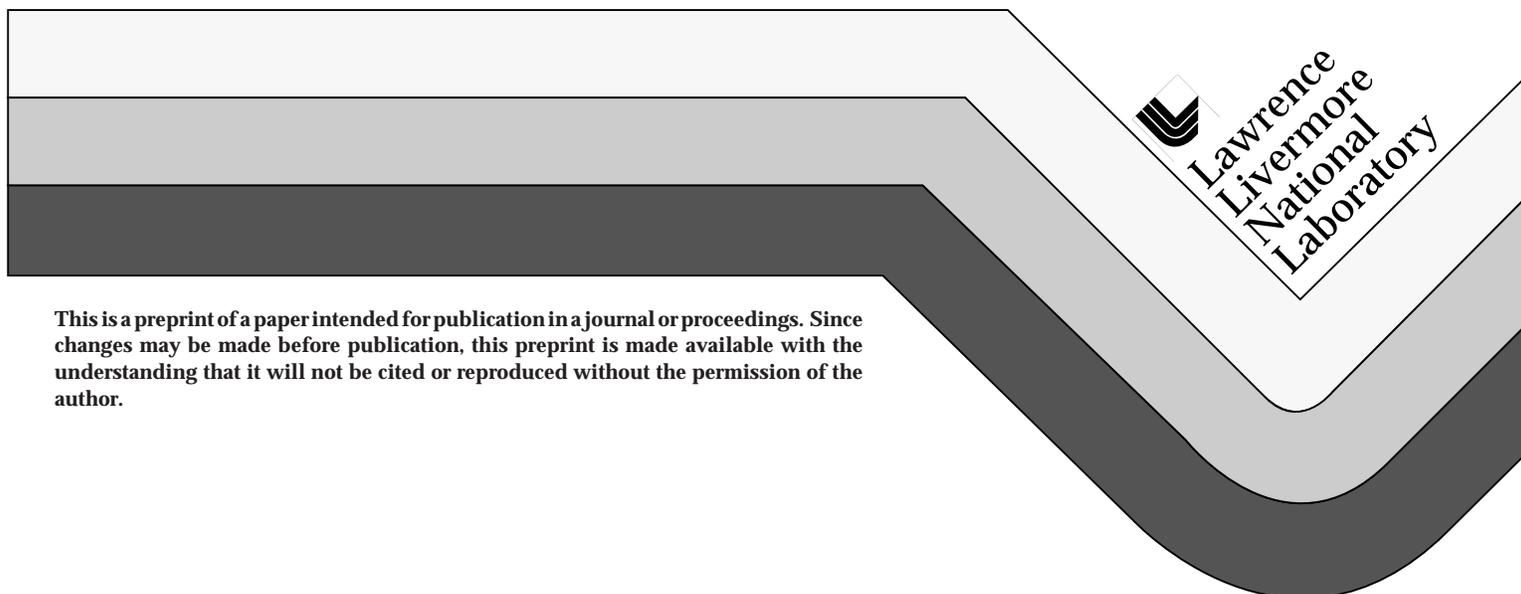


# Pathway and Kinetic Analysis on the Iso-Propyl Radical + O<sub>2</sub> Reaction System

J.W. Bozzelli  
W.J. Pitz

This paper was prepared for submittal to the  
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Pathway and Kinetic Analysis on the Iso-Propyl Radical + C  
System

Joseph W. Bozzelli  
Chemistry and Chemical Engineering Department  
New Jersey Institute of Technology  
Newark, NJ 07102

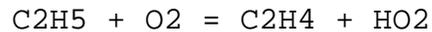
William J. Pitz  
Lawrence Livermore National Laboratories  
Livermore, CA 94551

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Recent work by Ignatyev et al. [1] using density functional theory suggested a fourth transition state (TST4), where direct production of  $\text{C}_2\text{H}_4 + \text{HO}_2$  can result via concerted elimination of  $\text{HO}_2$  from  $\text{C}_2\text{COOH}^\ddagger$ . This postulated reaction path does not proceed through the hydroperoxy-ethyl radical ( $\text{C}_2\text{COOH}$ ) intermediate. The existence of the cyclic transition state was first hypothesized by McAdam and Walker [2]. They reported that Mechanism (I) could not explain the observed pressure dependence of



at 298 K and the observed decrease in rate constant with increasing temperature from 653-773 K. They suggested the existence of a long-lived cyclic transition state and a concerted elimination of ethylene were consistent with these experimental observations. In subsequent work, Gulati and Walker [3] postulated the existence of an analogous, long-lived, cyclic transition state in the  $i\text{-C}_3\text{H}_7 + \text{O}_2$  system as well. However, Wagner [4], Bozzelli and Walker [5], Kaiser [6], Koert et al. [7] have shown that Mechanism I can explain the observed temperature and pressure dependencies.

The iso-propyl +  $\text{O}_2$  system is addressed in the present work. In this study, we analyze the propyl +  $\text{O}_2$  reaction system using thermochemical kinetics, Transition State Theory (TST), molecular thermodynamic properties, quantum Kassel analysis (quantum RRK) for  $k(E)$  and modified strong collision analysis for fall off. Cyclic transition states for hydrogen transfer and the  $\text{HO}_2$  concerted elimination from isopropylperoxy ( $\text{C}_3\text{H}_7\text{OO}^\ddagger$ ) are calculated using semi-empirical (MOPAC PM3) calculations [8] in addition to transition states for  $\text{HO}_2$  elimination and epoxide formation from hydroperoxy-isopropyl ( $\text{C}_3\text{H}_7\text{OOH}$ ). Computed rate constants for isopropyl +  $\text{O}_2$  are compared to the values of Gulati and Walker who measured the rate constants at 50 torr and over a temperature range of 653 to 773 K.

## APPROACH

Thermodynamic properties listed in Table 1 for the relevant reactants and stable parents were obtained by group additivity using THERM [9] with

updated H/C/O groups and bond dissociation groups [10]. Ab initio calculations (MP4/631G\*\*) and isodesmic reaction analysis were performed for selected peroxides [11]. Additional calculations show hydroperoxy radicals  $\text{C}_2\text{COOH}$  have C-H bond energy similar to that of a normal primary alkyl radical [12], in contrast to values reported by Ignatyev et al. which are 8 kcal/mole higher. The thermochemical data allow accurate calculation of reverse reaction rate constants by microscopic reversibility.

Entropies and heat capacities for relevant transition states are calculated using semi-empirical molecular orbital calculations (MOPAC-PM3). The vibrational frequency of the vibration from the reaction coordinate, hindered internal rotors, optical isomer and spin degeneracy are incorporated into the calculation of entropies and heat capacities. The transition state (TS) geometries calculated using the PM3 method are identified by the existence of only one imaginary frequency in the normal mode coordinate analysis.

The overall transition state for  $\text{HO}_2$  molecular elimination from the propyl peroxy radical is like the products ethylene (SP<sup>2</sup> like carbon-carbon double bond). The  $-\text{C}_2\text{H}_4-$  moiety is nearly planar, near SP<sup>2</sup> like structure, with the C-C distance closer to that of a carbon-carbon double bond. The  $\text{HO}_2$  group is nearly perpendicular to the plane of the  $-\text{C}_2\text{H}_4-$  and the C-O-H distances, to the hydrogen leaving the methyl carbon, are near 1.29 and 1.31 Å. The O=O bond is nearly that of a O=O double bond, Carbon-carbon and oxygen-oxygen bonds both shorten; O-C, O-H and C-O bonds become longer.

The transition state for H shift from isopropyl peroxy radical is non-planar, the carbon-hydrogen and O-O bonds become longer, the C-O and C-O bonds remain near constant in length, and  $\text{C}_2\text{H}_4$  moiety is nearly planar.

The  $\text{HO}_2$  elimination TST's extended  $\text{HO}_2$  moiety, further away from the methyl carbon, leads to lower vibrational frequencies and "looser" transition state reorganization. Energies are calculated in the PM3 case to be similar to the PM3 case (in kcal/mole), but these data are not used.

High pressure limit pre-exponential factors (Arrhenius A factor for bimolecular addition and combination reactions are obtained from literature and from trends in homologous series of reactions. A-factors for unimolecular reactions are calculated using transition state theory along with PM3-determined entropies of reactants and transition states

$$A^\infty = (eh_p T/k_b) \exp(\Delta S^\ddagger)$$

where  $h_p$  is Plank's constant,  $k_b$  is the Boltzmann constant, and  $\Delta S^\ddagger$  is  $S^\circ_{298,TS} - S^\circ_{298,reactant}$ . A-factors are listed in Table 2 as a function of temperature. Activation energies are derived from the endothermic reaction ( $\Delta U_{rxn}$ ) and from analogy to similar reactions with known energetics. Activation energies were estimated in a consistent manner with reference to the literature, experiments or theoretical calculation in each case. The activation energy for the forward reaction of internal H-atom shifts include analysis of Evans-Polanyi relationships for H-abstractions plus evaluation of ring-strain energy. The resultant high pressure rate constants for each reaction pathway are given in Table 2.

Rate constants and product channels for the multi-channel reaction of iso-propyl radicals with  $O_2$  and the reaction of important adducts were estimated with multifrequency quantum Kassel Theory (QRRK) [14,15] coupled with modified strong collision analysis of Gilbert et al. [16]. A fall-off and steady-state assumption for the adduct population at low pressures. A number of modifications have been made since the initial description of QRRK and falloff were published. These are described in Reference [17].

## RESULTS AND DISCUSSION

A potential energy diagram for the iso-propyl +  $O_2$  system is given in Figure 1. The four transition states calculated from the semi-empirical molecular orbital calculations are sketched at the top of the figure.

the barrier for the H-atom shift channel of C<sub>2</sub>COO. is estimated to be lower than the barrier for HO<sub>2</sub> molecular elimination. This is in contrast to the barrier for HO<sub>2</sub> molecular elimination. This is in contrast to Ignatyev et al. [1] who calculated that the barrier for H-atom shift is ca 8 kcal/mole higher than the barrier for HO<sub>2</sub> elimination. Ignatyev et al. calculate that the H shift TST is ca 8 kcal/mole higher than the HO<sub>2</sub> elimination pathway for the ethyl + O<sub>2</sub> system, using density functional calculations, B3LYP/6-31g\* level. Consideration of the H shift barrier similar to that of HO<sub>2</sub> molecular elimination is however justified. Ignatyev et al. calculated value for the stable C<sub>2</sub>.COOH alkyl hydroperoxy radical leads to a primary C-H bond energy of 109 kcal/mole; significantly higher than a normal primary, 101.6, or a C-H bond on a carbon with a hydroxyl group (96 kcal/mole). It is reasonable that the error in the functional calculation of C<sub>2</sub>.COOH carries over to the transition state shift to the peroxy group. Here the hybridization (SP<sup>3</sup> on C's) and atomic charges remain similar in both structures. A second supporting argument is the calculated activation energy (E<sub>a</sub>) for hydrogen shift to peroxy, Morokuma and Lin - modified G2 calculation [17], is 2 to 3 kcal/mole lower than E<sub>a</sub> for the corresponding HO<sub>2</sub> elimination. The lower values of E<sub>a</sub> for the H shift are also in agreement with the E<sub>a</sub> calculated by the methyl peroxy system, after allowance for ring strain in a 4 versus 5-membered ring is considered.

The A-factor (Table 2) for the elimination channel is about a factor of 10 higher than for H-shift due to a "looser" transition state for elimination compared to H-atom shift. This difference in A-factor results in a similar pre-exponential constant for elimination versus H shift as discussed below. The A-factors for unimolecular dissociation of C<sub>2</sub>.COOH differ by a factor of 15, also shown in Table 2. The transition state to propene oxide (C<sub>3</sub>H<sub>4</sub>O) + OH is much lower in energy than the TST to propene + HO<sub>2</sub>.

The calculated (chemical activation) rate constants of iso-propyl + O<sub>2</sub> as a function of temperature and at one atmosphere are given in Fig. 2. The dominant channel for iso-propyl + O<sub>2</sub> is to isopropylperoxy radical

(stabilization). The rate constant for this channel drops off at 1 temperature due to dissociation of  $C_2COO^\ddagger$  to reactants. The QRRK calculation for  $C_2COO$ . (stabilized) shows that it principally dissociates to reactants,  $C_2C. + O_2$ . The reaction



is in equilibrium above 600 K and a small amount of the reactants (percent) goes to products. The second channel shown in Fig. 2 is  $C_2C. + O_2$  to  $C_2C. + O_2$ . This is the fraction of the  $C_2C. + O_2$  that goes to  $C_2C.$  comes back to reactants rather than to products or stabilization ( $C_2C. + O_2$  HO<sub>2</sub> elimination ( $C_3H_6-E + HO_2$ ) and H-shift ( $C_3H_6-S + HO_2$ ) are the dominant channels to products. The labeling of  $C_3H_6-E$  and  $C_3H_6-S$  is to distinguish between propene made by the elimination channel versus H-shift channel. The rate constant for the elimination channel is a factor of 3 higher than the H-shift channel, as seen in Fig. 2. The difference is primarily due to the A-factor being higher for the elimination channel due to its "looser" transition state. The next channel shown is the one leading to the hydroperoxy-isopropyl radical ( $C_2.COOH$ ). The QRRK dissociation results (not shown) indicate that this radical principally proceeds to propene. One can add the  $C_2.COOH$  and  $C_3H_6-S + HO_2$  channels to get the total contribution of the H-shift channels to propene production, when the reaction of  $C_2.COOH$  with  $O_2$  is not important. The remaining product channels are small contributions, with the highest of these being the channel to acetylene oxide ( $C_2C_2O$ ) and OH whose rate constant increases at high temperature.

Results from QRRK calculations are compared to rate constant measurements of Gulati and Walker [3]. They examined the reaction of isobutyraldehyde, oxygen and nitrogen in a closed vessel at 653-773 torr. The isopropyl formyl radical formed from isobutyraldehyde rapidly decomposes to iso-propyl + CO. The yields of propene and propane from isobutyraldehyde oxidation were used to derive the rate constant for

propyl + O<sub>2</sub> = C<sub>3</sub>H<sub>6</sub> + HO<sub>2</sub>. Gulati and Walker extrapolated their propene yields back to zero extent of reaction, so that reverse reaction of HO<sub>2</sub> radicals should not play a role in interpretation of the data. A potential concern about the effect of reaction of molecular oxygen with C<sub>2</sub>COOH in interpreting the experimental results. If this reaction is important under their experimental conditions, it would lead to lower propene yields at higher oxygen concentrations. They examined a range of oxygen concentrations from 6-20% O<sub>2</sub> and did not report a decrease in propene yield with increasing O<sub>2</sub> level.

Results from the QRRK calculations are compared to the rate constants reported by Gulati and Walker. Three different cases were considered:

- 1) Inclusion of both HO<sub>2</sub> elimination and H-shift channels.
- 2) HO<sub>2</sub> elimination only
- 3) H-shift channel only

Activation energies for HO<sub>2</sub> elimination and/or H-shift were adjusted to give the iso-propyl + O<sub>2</sub> rate constant reported by Gulati and Walker. In case 1, the activation energies for HO<sub>2</sub> elimination and H shift are both 10 kcal/mole. The rate constants obtained are listed in Table 3 (Reaction 2 and 5). The rate constants are our current best estimate for these reactions. The rate constant obtained with Gulati and Walker for this case is shown in Fig. 3. The calculated curve exhibits a slightly positive activation energy compared to the slightly negative activation energy shown by the experimental results. The QRRK calculated curve includes contributions from both the HO<sub>2</sub> elimination channel and the H-shift channel. In these comparisons, the rate constant to the C<sub>2</sub>COOH channel was added into the total rate constant for propene + HO<sub>2</sub>. This is because the QRRK dissociation calculations for C<sub>2</sub>COOH show that the main fate of this radical is to form propene + HO<sub>2</sub>.

In case 2, the activation energy for the H-shift channel (Reaction 3) was raised 8 kcal/mole (turned H-shift channel off) above the HO<sub>2</sub> elimination channel (Reaction 2). The 8 kcal/mole was chosen to agree with the difference in the H-shift and HO<sub>2</sub> elimination barrier heights found

Ignatyev et al. [1]. The activation energy for HO<sub>2</sub> elimination was to be 29.0 kcal/mole where agreement with Gulati and Walker's rate constants was obtained. The calculated curve is nearly identical to that shown in Fig. 3. The resulting rate constants are given in Table 4.

In case 3, the activation energy for the HO<sub>2</sub> elimination channel (Reaction 2) was raised 8 kcal/mole above the H-shift channel (Reaction 1) in order to investigate the case where the H-shift channel dominates. The activation energy for the H-shift channel was found to be 26.9 kcal/mole. In addition, the activation energy of C<sub>2</sub>.COOH = C<sub>3</sub>H<sub>6</sub> + HO<sub>2</sub> (Reaction 7) was lowered from 20.7 to 18.2 kcal/mole which was the lower bound of our estimate for this activation energy. If the H-shift channel dominates, the barrier from C<sub>2</sub>.COOH to C<sub>3</sub>H<sub>6</sub> + HO<sub>2</sub> affects relative rates of further reaction with O<sub>2</sub> versus dissociation. The calculated curve is nearly identical to the one shown in Fig. 3.

The rate constant measurements of Gulati and Walker can be explained by HO<sub>2</sub> elimination or H-shift channels of iso-propyl + O<sub>2</sub>. The measurements do not distinguish between the two channels. Our current best estimate is to include both channels with the rate constants given in Table 3. Experimental data on epoxide product levels will provide the data to distinguish between these two reaction pathways.

## CONCLUSIONS

The properties of four transition states important to the reaction of iso-propyl with O<sub>2</sub> have been calculated and used to derive A-factors for the relevant reaction pathways. Activation energies for these pathways have been estimated. It was found that the transition state for HO<sub>2</sub> elimination has a looser transition state than that for the internal transfer of H. This leads to a higher A-factor for HO<sub>2</sub> elimination than for H-transfer. The estimated activation energies for HO<sub>2</sub> elimination and H-transfer are now to be both 29.8 kcal/mole based on agreement with the data of Gulati

Walker. However, the experimental data did not provide any further information to distinguish whether the main reaction pathway is HO<sub>2</sub> elimination or H-atom shift. Predictions of the rate constants for channels over a wide temperature range at 1 atm are given.

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Table 1: Thermochemical Properties of Important Species

SPECIES	$\Delta H_f(298 \text{ S})$	Cp	300	400	500	600	800	1000	
	kcal/ mole	cal/ mol-K	cal/ mol-K						
OH	9.49	43.88	7.16	7.08	7.05	7.05	7.15	7.33	7.87
HO2	3.80	54.73	8.37	8.95	9.48	9.96	10.78	11.43	12.47
CH3	34.82	46.38	9.26	10.05	10.81	11.54	12.90	14.09	16.26
CC*C	4.65	63.81	15.45	19.23	22.72	25.79	30.74	34.49	40.39
CCC.	23.67	69.29	17.11	21.27	25.14	28.53	33.95	38.14	44.70
C2C.	21.02	68.94	16.38	20.30	23.95	27.54	33.36	37.43	44.16
TIPRXXOH	19.00	83.21	24.53	29.11	33.24	36.75	42.32	46.51	53.31
TIPROXOH	18.00	78.11	23.31	28.69	33.04	36.97	42.82	46.83	53.51
TIPRYQE	16.20	76.86	23.63	29.20	34.02	38.01	44.13	48.55	55.28
TIPROOXH	16.20	75.82	23.09	29.03	34.09	38.23	44.40	48.81	55.00
CC.COOH	-0.21	89.98	24.29	29.34	33.62	37.68	43.92	48.40	-
CCC.OOH	-2.66	89.36	25.93	30.83	35.06	38.77	44.49	49.06	-
CCCOO	-10.46	85.76	23.74	28.83	33.17	36.98	42.95	47.88	-
CCCOO.	-10.46	85.76	23.74	28.83	33.17	36.98	42.95	47.88	-
C.CCOOH	2.44	88.95	25.02	30.31	34.81	38.67	44.51	49.11	-
C2COO.	-13.83	83.01	24.24	29.51	34.12	37.72	43.60	48.38	-
C2C.OOH	-8.43	88.77	26.51	31.04	35.22	38.60	44.19	48.73	-
C2.COOH	-0.93	88.96	25.52	30.99	35.76	39.41	45.16	49.61	-
CCOOC.	3.94	88.70	25.79	31.24	35.77	39.60	45.79	50.72	-
C.COOC	6.54	90.20	24.40	29.79	34.39	38.29	44.64	49.73	-
CC.OOC	3.44	87.72	25.31	30.31	34.64	38.39	44.62	49.68	-
C.COHC	-0.93	87.59	25.52	30.99	35.76	39.41	45.16	49.61	-
CC.OOHC	-8.43	88.77	26.51	31.04	35.22	38.60	44.19	48.73	-
CCYC2O	-21.87	66.79	17.30	22.37	27.10	30.64	36.29	40.30	-
CYCCCO	-19.24	66.25	14.80	20.07	24.91	28.99	35.24	39.70	-
C2C*O	-51.56	70.09	17.97	22.00	25.89	29.34	34.93	39.15	-

Notes: Dot denotes radical site on atom to left.

Carbon atoms are fully saturated with H-atoms.

\* = double bond

T = transition state

IPR = isopropyl

E = elimination

Y = cyclic

X = represents the elimination of the species after x

Table 2:  
A-factors for Various Key Reactions  
Calculated from Transition State Theory

Temperature (K)	A-factors			
	C2COO. $\Rightarrow$ C3H6 + HO2	C2COO. $\Rightarrow$ C2.COOH	C2.COOH $\Rightarrow$ C3H6 + HO2	C2.COOH $\Rightarrow$ CcyC2O + OH
300	7.68E+11	4.54E+11	9.34E+11	7.15E+10
400	9.56E+11	5.35E+11	1.01E+12	6.84E+10
500	1.19E+12	6.60E+11	9.94E+11	6.51E+10
600	1.47E+12	8.17E+11	9.55E+11	6.21E+10
800	2.13E+12	1.20E+12	8.75E+11	5.72E+10
1000	2.86E+12	1.60E+12	8.24E+11	5.34E+10
1200	3.61E+12	1.97E+12	7.96E+11	5.05E+10
1500	4.70E+12	2.43E+12	7.75E+11	4.71E+10
2000	6.65E+12	2.98E+12	7.99E+11	4.40E+10

Table 3:  
High-Pressure Rate Constants Used for QRRK Calculation of  
Isopropyl + O2  $\Rightarrow$  Products  
(Used as input for chemical activation and unimolecular dissoci  
calculations)

$$k = AT^n \exp(-E_a/RT) \quad (\text{mole-cm-kcal-sec units})$$

	Reaction	A	n	Ea
1	C2C. + O2 $\Rightarrow$ C2COO.	9.11E+12	0	0.00
- 1	C2COO. $\Rightarrow$ C2C. + O2	7.78E+14	0	32.14
2	C2COO. $\Rightarrow$ C3H6 + HO2	5.47E+08	1.208	29.81
3	C2COO. $\Rightarrow$ CCO.C + O	1.09E+15	0	58.90
4	C2COO. $\Rightarrow$ C2C*O + OH	1.22E+10	1	43.93
5	C2COO. $\Rightarrow$ C2.COOH	5.06E+08	1.14	29.85
- 5	C2.COOH $\Rightarrow$ C2COO.	2.56E+09	0.4436	17.33
7	C2.COOH $\Rightarrow$ C3H6 + HO2	1.01E+13	-0.1872	20.71
8	C2.COOH $\Rightarrow$ CcyC2O + OH	1.31E+12	-0.2781	19.72
9	C2.COOH $\Rightarrow$ C*COOH + CH3	3.89E+13	0	36.30

Notes: Dot denotes radical site on atom to left. Carbon atoms are saturated with H-atoms.

\* = double bond

cy = cyclic structure containing the atoms that follow

Table 4:  
High-Pressure Rate Constants Used for Cases 1 through 3

$$k = AT^n \exp(-Ea/RT) \quad (\text{mole-cm-kcal-sec units})$$

Case		Reaction	A	n	Ea
1	2	C2COO. => C3H6 + HO2	5.47E+08	1.208	29.81
	5	C2COO. => C2.COOH	5.06E+08	1.14	29.85
	- 5	C2.COOH => C2COO.	2.56E+09	0.4436	17.33
	7	C2.COOH => C3H6 + HO2	1.01E+13	-0.1872	20.71
2	2	C2COO. => C3H6 + HO2	5.47E+08	1.208	29.00
	5	C2COO. => C2.COOH	5.06E+08	1.14	37.00
	- 5	C2.COOH => C2COO.	2.56E+09	0.4436	25.33
	7	C2.COOH => C3H6 + HO2	1.01E+13	-0.1872	20.71
3	2	C2COO. => C3H6 + HO2	5.47E+08	1.208	34.89
	5	C2COO. => C2.COOH	5.06E+08	1.14	26.89
	- 5	C2.COOH => C2COO.	2.56E+09	0.4436	14.37
	7	C2.COOH => C3H6 + HO2	1.01E+13	-0.1872	18.21

Notes: Dot denotes radical site on atom to left. Carbon atoms are saturated with H-atoms.

\* = double bond

cy = cyclic structure containing the atoms that follow

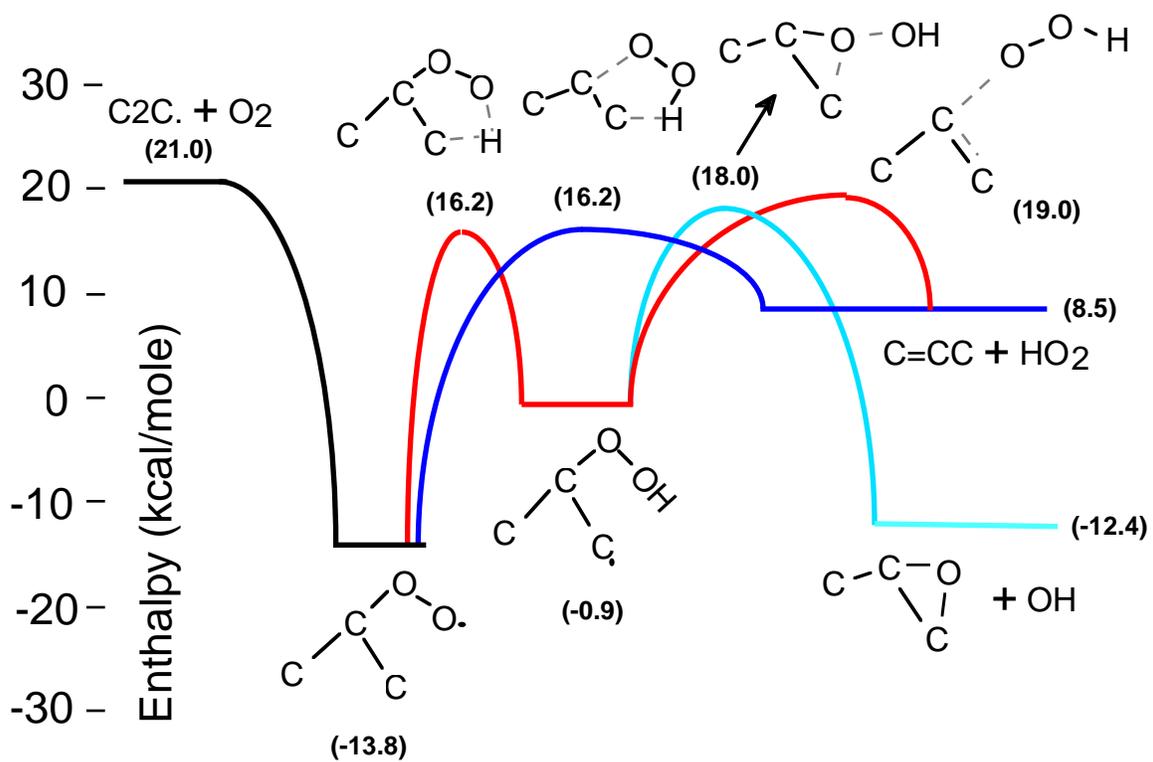


Fig. 1 Potential energy diagram of isopropyl + O<sub>2</sub> => products.

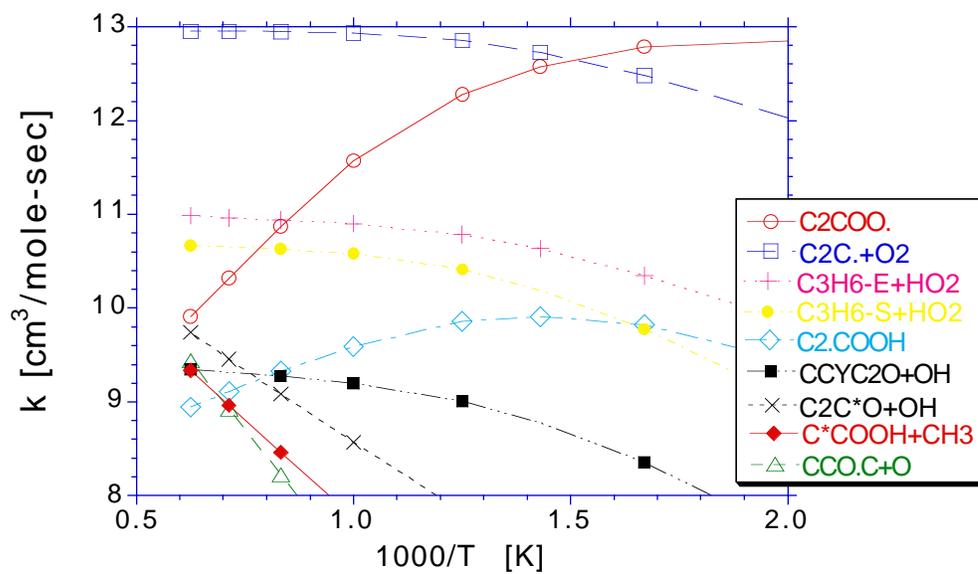


Fig. 2 Results of QRRK calculation of isopropyl + O<sub>2</sub> => products f pressure of 1 atm. C<sub>3</sub>H<sub>6</sub>-E denotes propene via the molecular elimi channel and C<sub>3</sub>H<sub>6</sub>-S denotes propene formed via the H-atom shift cha

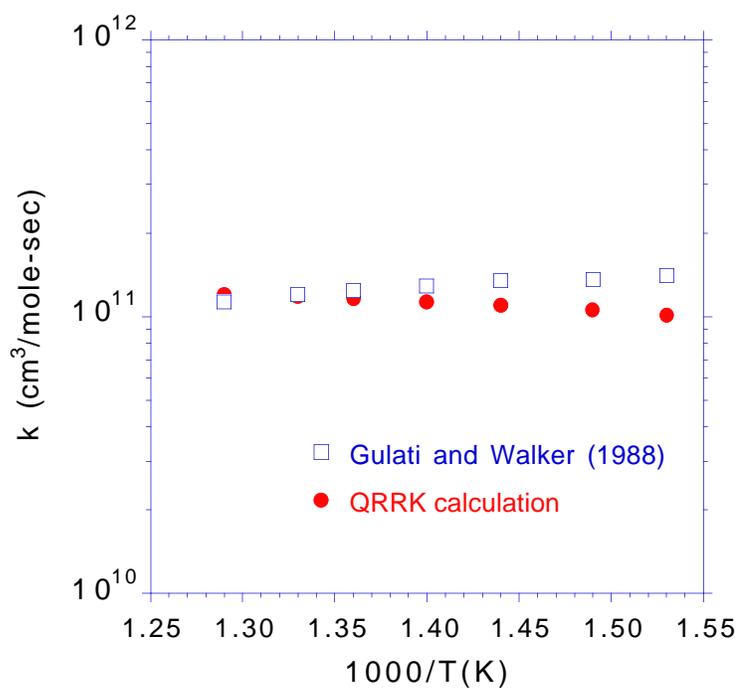


Fig. 3 Rate constant of isopropyl + O<sub>2</sub> => propene + H<sub>2</sub>O<sub>2</sub> calculated analysis and measured by Gulati and Walker [3]. The calculated rate constants include the contributions from internal H-atom transfer elimination. The product C<sub>2</sub>COOH was assumed to react to propene + which is its main fate.

*Technical Information Department • Lawrence Livermore National Laboratory*  
*University of California • Livermore, California 94551*

