARIFLEX.²⁶

Table V: 10 atm rate expressions in the form of Eq. 4 for primary unimolecular and recombination reactions involved in chain branching. Unimolecular reaction rate coefficients are in s^{-1} and recombination (or association) rate coefficients are in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$. A “-” in front of an equation number indicates the reverse reaction. Activation energies are in kcal/mol.

Reaction (Eq. #)	$k_{10atm}(T)$
<i>primary branching reactions</i>	
12	$4.46 \times 10^{32} T^{-6.54} e^{-4.2/RT}{}^a$
-12	$1.97 \times 10^{39} T^{-7.41} e^{-40.7/RT}{}^a$
13	$1.67 \times 10^{32} T^{-5.86} e^{-29.0/RT}$
15	$4.84 \times 10^{29} T^{-4.70} e^{-49.0/RT}$
16	$6.56 \times 10^{85} T^{-21.7} e^{-65.8/RT}{}^b$
<i>competing HPMF decomposition reactions</i>	
22	$7.08 \times 10^{32} T^{-5.62} e^{-49.6/RT}$
23	$4.31 \times 10^{34} T^{-6.45} e^{-35.1/RT}$
25	$6.15 \times 10^{21} T^{-2.31} e^{-55.0/RT}$
26	$6.52 \times 10^{19} T^{-1.53} e^{-65.3/RT}$
<i>decomposition reactions of short-lived intermediates</i>	
24	$2.00 \times 10^{23} T^{-3.37} e^{-11.7/RT}$
17	$3.31 \times 10^{13} T^{-1.52} e^{-10.9/RT}$
21	$4.68 \times 10^{14} T^{-1.20} e^{-3.3/RT}$
27	$1.57 \times 10^{27} T^{-4.44} e^{-31.1/RT}$
28	$3.26 \times 10^{31} T^{-6.63} e^{-36.2/RT}$
29	$7.73 \times 10^{27} T^{-4.82} e^{-25.0/RT}$
30	$3.27 \times 10^{27} T^{-4.72} e^{-22.2/RT}$
31	$2.70 \times 10^{34} T^{-6.75} e^{-12.4/RT}$
32	$6.85 \times 10^{32} T^{-5.83} e^{-10.9/RT}$
33	$1.34 \times 10^{23} T^{-2.79} e^{-70.5/RT}$
34	$4.74 \times 10^{23} T^{-3.23} e^{-70.4/RT}$

^aVRRKM calculation using VARIFLEX.²⁶ Varshni potential adjusted heat of reaction implied by Curran et al.^{4,5} group additivity estimates.

^bVRRKM calculation using VARIFLEX.²⁶

Table VI: 40 atm rate expressions in the form of Eq. 4 for primary unimolecular and recombination reactions involved in chain branching. Unimolecular reaction rate coefficients are in s^{-1} and recombination (or association) rate coefficients are in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$. A “-” in front of an equation number indicates the reverse reaction. Activation energies are in kcal/mol.

Reaction (Eq. #)	$k_{40\text{atm}}(T)$
<i>primary branching reactions</i>	
12	$1.55 \times 10^{25} T^{-4.06} e^{-2.38/RT}{}^a$
-12	$6.41 \times 10^{31} T^{-4.92} e^{-38.9/RT}{}^a$
13	$1.64 \times 10^{28} T^{-4.54} e^{-28.0/RT}$
15	$4.98 \times 10^{24} T^{-3.13} e^{-47.5/RT}$
16	$3.30 \times 10^{80} T^{-19.9} e^{-64.5/RT}{}^b$
<i>competing HPMF decomposition reactions</i>	
22	$5.79 \times 10^{27} T^{-4.00} e^{-48.1/RT}$
23	$1.86 \times 10^{30} T^{-5.03} e^{-34.0/RT}$
25	$6.04 \times 10^{17} T^{-1.052} e^{-53.8/RT}$
26	$1.76 \times 10^{16} T^{-0.42} e^{-64.2/RT}$
<i>decomposition reactions of short-lived intermediates</i>	
24	$4.21 \times 10^{24} T^{-3.58} e^{-12.5/RT}$
17	$1.42 \times 10^{16} T^{-1.93} e^{-11.7/RT}$
21	$1.72 \times 10^{15} T^{-1.18} e^{-3.8/RT}$
27	$9.61 \times 10^{22} T^{-3.08} e^{-30.0/RT}$
28	$3.91 \times 10^{31} T^{-6.24} e^{-37.0/RT}$
29	$4.45 \times 10^{25} T^{-4.01} e^{-24.7/RT}$
30	$6.77 \times 10^{26} T^{-4.35} e^{-22.5/RT}$
31	$7.71 \times 10^{40} T^{-8.52} e^{-14.2/RT}$
32	$7.09 \times 10^{25} T^{-3.78} e^{-7.6/RT}$
33	$3.35 \times 10^{19} T^{-1.64} e^{-69.5/RT}$
34	$5.11 \times 10^{19} T^{-1.96} e^{-69.2/RT}$

^aVRRKM calculation using VARIFLEX.²⁶ Varshni potential adjusted heat of reaction implied by Curran et al.^{4,5} group additivity estimates.

^bVRRKM calculation using VARIFLEX.²⁶

Table VII: 1 atm expressions for secondary chemistry of intermediates found in gas-phase ozonolysis of ethylene in terms of Eq. 4. Note that rate coefficients are in s^{-1} for unimolecular reactions or in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ for bimolecular reactions. These reactions are shown in Figure 9. SOZ stands for secondary ozonide (see Figure 9 for the chemical structure). All rate coefficients have been calculated with CHIMERA unless noted otherwise. Activation energies are in kcal/mol.

Reaction	k_{1atm}
<i>bimolecular reactions of CH₂OO:</i>	
<i>addition to CH₂O</i>	
SOZ \rightarrow CH ₂ OO + H ₂ C=O	$3.72 \times 10^{52} T^{-11.6} e^{-53.2/RT}$
SOZ \rightarrow SOZ-diradical	$2.50 \times 10^{32} T^{-6.32} e^{-23.8/RT}$
SOZ-diradical \rightarrow HOCH ₂ OC(=O)H	$8.57 \times 10^{13} T^{-1.03} e^{-3.9/RT}$
HOCH ₂ OC(=O)H \rightarrow HC(=O)OH + H ₂ C=O	$3.32 \times 10^{29} T^{-5.54} e^{-20.8/RT}$
<i>addition to H₂O</i>	
HOOCH ₂ OH \rightarrow CH ₂ OO + H ₂ O	$1.17 \times 10^{23} T^{-3.27} e^{-45.8/RT}$
HOOCH ₂ OH \rightarrow \cdot OH + \cdot OCH ₂ OH ^a	$1.37 \times 10^{73} T^{-18.5} e^{-52.3/RT}$

^aVRRKM rate expression calculated with VARIFLEX. Varshni parameters for potential are $D_e = 14772 \text{ cm}^{-1}$, $\beta = 0.662 \text{ \AA}^{-2}$, and $R_e = 1.413 \text{ \AA}$.

Table VIII: 10 atm expressions for secondary chemistry of intermediates found in gas-phase ozonolysis of ethylene in terms of Eq. 4. Note that rate coefficients are in s^{-1} for unimolecular reactions or in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ for bimolecular reactions. These reactions are shown in Figure 9. SOZ stands for secondary ozonide (see Figure 9 for the chemical structure). All rate coefficients have been calculated with CHIMERA unless noted otherwise. Activation energies are in kcal/mol.

Reaction	k_{10atm}
<i>bimolecular reactions of CH₂OO:</i>	
<i>addition to CH₂O</i>	
SOZ \rightarrow CH ₂ OO + CH ₂ O	$4.30 \times 10^{47} T^{-9.88} e^{-52.4/RT}$
SOZ \rightarrow SOZ-diradical	$1.98 \times 10^{30} T^{-5.43} e^{-24.0/RT}$
SOZ-diradical \rightarrow HOCH ₂ OC(=O)H	$2.52 \times 10^{14} T^{-0.89} e^{-4.5/RT}$
HOCH ₂ OC(=O)H \rightarrow HC(=O)OH + CH ₂ =O	$1.73 \times 10^{27} T^{-4.61} e^{-20.8/RT}$
<i>addition to H₂O</i>	
HOOCH ₂ OH \rightarrow CH ₂ OO + H ₂ O	$4.27 \times 10^{16} T^{-1.24} e^{-43.8/RT}$
HOOCH ₂ OH \rightarrow \cdot OH + \cdot OCH ₂ OH ^a	$1.67 \times 10^{73} T^{-18.2} e^{-53.7/RT}$

^aVRRKM rate expression calculated with VARIFLEX. Varshni parameters for potential are $D_e = 14772 \text{ cm}^{-1}$, $\beta = 0.662 \text{ \AA}^{-2}$, and $R_e = 1.413 \text{ \AA}$.

Table IX: 40 atm expressions for secondary chemistry of intermediates found in gas-phase ozonolysis of ethylene in terms of Eq. 4. Note that rate coefficients are in s^{-1} for unimolecular reactions or in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ for bimolecular reactions. These reactions are shown in Figure 9. SOZ stands for secondary ozonide (see Figure 9 for the chemical structure). All rate coefficients have been calculated with CHIMERA unless noted otherwise. Activation energies are in kcal/mol.

Reaction	k_{40atm}
<i>bimolecular reactions of CH₂OO:</i>	
<i>addition to CH₂O</i>	
SOZ → CH ₂ OO + CH ₂ O	$3.70 \times 10^{43} T^{-8.51} e^{-51.5/RT}$
SOZ → SOZ-diradical	$3.72 \times 10^{27} T^{-4.48} e^{-23.5/RT}$
SOZ-diradical → HOCH ₂ OC(=O)H	$1.05 \times 10^{15} T^{-0.96} e^{-5.0/RT}$
HOCH ₂ OC(=O)H → HC(=O)OH + CH ₂ =O	$2.67 \times 10^{24} T^{-3.64} e^{-20.3/RT}$
<i>addition to H₂O</i>	
HOOCH ₂ OH → CH ₂ OO + H ₂ O	$1.15 \times 10^{14} T^{-0.44} e^{-43.0/RT}$
HOOCH ₂ OH → ·OH + ·OCH ₂ OH ^a	$1.01 \times 10^{72} T^{-17.6} e^{-54.2/RT}$

^aVRRKM rate expression calculated with VARIFLEX. Varshni parameters for potential are $D_e = 14772 \text{ cm}^{-1}$, $\beta = 0.662 \text{ \AA}^{-2}$, and $R_e = 1.413 \text{ \AA}$.