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Analysis of Tertiary Butyl Radical + O_2, Isobutene + HO_2, Isobutene + OH, and Isobutene−OH Adducts + O_2: A Detailed Tertiary Butyl Oxidation Mechanism

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The reaction systems *tert*-butyl radical + O_2, isobutene + HO_2, isobutene + OH, and isobutene−OH adducts + O_2, which are important to understanding the oxidation chemistry of tertiary butyl radical ($C_3C^•$), are analyzed. Thermochemical parameters are determined by ab initio−Mϕller−Plesset (MP2(full)/6-31g(d)), complete basis set model chemistry (CBS-4 and CBS-q with MP2(full)/6-31g(d) and B3LYP/6-31g(d) optimized geometries), density functional (B3LYP/6-31g(d)), semiempirical MOPAC (PM3) molecular orbital calculations, and by group additivity estimation. Thermochemical kinetic parameters are developed for each elementary reaction path in these complex systems, and a chemical activation kinetic analysis using quantum Rice−Ramsperger−Kassel (QRRK) theory for $k(E)$ and master equation analysis for falloff is used to calculate rate constants as a function of pressure and temperature. An elementary reaction mechanism is constructed to model experimental data for oxidation of *tert*-butyl radical. Calculations for loss of *tert*-butyl precursor, 2,2,3,3-tetramethylbutane (C_3CCC_3), and production of isobutene and 2,2-dimethyloxirane from the mechanism are compared with experimental data reported in the literature. Reaction of *tert*-butyl radical ($C_3C^•$) with O_2 forms an energized *tert*-butyl peroxy adduct $C_3COO^{•}*$ which can dissociate back to reactants, dissociate to isobutene + HO_2, or isomerize to *tert*-butyl hydroperoxide ($C_3{}^•COOH$). This isomer can dissociate to either isobutene + HO_2 or 2,2-dimethyloxirane + OH, before it is stabilized. In the *tert*-butyl radical + O_2 reaction system, dissociation of the $[C_3COO^•]*$ adduct to isobutene + HO_2 via HO_2 molecular elimination is faster than the hydrogen shift to $C_3{}^•COOH$ by a factor of 86:1 at 773 K and 60 Torr. The reaction barrier (reaction enthalpy difference between TS4 and $C_3{}^•COOH$) for the $C_3{}^•COOH$ reaction to 2,2-dimethyloxirane + OH is calculated as 17.98 (19.06) kcal/mol at the CBS-q//MP2(full)/6-31g(d) level but is evaluated as 15.58 (18.06) kcal/mol by fitting experimental data. Data in parentheses are thermodynamic properties based on CBS-q//B3LYP/6-31g(d) calculation. Barriers for reactions of HO_2 + isobutene → $C_3{}^•COOH$ (HO_2 addition at CD/C2 carbon atom of isobutene, CD = carbon double bond) and HO_2 + isobutene → $C_2C^•COOH$ (HO_2 addition at CD/H2 carbon atom of isobutene) are respectively determined as 7.74 (7.38) and 10.69 (10.82) kcal/mol. 2,2-Dimethyloxirane is formed primarily by HO_2 addition to isobutene. OH addition to isobutene results in adducts which further react with O_2 to form acetone, formaldehyde, and the OH radical (Waddington mechanism) with these pathways also analyzed.

Introduction

Initial products from pyrolysis, oxidation, or photochemical reactions of saturated and unsaturated hydrocarbons are the corresponding radicals. Important reactions of these alkyl radicals in combustion and in atmospheric photochemistry are combination with molecular oxygen to form peroxy adducts which can undergo further reaction in energized (chemical activation) and stabilized states. These reactions are complex and difficult to study experimentally and present a source of controversy with regard to both pathway and reaction rates. While these reactions comprise the principal reaction paths of the hydrocarbon radical conversion in most hydrocarbon oxidation, combustion, and atmospheric photochemistry, they are relatively slow in the combustion environment and often a bottleneck to overall hydrocarbon conversion.

The C_2H_5 + O_2 reaction serves as an important reference in this study, as it has been studied the most extensively. It has been experimentally studied by Gutman et al.,[1,2] Kaiser et al.,[3] and Pilling et al.[4] Kinetics of the ethyl system has been analyzed by Bozzelli and Dean[5] using quantum RRK theory and by Wagner et al.[6] using variational RRKM theory for ethylene production and ethyl radical loss at pressures and temperatures relevant to the experimental data of Gutman's group.[1,2] These analyses postulate the formation of a chemically activated peroxy radical adduct. This energized adduct can be stabilized to $CCOO^•$, undergo unimolecular elimination to ethylene + HO_2, or isomerize through a cyclic five-member ring intermediate to a primary hydroperoxy alkyl radical (H shift). This hydroperoxy alkyl isomer can then react to C_2H_4 + HO_2 or to cyclic epoxide + OH. The H shift/HO_2 molecular elimination reaction in the ethyl system is analyzed by Bozzelli and Dean to be a bottleneck to ethyl conversion; a result of the low Arrhenius *A* factor (tight transition state) and a barrier similar to the reaction reforming the C_2H_5 + O_2, which has a higher *A* factor. The activation energy for the $C^•COOH$ reaction to C_2H_4 + HO_2 was evaluated as ΔH_{rxn} + 8 kcal/mol. This is, however, in disagreement with the value of ΔH_{rxn} + 17 kcal/mol, reported by Baldwin et al.,[7] and the range 12.7−14.1 kcal/mol reported by Gulati et al.[8] based on data from oxirane formation in larger molecules. Schaefer et al.[9] have recently reported a density

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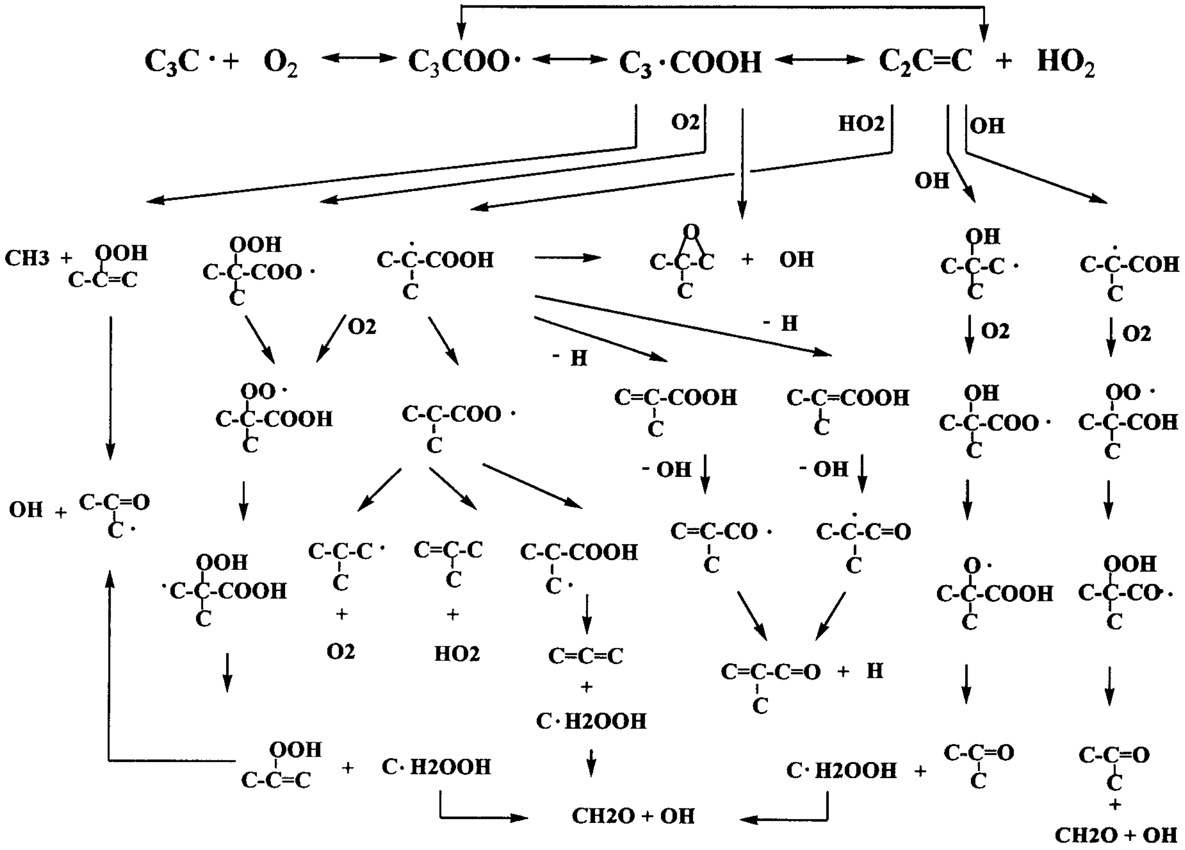


Figure 1. Important reaction pathways for *tert*-butyl radical oxidation.

functional (TZ2Pf UB3LYP) calculation value of 12.7 kcal/mol for reverse reaction ($C_2H_4 + HO_2 \rightarrow C^{\bullet}COOH$) barrier, and they reported barriers of 27.1 kcal/mol for the direct HO_2 molecular elimination from the ethyl peroxy radical ($CCOO^{\bullet}$) to $C_2H_4 + HO_2$. They also report an activation energy of 37.0 kcal/mol to reach the five-member ring intramolecular H shift transition state from $CCOO^{\bullet}$ to ethyl hydroperoxy radical ($C^{\bullet}COOH$). Jungkamp et al.[10] studied reactions in the atmospheric oxidation of *n*-butane and calculated reaction activation energies at various levels of theory. They report 0 K activation energies for intramolecular H-shift reactions of 2-butylperoxy radical abstracting primary and 1-butylperoxy radical abstracting secondary hydrogen atoms by a peroxy group through a six-member ring transition state as 24.3 and 20.3 kcal/mol, respectively, at CBS-q//B3LYP/6-31g(d,p) level of theory.

Few experimental studies on the *tert*-butyl radical reaction with O_2 have been reported. The research group of Atri and Baldwin[11,12] studied the thermal decomposition of 2,2,3,3-tetramethylbutane in the presence of oxygen at temperatures from 673 to 815 K and pressures from 50 to 600 Torr, in flow reactors (both KCl and boric acid coated vessels), at slow flow, up to several minute reaction times. They report rate constants for C_3C-CC_3 bond cleavage and for HO_2 abstraction of hydrogen from the primary C−H bonds on the 2,2,3,3-tetramethylbutane. They also report concentration profiles for selected *tert*-butyl radical reaction products as well as 2,2,3,3-tetramethylbutane loss versus reaction time. Atri and Baldwin[11,12] formulate a mechanism for kinetic evaluation using steady-state approximations on the *tert*-butyl radical + O_2 reaction system. The model includes peroxy formation, reverse dissociation, isomerization (hydrogen atom transfer, nonreversible), and isomer decomposition to form a cyclic ether + OH from the alkyl hydroperoxide radical (isomer) plus abstraction reactions of HO_2 and OH radicals. Their interpretation of experimental data shows that *tert*-butyl radicals are major products formed from the reaction of 2,2,3,3-tetramethylbutane decomposition and ~1% of *tert*-butyl radicals further react with O_2 to cyclic ether + OH for their reaction times.

Evans et al.[13] studied the rate constants for the reaction of *tert*-butyl radicals formed from the decomposition of 2,2,3,3-tetramethylbutane in the presence of H_2 and O_2 in KCl-coated reaction vessels. They measured the relative yields of isobutene and isobutane in the early stages of reaction over the temperature range 713−813 K and analyzed the data using steady state and equilibrium relationships. They report rate constants of the reactions $C_3C^{\bullet} + O_2 \Leftrightarrow$ isobutene + HO_2 and $C_3C^{\bullet} + H_2 \Leftrightarrow$ isobutane + H, and make comparisons with rate constants for analogous reactions.

Lenhardt et al.[14] have studied rate constants for reactions of normal, secondary, tertiary, and 3-hydroxy *s*-butyl radicals with O_2 at 300 K and low pressure, 1−4 Torr. Butyl radicals were generated by flash photolysis of butyl iodides using a xenon flash lamp. The initial concentration of butyl radicals was low (below 10^{11} radicals cm^{-3}) to reduce the importance of radical−radical combination. They monitored the pseudo-first-order decay of the butyl radicals as a function of oxygen using mass spectrometry. Their experimental results show no measurable pressure dependence for rate constants of butyl radical + O_2 recombination over the small pressure range of 1−4 Torr. They used adiabatic channel model calculations to interpret their results and report the high-pressure limit rate constant for combination of *tert*-butyl + O_2 as $k = 1.41 \times 10^{13}$ cm^3 mol^{-1} s^{-1}.

Slagle et al.[15] studied the gas-phase equilibrium reaction of *tert*-butyl radical with molecular oxygen to form the peroxy radical over temperature range from 550 to 580 K and pressures

TABLE 1: Total Energies (*E*, Hartree), Zero-Point Energies (ZPE, Hartree, unscaled), and Thermal Corrections to Enthalpies ($H_{thermal}$, kcal/mol)

	geometry[a]	total energy 0 K (hartree)	CBS4 energy 0 K (hartree)	CBS-q energy 0 K (hartree)	ZPVE[b] (hartree)	thermal corr[c] (kcal/mol)
O_2	B3LYP	−150.3200379	−150.1712192	−150.1894687	0.0037790	2.08
	MP2	−149.9543197	−150.1698796	−150.1886165	0.0032180	2.08
HO_2	B3LYP	−150.8991541	−150.7471229	−150.7692372	0.0140230	2.38
	MP2	−150.5023650	−150.7472364	−150.7691685	0.0143970	2.38
$C_3C^•$	B3LYP	−157.7983253	−157.4847320	−157.5152719	0.1172620	4.60
	MP2	−157.1957939	−157.4840491	−157.5143749	0.1208430	4.42
$C_3COO^•$	B3LYP	−308.1729037	−307.7123770	−307.7647070	0.1278390	5.32
	MP2	−307.2013203	−307.7124269	−307.7640157	0.1313710	5.13
$C_3{}^•CQ$	B3LYP	−308.1277093	−307.6813989	−307.7295115	0.1243930	5.85
	MP2	−307.1674984	−307.6804133	−307.7279854	0.1284340	5.69
$C_2C{=}C$	B3LYP	−157.2272862	−156.9257269	−156.9561072	0.1084940	3.92
	MP2	−156.6463970	−156.9258866	−156.9561746	0.1106620	3.90
TS1	B3LYP	−308.1235557	−307.6641159	−307.7186974	0.1215310	5.33
	MP2	−307.1436192	−307.6661269	−307.7193443	0.1252530	5.12
TS2	B3LYP	−308.1044353	−307.6542136	−307.7043273	0.1213150	4.92
	MP2	−307.1288762	−307.6517572	−307.7017197	0.1260070	4.71
TS3	B3LYP	−308.1107498	−307.6536277	−307.7126306	0.1237190	5.70
	MP2	−307.1231334	−307.6534212	−307.7117598	0.1277380	5.50
TS4	B3LYP	−308.1121421	−307.6392894	−307.7058520	0.1228820	5.62
	MP2	−307.1188941	−307.6460046	−307.7071357	0.1268270	5.33
$C_2C^•COOH$	B3LYP	−308.1343836	−307.6822240	−307.7298523	0.1256230	5.97
	MP2	−307.1666503	−307.6819361	−307.7294981	0.1286010	5.90
$C_2CCOO^•$	B3LYP	−308.1632657	−307.6984653	−307.7503242	0.129112	5.24
	MP2	−307.1881332	−307.6979195	−307.7490726	0.1324170	5.16
$C_2{}^•CCOOH$	B3LYP	−308.1200886	−307.6729020	−307.7199649	0.125108	5.95
	MP2	−307.1576780	−307.6725188	−307.7195564	0.1278980	5.86
TS5	B3LYP	−308.1137740	−307.6483930	−307.7073561	0.124175	5.83
	MP2	−307.1220775	−307.6494883	−307.7073123	0.1281360	5.66
TS6	B3LYP	−308.1164419	−307.6360605	−307.7035120	0.123276	6.0
	MP2	−307.1158846	−307.6455639	−307.7064356	0.1273560	6.65
TS7	B3LYP	−308.1066583	−307.6514605	−307.7027579	0.122524	4.98
	MP2	−307.1262664	−307.6473950	−307.6994882	0.1271550	4.77
TS8	B3LYP	−308.1145911	−307.6608680	−307.7111833	0.122972	4.68
	MP2	−307.1360371	−307.6590087	−307.7108057	0.1270320	4.51
TS9	B3LYP	−308.1097740	−307.6443304	−307.7021652	0.121833	5.29
	MP2	−307.1310841	−307.6468554	−307.6988988	0.1271380	5.05
TS12	B3LYP	−308.0809123	−307.6204060	−307.6782392	0.123323	5.55
	MP2	−307.0955402	−307.6208411	−307.6774771	0.1265470	5.46
TS13	MP2	−157.126503	−157.4189205	−157.4551846	0.1133000	4.30

[a] Using 6-31g* basis set. [b] Unscaled zero-point vibrational energies in hartree. In the calculation of reaction enthalpies, ZPVE is scaled by 0.9661 and 0.9806 for MP2(full)/6-31g(d) and B3LYP/6-31g(d) levels, respectively. [c] Thermal corrections in kcal/mol. Thermal corrections are calculated as follows for $T = 298.15$ K: $H°_T - H°_0 = H_{trans}(T) + H_{rot}(T) + \Delta H_{vib}(T) + RT$; $H_{trans}(T) = (^3/_2)RT$, $H_{rot}(T) = (^3/_2)RT$, $\Delta H_{vib}(T) = N_A h \sum \upsilon_i/(\exp(h\upsilon_i/kT) - 1)$, where N_A is the Avogadro constant, *h* is the Plant constant, *k* is the Boltzman constant, and υ_i are vibrational frequencies.

from 1 to 5 Torr. They monitored the reaction of *tert*-butyl radical + O_2 to equilibrium using photoionization mass spectrometry and reported the enthalpy change for $C_3C^• + O_2 \Leftrightarrow C_3COO^•$ equilibrium reaction by using a third law procedure combining the measured equilibrium constants with calculated or estimated entropy change for the reaction.

In this study, we perform a thermochemical analysis on the reaction of *tert*-butyl radical with O_2, in addition to analysis on a subset of reactions that relate to stable product formation from *tert*-butyl + O_2 reaction.

The reaction systems analyzed includes

$$\textit{tert}\text{-butyl radical} + O_2 \rightarrow \text{products}$$

$$\text{isobutene} + HO_2 \rightarrow \text{products}$$

$$\text{isobutene} + OH \rightarrow \text{products}$$

$$\text{isobutene}{-}OH + O_2 \rightarrow \text{products}$$

Reaction path analysis, reaction barrier, pre-exponential factor, and thermochemical properties of each elementary reaction step are evaluated for reactions of *tert*-butyl radical in an oxidizing atmosphere under moderate to low-temperature combustion conditions. Important reaction pathways are shown in Figure 1. We utilize a chemical activation kinetics treatment incorporating quantum Rice−Ramsperger−Kassel (QRRK) theory for *k*(*E*) and master equation analysis[16a−c] as discussed by Gilbert and Gilbert's UNIMOL manual for falloff of the energized adduct. A similar multichannel unimolecular quantum RRK and master equation falloff analysis are used for dissociation of the stabilized adducts. An elementary reaction mechanism is developed and used to model data of the Baldwin and Walker research group where tertiary butyl radical comes from the unimolecular decomposition of the 2,2,3,3-tetramethylbutane in the presence of O_2. Calculations for loss of *tert*-butyl precursor, 2,2,3,3-tetramethylbutane, and production of isobutene and 2,2-dimethyloxirane show good agreement with experimental data of Atri et al.[11] Data on $C_3C^• \rightarrow C_2C{=}C + H$ are in good agreement with data of Knyazev et al.[17] Calculated rate constants for channels of chemical activation reaction systems are reported for pressures of 0.076, 0.76, 7.6, 60, 760, and 7600 Torr.

Method

Thermodynamic Properties. Geometry optimizations and frequency calculations for reactants, intermediates, and transition states in the *tert*-butyl radical + O_2 and isobutene + HO_2 reaction systems are performed using ab initio−Mϕller−Plesset

TABLE 2: Reaction Enthalpies[a]

	//MP2(full)/6-31g(d)		//B3LYP/6-31g(d)	
	CBS-4	CBS-q	CBS-4	CBS-q
$C_3^{\bullet}COOH + CCOOH \Leftrightarrow C_3COOH + C^{\bullet}COOH$	−1.06	−1.10	−0.68	−0.52
$C_2^{\bullet}CCOOH + CCOOH \Leftrightarrow C_2CCOOH + C^{\bullet}COOH$	0.27	0.27	0.28	0.23
$C_2C^{\bullet}COOH + CCOOH \Leftrightarrow C_2CCOOH + C^{\bullet}COOH$	6.16	6.46	6.13	6.41
$C_2CCOO^{\bullet} + COOH \Leftrightarrow C_2CCOOH + COO^{\bullet}$	0.44	0.43	0.64	0.70
$C_2C{=}C + HO_2 \Leftrightarrow$ TS1	2.90	2.59	3.86	3.20
$C_3^{\bullet}COOH \Leftrightarrow$ TS2	15.88	15.49	15.20	14.88
$C_2C{=}C + HO_2 \Leftrightarrow$ TS3	6.30	7.74	5.42	7.38
$C_2C{=}C + HO_2 \Leftrightarrow$ TS4	8.15	10.47	8.49	11.55
$C_2C{=}C + HO_2 \Leftrightarrow$ TS5	9.11	10.69	8.89	10.82
$C_2C{=}C + HO_2 \Leftrightarrow$ TS6	9.11	11.23	10.31	13.40
$C_2C^{\bullet}COOH \Leftrightarrow$ TS7	19.42	17.68	17.13	16.01
$C_2^{\bullet}CCOOH \Leftrightarrow$ TS8	6.18	4.13	5.65	4.24
$C_2C{=}C + HO_2 \Leftrightarrow$ TS9	14.71	15.31	12.42	13.54
$C_2^{\bullet}CCOOH \Leftrightarrow$ TS12	27.03	26.00	26.86	25.79

[a] Reaction enthalpies include thermal correction and zero-point energy correction.

(MP2) and B3LYP functional theory. Semiempirical PM3 molecular orbital calculations are performed to evaluate entropy and heat capacity for important transition states and other relevant species of the isobutene−OH adducts + O_2 reaction system. The structures calculated from MP2(full)/6-31g(d), B3LYP/6-31g(d), and PM3 are provided as Supporting Information. Zero-point vibrational energies (ZPVE), vibrational frequencies, and thermal contributions to enthalpy and entropy from harmonic frequencies are scaled with factors as recommended by Scott et al.[23] Entropies and heat capacities are calculated from scaled vibrational degrees of freedom. The method of Pitzer and Gwinn[24] is used for thermodynamic analysis of S and Cp(T) contribution from hindered internal rotors. The numbers of optical isomers and spin degeneracy of unpaired electrons are incorporated. Transition state (TS) geometries are identified by the existence of only one imaginary frequency in the normal mode coordinate analysis, evaluation TS geometry, and transition state theory (TST[25]) reaction coordinate vibration information. Ab initio and semiempirical (PM3) molecular orbital calculations were performed using the Gaussian94[26] and MOPAC 6.0[27] programs, respectively.

Total energies, zero-point vibrational energies, and thermal contributions to enthalpy calculated by MP2(full)/6-31g(d), B3LYP/ 6-31g(d), and complete basis set (CBS-4 and CBS-q) model chemistries[28−30] for the species of *tert*-butyl radical ($C_3C^{\bullet}$) + O_2 and isobutene ($C_2C{=}C$) + HO_2 reaction systems are listed in Table 1. The CBS-4 and CBS-q calculations are performed using geometry optimizations at MP2(full)/ 6-31g(d) and B3LYP/ 6-31g(d) levels of theory. Reaction enthalpies determined at different theory levels are listed in Table 2. CBS-q results using either MP2(full)/ 6-31g(d) or B3LYP/ 6-31g(d) optimized geometries are similar, where differences are within 2.4 kcal/mol. We choose the CBS-q//MP2(full)/ 6-31g(d) calculation for discussion and kinetic analysis for $C_3C^{\bullet} + O_2$ and $C_2C{=}C + HO_2$ reaction systems. CBS-q calculations are chosen because Jungkamp et al.,[10,31] Petersson et al.,[32] and our group[33] have shown that they result in reasonable, accurate thermodynamic enthalpy data for these molecular systems. CBS-q and G2(MP2) are probably the best methods for these (five or six heavy atoms) systems and CBS-q requires ca. two-thirds of the computation time of G2(MP2).

Thermodynamic parameters $-\Delta H_f°_{298}$, $S°_{298}$, and Cp(300) to Cp(1500) for species in the reaction schemes are listed in Table 3a. Thermodynamic parameters of molecules and radicals with the exception of species calculated from ab initio and PM3 are calculated from group additivity using THERM[18] with peroxy,[19,20] cyclic,[21] and hydrogen bond increment (HBI) groups[22] parameters. We use heats of formation calculated from group additivity instead of those from PM3 calculations. The OO symbol is a group notation for peroxides. Peroxy groups were developed by Lay et al.[20,21] Hydrogen bond increment (HBI) groups are used to calculate thermodynamic properties of radicals.[22] The HBI group technique is based on known thermodynamic properties of the parent molecule and calculated changes that occur upon formation of radicals via loss of a H atom. The HBI group incorporates evaluated carbon hydrogen (C−H) (or oxygen−H) bond energies for ΔH_f of the respective radical, and entropy and heat capacity changes that result from loss or changes in vibration frequencies, internal rotation, and spin degeneracy when a hydrogen atom is removed from the specific carbon site. HBI groups are described in ref 22 and listed in Table 3b. The thermochemical data allow calculation of reverse reaction rate constants by microscopic reversibility.

Kinetic Calculations. Unimolecular dissociation and isomerization reactions of the chemically activated and stabilized adducts resulting from addition or combination reactions are analyzed by first constructing potential energy diagrams for the reaction system. Thermodynamic parameters, $\Delta H_f°_{298}$, $S°_{298}$, Cp(T), reduced vibration frequency sets, and Lennard Jones parameters for species in each reaction path are presented.

High-pressure rate constants for each channel are obtained from literature or referenced estimation techniques. Kinetics parameters for unimolecular and bimolecular (chemical activation) reactions are then calculated using multifrequency QRRK analysis for $k(E)$.[38−40] The master equation analysis[16a−c] as discussed by Gilbert is used for falloff (β collision) with the steady-state assumption on the energized adduct(s). $(\Delta E)°_{down}$ of 1000 cal/mol[83,84] is used for master equation analysis, N_2 is the third body.

Reactions which involve a change in number of moles, such as unimolecular dissociation, have energy of activation calculated as ΔU_{rxn} plus an E_a for the reverse addition, where U is internal energy (E_a reverse is usually 0.0 for simple association reactions). Enthalpies and E_a's, in the text and in potential energy diagrams, are at 298 K, while those in the tables listing data input to the chemical activation reactions are for 800 K, which we select as representative of modeled combustion experiments. The rate constants $k = AT^n \exp(-E_a/RT)$ for QRRK calculated chemical activation and unimolecular dissociation reaction in Table 4, the *tert*-butyl radical oxidation mechanism, are obtained by fitting the QRRK calculated rate constants in the temperature range from 500 to 900 K and pressures of 0.076, 0.76, 7.6, 60, 760, and 7600 Torr in N_2 bath gas.

Input Information Requirements for QRRK Calculation. Pre-exponential factors (A_∞s), are calculated using canonical TST[25] along with MP2, DFT, or PM3-determined entropies of intermediates and TSs for the reactions where thermodynamic properties of TS are available. High-pressure limit pre-exponential factors for combination reactions are obtained from the literature and from trends in homologous series of reactions. Activation energies come from complete basis model calculations CBS-q plus evaluated endothermicity of reaction ΔU_{rxn}, from analysis of Evans Polanyi relationships for abstractions plus evaluation of ring strain energy, and from analogy to similar reactions with known energies. Thermodynamic properties are provided for each system.

TABLE 3.

A. Thermodynamic Properties[e]

species	$\Delta H^\circ_{f\,298}$	S°_{298}	Cp_{300}	Cp_{400}	Cp_{500}	Cp_{600}	Cp_{800}	Cp_{1000}	Cp_{1500}
N2	0	45.7	6.65	6.86	6.99	7.1	7.31	7.61	7.98
H	52.1	27.3	4.9	4.9	4.9	4.9	4.9	4.9	4.9
H2	0	31.2	6.89	6.97	7.05	7.13	7.27	7.4	7.69
X	59.52	38.4	5	5	5	5	5	5	5
Y	9.5	43.8	6.79	6.86	6.93	7	7.14	7.28	7.61
O	59.52	38.4	5	5	5	5	5	5	5
O2	0	49	6.82	7.15	7.36	7.51	7.82	8.24	8.69
OH	9.5	43.8	6.79	6.86	6.93	7	7.14	7.28	7.61
H2O	−57.8	43.72	8.21	8.91	9.59	10.21	11.29	12.07	12.96
HO2	3.5	54.7	8.29	8.77	9.23	9.67	10.47	11.13	12.23
H2O2	−32.6	55.71	10.69	11.84	12.77	13.51	14.6	15.34	16.57
CH3	34.8	46.3	9.13	9.94	10.71	11.44	12.78	13.93	16.01
CH4	−17.9	44.4	8.8	9.87	11	12.16	14.43	16.48	20.08
CO	−26.4	47.2	6.71	6.89	7.06	7.23	7.53	7.79	8.29
CO2	−94.02	51	9.18	9.81	10.44	11.04	12.11	12.93	13.79
Using THERM Group Additivity									
CH2O	−26	50.92	8.48	9.49	10.51	11.51	13.33	14.82	16.98
HCO	10.4	53.6	8.65	9	9.39	9.8	10.6	11.33	12.49
CH3OH	−48	57.31	10.51	12.46	14.31	16.04	19.06	21.46	25.11
CH3O•	3.96	55.85	9.62	11.19	12.7	14.14	16.7	18.74	21.69
C•H2OH	−3.6	60.42	11.68	13.25	14.58	15.69	17.44	18.74	20.94
CH3OOH	−31.8	64.97	15.91	18.35	20.48	22.34	25.36	27.62	31.05
CH3OO	4.3	65.19	13.92	15.49	16.95	18.29	20.66	22.62	25.95
C•H2OOH	14.6	68.26	16.57	18.39	19.95	21.27	23.36	24.86	27.04
C*C*O	−11.74	57.83	12.7	14.79	16.45	17.78	19.68	20.95	22.96
CC*O	−39.18	63.14	13.17	15.83	18.26	20.47	24.19	27.06	31.22
CC•*O	−2.28	64.26	12.29	14.4	16.32	18.07	21.02	23.31	26.64
CCC	−25.33	64.51	17.88	22.74	27.05	30.86	37.13	41.91	49.28
CC•C	21.02	70.32	16.26	20.4	24.15	27.51	33.17	37.53	44.14
C*CC	4.65	63.82	15.45	19.32	22.74	25.75	30.72	34.51	40.34
CC•*C	61.56	65.63	15.09	18.09	20.8	23.24	27.37	30.59	35.58
C*CC•	40.75	63.44	14.87	18.65	21.88	24.63	28.95	32.09	36.77
C*C*C	45.92	58.31	14.19	17.22	19.8	21.99	25.46	28.02	32.03
C#CC	44.28	59.29	13.98	16.64	19.07	21.28	25	27.86	31.94
C#CC•	81.59	60.96	13.76	16.1	18.09	19.79	22.47	24.42	27.31
CCC*O	−44.5	72.74	19.37	23.37	26.92	30.06	35.25	39.19	45.2
CC•C*O	−4.7	70.37	18.07	21.88	25.19	28.06	32.66	36.06	41.08
C2C*O	−51.56	70.1	17.92	22.13	25.92	29.3	34.92	39.19	45.45
C2•C*O	−9.26	72.5	18.29	22.29	25.76	28.75	33.51	36.93	41.75
C*C(C)OH	−38.81	72.63	19.11	23.28	26.94	30.15	35.36	39.24	45
CCYCCO	−21.87	68.17	17.37	22.57	26.94	30.62	36.3	40.32	46.31
CCYC•CO	24.48	72.61	15.77	20.22	24.03	27.29	32.38	35.96	40.98
C2COOH	−49.98	81.34	26.32	32.11	37.07	41.3	47.94	52.75	59.86
C2C•OOH	−8.48	87.32	26.46	30.82	34.68	38.09	43.69	47.96	54.55
C*C(C)Q	−15.57	82.85	23.54	28.17	32.12	35.49	40.8	44.66	50.41
C*C(C)Q•	20.53	83.07	21.57	25.29	28.54	31.38	36.05	39.68	45.58
C*C*CQ	26.6	77.13	22.32	26.43	29.8	32.55	36.58	39.26	42.98
CC*OCOOH	−70.32	90.59	27.1	31.82	35.98	39.62	45.54	49.93	56.2
CC*OCOO•	−34.21	90.81	25.06	28.94	32.44	35.57	40.86	44.96	51.11
C•C*OCOOH	−28.01	91.61	27.09	31.55	35.38	38.67	43.82	47.46	52.31
C3C	−32.5	70.44	23.17	29.65	35.33	40.29	48.37	54.46	63.76
C3C•	11.7	75.68	22.31	27.25	31.87	36.14	43.55	49.44	58.37
C3•C	16.5	77.41	22.4	28.27	33.42	37.91	45.22	50.71	59.11
C2C*C	−3.8	70	21.58	26.74	31.3	35.31	41.9	46.91	54.64
C2•C*C	32.3	71	20.99	26.11	30.47	34.2	40.1	44.44	51.16
C2C*C•	55.3	72.76	21.39	25.94	29.92	33.4	39.09	43.41	50.12
C3COH	−75.11	78.02	27.23	34.24	40.21	45.29	53.3	59.19	68.35
C3CO•	−23.14	76.56	26.25	32.93	38.6	43.4	50.92	56.39	64.77
C3•COH	−26.1	84.99	26.46	32.86	38.29	42.9	50.15	55.45	63.71
C2CCOH	−68.31	83.26	26.19	33.12	39.1	44.25	52.49	58.58	67.92
C2C•COH	−24.1	88.5	25.35	30.72	35.64	40.09	47.66	53.56	62.54
C2CCO•	−16.34	81.8	25.2	31.81	37.49	42.37	50.11	55.78	64.35
C2CC*O	−51.2	79.66	23.57	29.64	34.9	39.43	46.67	51.96	59.79
C2C•C*O	−13.5	77.95	24.14	29.29	33.76	37.63	43.86	48.51	55.61
C2C*COH	−45.93	79.06	25.53	31.3	36.21	40.39	46.98	51.82	59.37
C*C(C)COH	−38.26	82.02	24.73	30.24	35.07	39.28	46.1	51.2	58.91
C*C(C)CO•	13.7	80.56	23.77	28.96	33.49	37.42	43.74	48.41	55.37
C*CICC*O	−27.34	74.65	23.18	28.32	32.61	36.2	41.71	45.61	51.52
C*CICC•*O	3.56	73.26	22.96	27.39	31.02	34.01	38.52	41.7	46.8
C2C*C*O	−28.06	73.98	24.27	28.96	32.92	36.26	41.48	45.29	51.24
C2CYC2O	−31.47	71.09	23.1	29.9	35.6	40.38	47.73	52.94	60.74
C2CYCC•O	10.43	73.61	22.97	29.14	34.26	38.5	44.93	49.44	56.23

TABLE 3. (Continued)

A. Thermodynamic Properties[e] (Continued)

species	$\Delta H°_{f\,298}$	$S°_{298}$	Cp_{300}	Cp_{400}	Cp_{500}	Cp_{600}	Cp_{800}	Cp_{1000}	Cp_{1500}
Using THERM Group Additivity (Continued)									
CCYCOCC	−28.54	73.69	20.89	27.95	33.95	39.03	46.94	52.59	60.95
CCYC$^{\bullet}$COC	17.99	78.24	19.07	24.75	29.81	34.29	41.66	47.21	55.35
C*CYCCOC	4.97	69	18.72	24.34	29.23	33.47	40.21	45.08	52.01
C2$^{\bullet}$CYC2O	17.53	77.26	22.33	28.51	33.68	37.99	44.57	49.2	56.09
C*CIC$^{\bullet}$C*O	8.76	74.27	22.59	27.68	31.8	35.1	39.91	43.14	48.02
C3COOH	−59.40	84.24	32.35	39.67	45.85	51.06	59.16	65.01	73.96
C2CCOOH	−52.70	91.92	31.02	38.56	45.04	50.56	58.93	65.33	74.18
C2C*CQ	−23.92	87.27	29.8	36.03	41.35	45.88	53	58.11	65.6
C*C(C)CQ	−24.38	90.11	30.26	36.22	41.32	45.67	52.56	57.59	65.2
CC(CO$^{\bullet}$)CO	−35.04	90.22	25.71	31.8	37.01	41.44	48.37	53.35	60.64
C*CICOOC$^{\bullet}$	31	95.08	27.92	33.77	38.76	43	49.67	54.48	61.45
C2CYCCOO	−16.51	76.71	25.37	32.93	39.26	44.54	52.61	58.23	66.4
C2$^{\bullet}$CYCCOO	32.49	81.51	24.6	31.55	37.34	42.16	49.45	54.49	61.77
CCYCCOOC	−28.68	75.42	23.82	31.85	38.55	44.14	52.62	58.5	66.98
CCYC$^{\bullet}$COOC	15.22	77.14	23.78	31.27	37.4	42.41	49.81	54.82	62.17
CCYCC$^{\bullet}$OOC	17.32	77.14	23.78	31.27	37.4	42.41	49.81	54.82	62.17
C*C(C)CQ$^{\bullet}$	11.72	92.51	28.23	33.32	37.74	41.57	47.79	52.52	60.03
C*C(C$^{\bullet}$)CQ	11.72	89.73	29.75	35.65	40.57	44.64	50.83	55.15	61.48
C*C(C)C$^{\bullet}$Q	9.12	88.48	28.7	34.38	39.22	43.34	49.77	54.38	61.06
C2CQCOH	−95.49	97.06	35.53	43.15	49.55	54.91	63.19	69.12	78.27
C2COHCQ	−96.3	98.46	35.62	43.24	49.67	55.09	63.53	69.59	78.76
C2C(Q)C*O	−75.44	94.38	32.5	39.72	45.81	50.91	58.71	64.1	71.51
C3QCQ	−80.88	104.68	40.79	48.67	55.29	60.82	69.33	75.33	84.23
C2CQCQ$^{\bullet}$	−44.77	104.9	38.72	45.76	51.72	56.76	64.63	70.34	79.13
C2CQ$^{\bullet}$CQ	−44.77	104.9	38.72	45.76	51.72	56.76	64.63	70.34	79.13
C2$^{\bullet}$CQCQ	−31.87	109.63	40.14	47.37	53.42	58.46	66.17	71.58	79.57
C2CQC$^{\bullet}$Q	−36.97	108.5	40.91	47.81	53.64	58.55	66.14	71.53	79.54
CYC6H6	19.8	64.25	19.53	26.69	32.68	37.67	45.3	50.6	58.17
C*CCCC*C	20.18	88.59	28.69	36.57	43.28	48.98	57.91	64.37	74.28
C2C*CC2	−20.12	90.51	32.93	40.7	47.58	53.65	63.65	71.26	82.94
C2*CCCC*C	11.73	98.33	34.84	43.99	51.83	58.52	69.09	76.81	88.57
C*C(C)CC3	−22.52	90.93	37.93	48.53	57.51	65.1	76.92	85.37	98.01
C3CCC2	−49.2	91.79	39.91	51.57	61.5	69.95	83.18	92.74	107.06
C3CC$^{\bullet}$C2	−4.8	97.03	39.09	49.18	58.04	65.79	78.36	87.71	101.67
C3CCQC2	−74.79	106.96	49.25	61.61	71.97	80.63	93.91	103.28	117.35
C3$^{\bullet}$CCQC2	−25.78	113.94	48.46	60.22	70.05	78.24	90.75	99.54	112.69
C3CCQ$^{\bullet}$C2	−38.68	107.18	47.17	58.7	68.4	76.56	89.21	98.29	112.25
C3CCC3	−53.92	93.43	45.88	59.59	71.13	80.81	95.69	106.16	121.6
C3$^{\bullet}$CCC3	−4.92	101.78	45.11	58.21	69.21	78.42	92.53	102.42	116.95
DIC2$^{\bullet}$C*C	3.28	104.51	40.98	51.42	60.39	68.07	80.26	89.21	102.88
C3CCC3Q	−75	115.25	54.37	68.61	80.57	90.57	105.9	116.63	132.29
C3CCC3Q$^{\bullet}$	−38.89	115.47	52.33	65.71	77	86.51	101.2	111.64	127.2
C3CCC2$^{\bullet}$CQ	−25.99	120.59	53.87	67.3	78.57	88	102.45	112.57	127.43
C3COOCC3	−83.45	112.76	53.76	67.89	79.81	89.85	105.43	116.59	133.14
C2CCOOTB	−78.67	120.83	52.77	66.78	78.7	88.8	104.59	115.98	132.79
C2C$^{\bullet}$COOTB	−34.46	125.42	52.18	64.69	75.55	84.94	100	111.11	127.48
Using PM3 Molecular Orbital Calculation for Key Reaction Species and Transition States[a]									
C2COHCQ$^{\bullet}$	−60.19	96.02	32.85	40.56	47.20	52.53	60.33	65.80	74.22
TS10		84.30	30.26	38.86	46.23	52.17	60.82	66.77	75.57
C2CO$^{\bullet}$CQ	−44.33	96.60	33.58	41.37	47.90	53.09	60.55	62.65	73.37
C2CQ$^{\bullet}$COH	−59.38	96.14	33.23	40.71	47.14	52.34	60.06	65.55	74.06
TS11		84.71	30.51	39.07	46.39	52.29	60.90	66.83	75.61
C2CQCO$^{\bullet}$	−43.52	95.17	34.49	42.65	49.60	55.14	62.98	68.18	75.80
C2$^{\bullet}$COHCQ	−47.29	100.36	34.66	42.21	48.50	53.47	60.69	65.74	73.58
C2$^{\bullet}$CQCOH	−46.48	103.99	35.12	42.76	49.13	54.19	61.48	66.47	74.10
C2CQC$^{\bullet}$OH	−53.58	100.10	35.47	42.78	49.03	54.07	61.39	66.40	74.06
TS14		86.75	30.94	39.46	46.65	52.39	60.75	66.53	75.23
TS15		91.89	32.04	40.16	46.96	52.41	60.40	66.00	74.47
TS16		89.51	32.70	40.83	47.69	53.15	61.06	66.52	74.75
Using CBS-q//MP2(full)/6-31G* Calculation for Species and Transition States of $C_3C^{\bullet} + O_2$ and $C_2C{=}C + HO_2$ Reaction Systems									
C3COO$^{\bullet}$	−25.16[b]	82.98	28.7	35.43	41.42	46.43	54.08	59.63	68.43
TS1	2.29	82.16	27.41	34.31	40.52	45.78	53.84	59.65	68.63
TS2	7.68	79.83	26.54	33.86	40.34	45.75	53.92	59.73	68.67
C3$^{\bullet}$COOH	−7.81[c]	91.60	30.28	37.07	43.05	47.99	55.34	60.49	68.49
TS3	7.44	89.35	28.18	34.8	40.67	45.57	52.98	58.32	66.75
TS4	7.77 [d]	85.61	28.48	35.3	41.17	45.98	53.25	58.56	67.15
TS5	10.39	89.59	27.47	34.03	39.97	44.97	52.59	58.06	66.66
TS6	10.93	87.24	27.69	34.06	39.9	44.85	52.49	58.09	67.02
C2C$^{\bullet}$COOH	−8.37[c]	97.15	27.75	33.69	39.52	44.63	52.63	58.44	67.54
C2CCOO$^{\bullet}$	−19.07[c]	89.20	27.69	34.29	40.26	45.28	53.08	58.84	67.99

TABLE 3. (Continued)

A. Thermodynamic Properties[e] (Continued)

species	$\Delta H^{\circ}_{f\,298}$	S°_{298}	Cp_{300}	Cp_{400}	Cp_{500}	Cp_{600}	Cp_{800}	Cp_{1000}	Cp_{1500}
Using CBS-q//MP2(full)/6-31G* Calculation for Species and Transition States of $C_3C^{\bullet} + O_2$ and $C_2C{=}C + HO_2$ Reaction Systems (Continued)									
TS7	9.31	80.20	25.61	32.68	39.21	44.76	53.24	59.29	68.52
TS8	1.95	78.60	24.75	32.18	38.96	44.7	53.43	59.67	69.15
TS9	15.01	82.00	26.54	33.42	39.68	45.02	53.24	59.19	68.38
C2$^{\bullet}$CCOOH	−2.18[c]	95.98	30.27	36.83	42.72	47.61	54.91	60.11	68.26
TS12	23.82	94.86	27.91	34.69	40.68	45.68	53.22	58.64	67.09
TS13	48.82	74.88	22.96	28.09	32.85	37.04	43.85	49.04	57.38
Using CBS-q//B3LYP/6-31G* Calculation for Species and Transition States of $C_3C^{\bullet} + O_2$ and $C_2C{=}C + HO_2$ Reaction Systems									
C3COO$^{\bullet}$	−25.16[b]	83.85	29.84	36.86	42.97	47.99	55.55	60.99	69.43
TS1	2.9	83.88	28.73	35.85	42.16	47.43	55.39	61.06	69.66
TS2	7.07	81.11	28.37	36.09	42.66	47.98	55.86	61.40	69.81
C3$^{\bullet}$COOH	−7.81[c]	92.50	31.67	38.84	44.92	49.82	56.99	61.96	69.55
TS3	7.08	89.67	28.61	35.35	41.27	46.19	53.59	58.90	67.21
TS4	10.25[d]	87.24	30.11	37.08	42.92	47.65	54.74	59.90	68.14
TS5	10.52	90.63	28.69	35.58	41.64	46.65	54.15	59.49	67.72
TS6	13.1	92.04	29.08	35.64	41.53	46.45	53.99	59.47	68.06
C2C$^{\bullet}$COOH	−8.37[c]	97.77	28.62	34.89	40.86	46.01	53.99	59.71	68.42
C2CCOO$^{\bullet}$	−19.07[c]	89.89	28.73	35.68	41.80	46.85	54.57	60.21	69.01
TS7	7.64	81.61	27.18	34.67	41.32	46.85	55.13	60.95	69.68
TS8	2.06	79.79	26.43	34.25	41.09	46.75	55.23	61.21	70.21
TS9	13.24	83.71	28.61	35.79	42.14	47.43	55.38	61.03	69.62
C2$^{\bullet}$CCOOH	−2.18[c]	96.62	31.12	37.97	43.97	48.89	56.15	61.29	69.18
TS12	23.61	95.32	28.65	35.52	41.51	46.47	53.94	59.29	67.58

B. Hydrogen Atom Bond Increments Group for Hydrocarbon Radicals[i]

	$D^{\circ}(R-H)$	$\Delta S^{\circ}_{int,298}$[f]	ΔCp_{300}	ΔCp_{400}	ΔCp_{500}	ΔCp_{600}	ΔCp_{800}	ΔCp_{1000}	ΔCp_{1500}
P[g]	101.1	2.61	−0.77	−1.36	−1.91	−2.4	−3.16	−3.74	−4.66
S[h]	98.45	4.44	−1.5	−2.33	−3.1	−3.39	−3.75	−4.45	−5.2
tertalkyl	96.5	5.24	−0.78	−2.48	−3.55	−4.15	−4.75	−5.02	−5.39
CCJC	98.45	4.51	−1.3	−2.36	−3.02	−3.44	−3.98	−4.36	−4.99
neopentyl	101.1	3.03	−0.59	−1.32	−2.05	−2.65	−3.5	−4.06	−4.87
VIN	111.2	1.39	−0.19	−0.75	−1.36	−1.92	−2.82	−3.49	−4.53
VIN_S	109	1.81	−0.34	−1.21	−1.94	−2.52	−3.34	−3.91	−4.76
ALLYL_P	88.2	−2.56	−0.62	−0.56	−0.78	−1.12	−1.84	−2.46	−3.49
ALLYL_S	85.6	−3.81	−1.54	−1.82	−2.08	−2.32	−2.75	−3.14	−3.85
C≡CCJ	89.4	−0.51	−0.84	−1.17	−1.56	−1.95	−2.7	−3.31	−5.31
CYC4	98.45	1.68	−0.35	−0.6	−1.02	−1.51	−2.45	−3.2	−4.12
CYC5H9	98.1	1.72	−0.06	−0.52	−1.11	−1.74	−2.85	−3.69	−4.83
CYCJC3O2	96	1.72	−0.06	−0.52	−1.11	−1.74	−2.85	−3.69	−4.83
ROJ	104.06	−1.46	−0.98	−1.3	−1.61	−1.89	−2.38	−2.8	−3.59
RC═COJ	88	−1.11	−1.34	−1.99	−2.48	−2.79	−3.13	−3.33	−3.79
CJOH	96.5	0.93	1.28	0.93	0.2	−0.55	−1.83	−2.77	−4.17
CCJOH	94	0.78	0.33	−0.3	−1.02	−1.67	−2.67	−3.39	−4.49
CCJOR	94	1.15	−0.13	−0.67	−1.31	−1.89	−2.82	−3.49	−4.54
C2CJOR	92.8	2.46	−1.49	−2.88	−3.9	−4.51	−5.09	−5.32	−5.58
CCJCHO	91.9	−2.37	−1.36	−1.57	−1.73	−1.89	−2.66	−3.11	−3.5
C2CJCHO	89.8	−1.71	0.62	−0.2	−1.23	−1.82	−2.87	−3.47	
ROOJ	88.2	0.22	−2.05	−2.84	−3.55	−4.09	−4.72	−4.97	−5.08
CJOOH	98.5	1.11	0.62	0.09	−0.53	−1.09	−2.01	−2.75	−4.01
CCJOOH	96	3.82	0.14	−0.84	−1.66	−2.3	−3.18	−3.79	−4.7
C2CJOOH	93.6	5.98	0.22	−1.31	−2.45	−3.21	−4.13	−4.62	−5.24
CJCOOH	102.87	2.73	−0.66	−1.28	−1.86	−2.35	−3.14	−3.72	−4.65
C2JCOOH	101.1	2.76	−0.65	−1.28	−1.88	−2.38	−3.16	−3.75	−4.67
C2CJCOOH	96.44	4.59	−0.49	−2.12	−3.22	−3.88	−4.53	−4.87	−5.31
C2JC*O	94.4	−1.16	0.32	0.19	−0.15	−0.57	−1.43	−2.22	−3.67
CCJ*O	89	1.12	−0.83	−1.43	−1.96	−2.42	−3.16	−3.73	−4.64
C*CCJ*O	83	−1.39	−0.19	−0.85	−1.59	−2.21	−3.21	−3.89	−4.6
OJC═O	104	0.79	−1.31	−1.87	−2.32	−2.69	−3.28	−3.74	−4.56
C3COOJ	85.3[b]	0.22	−2.05	−2.84	−3.55	−4.09	−4.72	−4.97	−5.08
C3JCOOH	103.69	3.15	−0.48	−1.24	−2	−2.6	−3.47	−4.04	−4.87

[a] ΔH°_{f298} from THERM. [b] Reference 46. [c] Calculated from average values of ΔH_{rxn} of isodesmic reactions (list in Table 2) at CBS-q//MP2(full)/6-31g* and CBS-q//B3LYP/6-31g* levels. [d] Best fit with experimental data. [e] Units: Hf, kcal/mol; S and Cp(T), cal/mol. [f] Includes electronic spin degeneracy. [g] The general group for all kinds of primary alkyl radicals. [h] The general group for all kinds of secondary alkyl radicals. [i] Units: $D^{\circ}(R-H)$, kcal/mol; $\Delta S^{\circ}_{int,298}$ and $\Delta Cp(T)$, cal/mol.

Reduced sets of three vibration frequencies and their associated degeneracies are computed from fits to heat capacity data, as described by Ritter and Bozzelli et al.[34,35] These have been shown by Ritter to accurately reproduce molecular heat capacities, Cp(T), and by Bozzelli et al.[35] to yield accurate ratios of density of states to partition coefficient, $\rho(E)/Q$.

Lennard-Jones parameters, σ (angstroms) and ϵ/k (Kelvin), are obtained from tabulations[36] and from a calculation method

TABLE 4: Detail Mechanism[a,v]

reactions	*A*	*n*	E_a	atm	
C3CCC3 = 2C3C•	2.31E+49	−10.18	81198	0.0001	*a*
C3CCC3 = 2C3C•	3.41E+29	−3.97	74131	0.001	*a*
C3CCC3 = 2C3C•	3.20E+23	−2.09	71948	0.01	*a*
C3CCC3 = 2C3C•	2.67E+23	−2.07	71920	0.079	*a*
C3CCC3 = 2C3C•	2.61E+23	−2.07	71916	1	*a*
C3CCC3 = 2C3C•	2.60E+23	−2.07	71916	10	*a*
C3CCC3 = C3CC•C2 + CH3	2.57E+53	−10.89	93667	0.0001	*a*
C3CCC3 = C3CC•C2 + CH3	3.79E+41	−7.18	89490	0.001	*a*
C3CCC3 = C3CC•C2 + CH3	2.45E+41	−7.12	89423	0.01	*a*
C3CCC3 = C3CC•C2 + CH3	2.34E+41	−7.11	89417	0.079	*a*
C3CCC3 = C3CC•C2 + CH3	2.33E+41	−7.11	89416	1	*a*
C3CCC3 = C3CC•C2 + CH3	2.33E+41	−7.11	89416	10	*a*
C3CC•C2 = C2C*CC2 + CH3	8.40E+49	−13.21	27397	0.0001	*a*
C3CC•C2 = C2C*CC2 + CH3	3.16E+57	−15.11	31725	0.001	*a*
C3CC•C2 = C2C*CC2 + CH3	3.36E+76	−20.52	40951	0.01	*a*
C3CC•C2 = C2C*CC2 + CH3	8.75E+81	−21.75	45269	0.079	*a*
C3CC•C2 = C2C*CC2 + CH3	1.13E+75	−19.14	45413	1	*a*
C3CC•C2 = C2C*CC2 + CH3	2.52E+53	−12.15	39038	10	*a*
C3CC•C2+O2 = C3CCQ•C2	1.19E+213	−65.24	58174	0.0001	*a*
C3CC•C2+O2 = C3CCQ•C2	3.66E+228	−69.33	67132	0.001	*a*
C3CC•C2+O2 = C3CCQ•C2	7.03E+84	−22.92	23907	0.1	*a*
C3CC•C2+O2 = C3CCQ•C2	1.52E+223	−66.29	72750	0.079	*a*
C3CC•C2+O2 = C3CCQ•C2	7.80E+171	−49.82	57092	1	*a*
C3CC•C2+O2 = C3CCQ•C2	7.10E+99	−27.2	31884	10	*a*
C3CC•C2+O2 = C3•CCQC2	1.79E+174	−55.28	41687	0.0001	*a*
C3CC•C2+O2 = C3•CCQC2	1.09E+176	−55.33	43504	0.001	*a*
C3CC•C2+O2 = C3•CCQC2	1.57E+70	−18.87	21902	0.1	*a*
C3CC•C2+O2 = C3•CCQC2	1.28E+139	−43.21	31156	0.079	*a*
C3CC•C2+O2 = C3•CCQC2	1.16E+94	−29.08	14837	1	*a*
C3CC•C2+O2 = C3•CCQC2	1.54E+84	−25.73	13445	10	*a*
C3CC•C2+O2 = C2C*C + C2C•OOH	3.45E+40	−9.18	8041	0.0001	*a*
C3CC•C2+O2 = C2C*C + C2C•OOH	3.99E+52	−12.8	13715	0.001	*a*
C3CC•C2+O2 = C2C*C + C2C•OOH	9.34E+82	−21.52	32873	0.1	*a*
C3CC•C2+O2 = C2C*C + C2C•OOH	9.31E+83	−21.96	31384	0.079	*a*
C3CC•C2+O2 = C2C*C + C2C•OOH	8.83E+70	−17.56	31156	1	*a*
C3CC•C2+O2 = C2C*C + C2C•OOH	6.52E+41	−8.25	24851	10	*a*
C3CCQ•C2 = C3•CCQC2	4.63E+61	−16.78	32482	0.0001	*a*
C3CCQ•C2 = C3•CCQC2	1.74E+72	−19.61	38734	0.001	*a*
C3CCQ•C2 = C3•CCQC2	1.62E+83	−23.03	42708	0.1	*a*
C3CCQ•C2 = C3•CCQC2	1.86E+63	−16.15	39332	0.079	*a*
C3CCQ•C2 = C3•CCQC2	2.09E+52	−12.64	35975	1	*a*
C3CCQ•C2 = C3•CCQC2	1.76E+52	−12.62	35955	10	*a*
C3•CCQC2 = C2C*C + C2C•OOH	7.88+247	−70.96	125322	0.0001	*a*
C3•CCQC2 = C2C*C + C2C•OOH	5.68E−92	33.18	−11264	0.001	*a*
C3•CCQC2 = C2C*C + C2C•OOH	1.39E+42	−10.01	19934	0.1	*a*
C3•CCQC2 = C2C*C + C2C•OOH	1.53E−158	51.94	−54622	0.079	*a*
C3•CCQC2 = C2C*C + C2C•OOH	3.38E+48	−11.64	23836	1	*a*
C3•CCQC2 = C2C*C + C2C•OOH	3.21E+59	−14.58	30306	10	*a*
C3•CCC3 = C3C• + C2C*C	1.96E+214	−61.98	97828	0.0001	*a*
C3•CCC3 = C3C• + C2C*C	7.95E−91	31.91	−20468	0.001	*a*
C3•CCC3 = C3C• + C2C*C	8.56E−286	91.72	−99515	0.01	*a*
C3•CCC3 = C3C• + C2C*C	1.77E−166	54.34	−58900	0.079	*a*
C3•CCC3 = C3C• + C2C*C	2.44E+40	−9.22	19312	1	*a*
C3•CCC3 = C3C• + C2C*C	8.16E+51	−12.34	25811	10	*a*
C3•CCC3 + O2 = C3CCC3Q•	1.16E+286	−87.31	87423	0.0001	*a*
C3•CCC3 + O2 = C3CCC3Q•	2.00E+107	−30.44	28925	0.001	*a*
C3•CCC3 + O2 = C3CCC3Q•	7.72E+288	−86.85	96164	0.01	*a*
C3•CCC3 + O2 = C3CCC3Q•	6.55E+255	−76.09	86886	0.079	*a*
C3•CCC3 + O2 = C3CCC3Q•	2.57E+181	−52.61	61688	1	*a*
C3•CCC3 + O2 = C3CCC3Q•	6.52E+96	−26.2	31120	10	*a*
C3•CCC3 + O2 = C3CCC2•CQ	2.74E+244	−76.67	70708	0.0001	*a*
C3•CCC3 + O2 = C3CCC2•CQ	2.72E+85	−23.63	26094	0.001	*a*
C3•CCC3 + O2 = C3CCC2•CQ	3.43E+202	−62.89	57183	0.01	*a*
C3•CCC3 + O2 = C3CCC2•CQ	1.11E+148	−45.92	35676	0.079	*a*
C3•CCC3 + O2 = C3CCC2•CQ	6.08E+117	−36.23	25081	1	*a*
C3•CCC3 + O2 = C3CCC2•CQ	8.72E+131	−39.99	35083	10	*a*
C3•CCC3 + O2 = C3CC*C(C) + C•H2OOH	2.20E+46	−10.38	17212	0.0001	*a*
C3•CCC3 + O2 = C3CC*C(C) + C•H2OOH	2.07E+68	−16.96	27765	0.001	*a*
C3•CCC3 + O2 = C3CC*C(C) + C•H2OOH	2.25E+83	−21.41	35488	0.01	*a*
C3•CCC3 + O2 = C3CC*C(C) + C•H2OOH	1.45E+95	−24.72	43783	0.079	*a*
C3•CCC3 + O2 = C3CC*C(C) + C•H2OOH	9.48E+80	−19.82	44827	1	*a*
C3•CCC3 + O2 = C3CC*C(C) + C•H2OOH	3.88E+27	−2.88	31309	10	*a*
C3CCC3Q• = C3CCC2•CQ	6.69E+64	−17.69	34239	0.0001	*a*

TABLE 4. (Continued)

reactions	*A*	*n*	E_a	atm	
C3CCC3Q• = C3CCCC•CQ	1.25E+60	−16.66	31516	0.001	*a*
C3CCC3Q• = C3CCC2•CQ	1.53E+70	−18.44	41398	0.01	*a*
C3CCC3Q• = C3CCC2•CQ	7.04E+63	−16.34	39899	0.079	*a*
C3CCC3Q• = C3CCC2•CQ	6.42E+63	−16.32	39897	1	*a*
C3CCC3Q• = C3CCC2•CQ	6.37E+63	−16.32	39897	10	*a*
C3CCC2•CQ = C3CC*C(C) + C•H2OOH	9.64+122	−30.83	98269	0.0001	*a*
C3CCC2•CQ = C3CC*C(C) + C•H2OOH	1.26E+35	−7.87	26953	0.001	*a*
C3CCC2•CQ = C3CC*C(C) + C•H2OOH	2.71E+24	−5.76	17527	0.01	*a*
C3CCC2•CQ = C3CC*C(C) + C•H2OOH	1.67E+41	−10.01	25809	0.079	*a*
C3CCC2•CQ = C3CC*C(C) + C•H2OOH	2.95E+59	−14.65	36999	1	*a*
C3CCC2•CQ = C3CC*C(C) + C•H2OOH	3.84E+45	−9.89	34385	10	*a*
C3C• = C2C*C + H	3.35E+66	−17.52	50901	0.0001	*a*
C3C• = C2C*C + H	4.92E+62	−15.96	51043	0.001	*a*
C3C• = C2C*C + H	2.06E+54	−13.03	49591	0.01	*a*
C3C• = C2C*C + H	2.10E+42	−9.11	46246	0.079	*a*
C3C• = C2C*C + H	5.98E+26	−4.18	41144	1	*a*
C3C• = C2C*C + H	6.37E+18	−1.67	38351	10	*a*
C3C• + O2 = C3COO•	3.85E+95	−28.26	19183	0.0001	*a*
C3C• + O2 = C3COO•	3.38E+97	−28.24	21830	0.001	*a*
C3C• + O2 = C3COO•	4.05E+96	−27.41	23610	0.01	*a*
C3C• + O2 = C3COO•	6.17E+92	−25.79	24226	0.079	*a*
C3C• + O2 = C3COO•	1.11E+80	−21.37	21980	1	*a*
C3C• + O2 = C3COO•	2.50E+58	−14.35	15682	10	*a*
C3C• + O2 = C3CO• + O	4.61E+24	−3.89	29994	0.0001	*a*
C3C• + O2 = C3CO• + O	4.61E+24	−3.89	29994	0.001	*a*
C3C• + O2 = C3CO• + O	4.61E+24	−3.89	29994	0.01	*a*
C3C• + O2 = C3CO• + O	4.61E+24	−3.89	29994	0.079	*a*
C3C• + O2 = C3CO• + O	4.74E+24	−3.89	30000	1	*a*
C3C• + O2 = C3CO• + O	5.86E+26	−4.52	30982	10	*a*
C3C• + O2 = C2C*C + HO2 (via TS1)	3.57E+18	−2.41	7	0.0001	*a*
C3C• + O2 = C2C*C + HO2 (via TS1)	6.54E+23	−3.99	2515	0.001	*a*
C3C• + O2 = C2C*C + HO2 (via TS1)	7.09E+32	−6.66	7193	0.01	*a*
C3C• + O2 = C2C*C + HO2 (via TS1)	1.02E+41	−9.02	12126	0.079	*a*
C3C• + O2 = C2C*C + HO2 (via TS1)	1.08E+45	−10.02	16779	1	*a*
C3C + O2 = C2C*C + HO2 (via TS1)	2.64E+35	−6.85	16296	10	*a*
C3C• + O2 = C3•COOH	7.85E+81	−25.06	16825	0.0001	*a*
C3C• + O2 = C3•COOH	2.56E+88	−26.56	20692	0.001	*a*
C3C• + O2 = C3•COOH	6.91E+95	−28.34	25542	0.01	*a*
C3C• + O2 = C3•COOH	6.64E+104	−30.61	31505	0.079	*a*
C3C• + O2 = C3•COOH	1.52E+114	−32.79	39761	1	*a*
C3C• + O2 = C3•COOH	4.11E+101	−28.22	40560	10	*a*
C3C• + O2 = C2C*C + HO2 (via TS2)	4.73E+09	0.04	656	0.0001	*a*
C3C• + O2 = C2C*C + HO2 (via TS2)	1.47E+12	−0.71	1821	0.001	*a*
C3C• + O2 = C2C*C + HO2 (via TS2)	5.37E+19	−2.97	5483	0.01	*a*
C3C• + O2 = C2C*C + HO2 (via TS2)	1.07E+32	−6.61	11831	0.079	*a*
C3C• + O2 = C2C*C + HO2 (via TS2)	4.73E+49	−11.71	22557	1	*a*
C3C• + O2 = C2C*C + HO2 (via TS2)	1.25E+51	−11.72	28708	10	*a*
C3C• + O2 = C2CYC2O + OH	1.16E+08	0.3	762	0.0001	*a*
C3C• + O2 = C2CYC2O + OH	2.74E+10	−0.41	1871	0.001	*a*
C3C• + O2 = C2CYC2O + OH	5.67E+17	−2.6	5403	0.01	*a*
C3C• + O2 = C2CYC2O + OH	8.67E+29	−6.21	11667	0.079	*a*
C3C• + O2 = C2CYC2O + OH	6.03E+47	−11.37	22433	1	*a*
C3C• + O2 = C2CYC2O + OH	3.66E+49	−11.49	28707	10	*a*
C3C• + O2 = C*C(C)Q + CH3	5.35E+12	−0.52	21335	0.0001	*a*
C3C• + O2 = C*C(C)Q + CH3	5.34E+12	−0.52	21334	0.001	*a*
C3C• + O2 = C*C(C)Q + CH3	5.31E+12	−0.52	21333	0.01	*a*
C3C• + O2 = C*C(C)Q + CH3	5.10E+12	−0.52	21324	0.079	*a*
C3C• + O2 = C*C(C)Q + CH3	2.14E+14	−1.01	22065	1	*a*
C3C• + O2 = C*C(C)Q + CH3	3.33E+31	−6.11	30834	10	*a*
C3COO• = C3CO• + O	1.45E+57	−20.16	67718	0.0001	*a*
C3COO• = C3CO• + O	6.61E+63	−21.46	69284	0.001	*a*
C3COO• = C3CO• + O	6.16E+71	−23.09	70721	0.01	*a*
C3COO• = C3CO• + O	5.06E+78	−24.35	71390	0.079	*a*
C3COO• = C3CO• + O	1.59E+88	−25.87	74262	1	*a*
C3COO• = C3CO• + O	2.40E+91	−25.44	78745	10	*a*
C3COO• = C2C*C + HO2	1.41E+70	−19.09	42021	0.0001	*a*
C3COO• = C2C*C + HO2	1.11E+71	−18.98	44128	0.001	*a*
C3COO• = C2C*C + HO2	1.67E+70	−18.4	45496	0.01	*a*
C3COO• = C2C*C + HO2	6.81E+64	−16.48	44856	0.079	*a*
C3COO• = C2C*C + HO2	2.15E+51	−12.05	41259	1	*a*
C3COO• = C2C*C + HO2	5.78E+34	−6.77	35933	10	*a*
C3COO• = C3•COOH	6.74E+71	−20.65	45123	0.0001	*a*
C3COO• = C3•COOH	2.42E+74	−20.85	48008	0.001	*a*

TABLE 4. (Continued)

reactions	*A*	*n*	E_a	atm	
C3COO• = C3•COOH	1.67E+76	−20.92	50715	0.01	*a*
C3COO• = C3•COOH	7.76E+73	−19.8	51710	0.079	*a*
C3COO• = C3•COOH	2.40E+63	−16.13	50020	1	*a*
C3COO• = C3•COOH	6.85E+45	−10.43	45000	10	*a*
C3•COOH = C2C*C + HO2	2.51E+55	−14.89	31072	0.0001	*a*
C3•COOH = C2C*C + HO2	2.89E+56	−14.91	31108	0.001	*a*
C3•COOH = C2C*C + HO2	9.79E+57	−15.06	31421	0.01	*a*
C3•COOH = C2C*C + HO2	1.47E+61	−15.74	32749	0.079	*a*
C3•COOH = C2C*C + HO2	1.27E+65	−16.54	35469	1	*a*
C3•COOH = C2C*C + HO2	1.94E+61	−14.98	35911	10	*a*
C3•COOH = C2CYC2O + OH	1.03E+54	−14.72	31069	0.0001	*a*
C3•COOH = C2CYC2O + OH	1.19E+55	−14.73	31105	0.001	*a*
C3•COOH = C2CYC2O + OH	4.02E+56	−14.89	31418	0.01	*a*
C3•COOH = C2CYC2O + OH	5.94E+59	−15.56	32745	0.079	*a*
C3•COOH = C2CYC2O + OH	4.62E+63	−16.35	35455	1	*a*
C3•COOH = C2CYC2O + OH	4.92E+59	−14.74	35861	10	*a*
C3•COOH = C*C(C)Q + CH3	1.54E+42	−13.33	38434	0.0001	*a*
C3•COOH = C*C(C)Q + CH3	1.68E+43	−13.34	38367	0.001	*a*
C3•COOH = C*C(C)Q + CH3	7.95E+44	−13.53	38000	0.01	*a*
C3•COOH = C*C(C)Q + CH3	7.17E+51	−15.21	38806	0.079	*a*
C3•COOH = C*C(C)Q + CH3	3.85E+66	−18.58	45141	1	*a*
C3•COOH = C*C(C)Q + CH3	2.68E+71	−18.84	51500	10	*a*
C3C• + HO2 = C3COOH	1.25E+87	−28.46	16417	0.0001	*a*
C3C• + HO2 = C3COOH	2.40E+93	−29.42	17029	0.001	*a*
C3C• + HO2 = C3COOH	5.68E+100	−30.46	19703	0.01	*a*
C3C• + HO2 = C3COOH	5.10E+102	−29.9	23042	0.079	*a*
C3C• + HO2 = C3COOH	4.40E+91	−25.31	23617	1	*a*
C3C• + HO2 = C3COOH	7.09E+63	−16.03	16793	10	*a*
C3C• + HO2 = C3CO• + OH	2.01E+13	0	1	0.0001	*a*
C3C• + HO2 = C3CO• + OH	2.01E+13	0	1	0.001	*a*
C3C• + HO2 = C3CO• + OH	2.08E+13	−0.01	8	0.01	*a*
C3C• + HO2 = C3CO• + OH	4.62E+14	−0.41	631	0.079	*a*
C3C• + HO2 = C3CO• + OH	1.49E+27	−4.12	7000	1	*a*
C3C• + HO2 = C3CO• + OH	1.09E+29	−4.45	10900	10	*a*
C3COOH = C3CO• + OH	6.71E+91	−24.81	66151	0.0001	*a*
C3COOH = C3CO• + OH	3.08E+85	−22.44	65835	0.001	*a*
C3COOH = C3CO• + OH	2.06E+74	−18.63	63592	0.01	*a*
C3COOH = C3CO• + OH	8.01E+57	−13.33	58764	0.079	*a*
C3COOH = C3CO• + OH	8.57E+35	−6.37	51464	1	*a*
C3COOH = C3CO• + OH	1.48E+22	−2.05	46620	10	*a*
C3CO• = C2C*O + CH3	1.65E+30	−6.31	21178	0.0001	*a*
C3CO• = C2C*O + CH3	7.11E+31	−6.48	21558	0.001	*a*
C3CO• = C2C*O + CH3	3.58E+59	−13.75	38110	0.01	*a*
C3CO• = C2C*O + CH3	2.40E+62	−13.94	41560	0.079	*a*
C3CO• = C2C*O + CH3	5.73E+37	−8.91	12887	1	*a*
C3CO• = C2C*O + CH3	5.13E+45	−10.92	17112	10	*a*
C3C• + C3COO• = C3COOCC3	2.15E+177	−58.75	38031	0.0001	*a*
C3C• + C3COO• = C3COOCC3	8.88E+198	−64.26	44644	0.001	*a*
C3C• + C3COO• = C3COOCC3	1.19E+218	−68.63	53622	0.01	*a*
C3C• + C3COO• = C3COOCC3	2.40E+221	−68.17	59541	0.079	*a*
C3C• + C3COO• = C3COOCC3	8.81E+197	−59.25	58278	1	*a*
C3C• + C3COO• = C3COOCC3	4.09E+140	−40.37	42894	10	*a*
C3C• + C3COO• = C3CO• + C3CO•	1.00E+13	0	0	0.0001	*a*
C3C• + C3COO• = C3CO• + C3CO•	1.00E+13	0	0	0.001	*a*
C3C• + C3COO• = C3CO• + C3CO•	1.02E+13	0	5	0.01	*a*
C3C• + C3COO• = C3CO• + C3CO•	7.93E+13	−0.27	406	0.079	*a*
C3C• + C3COO• = C3CO• + C3CO•	4.52E+27	−4.4	6833	1	*a*
C3C• + C3COO• = C3CO• + C3CO•	1.85E+46	−9.84	17253	10	*a*
C3COOCC3 = C3CO• + C3CO•	2.83E+105	−29.71	56380	0.0001	*a*
C3COOCC3 = C3CO• + C3CO•	3.66E+114	−32	62489	0.001	*a*
C3COOCC3 = C3CO• + C3CO•	9.88E+115	−31.93	65877	0.01	*a*
C3COOCC3 = C3CO• + C3CO•	1.41E+105	−28.18	64167	0.079	*a*
C3COOCC3 = C3CO• + C3CO•	1.31E+75	−18.54	54983	1	*a*
C3COOCC3 = C3CO• + C3CO•	3.70E+43	−8.6	44127	10	*a*
C2C*C + C3COO• = C2C•COOTB	9.54E+146	−47.1	34366	0.0001	*a*
C2C*C + C3COO• = C2C•COOTB	2.63E+02	0.78	−5471	0.001	*a*
C2C*C + C3COO• = C2C•COOTB	1.13E+20	−4.16	2943	0.01	*a*
C2C*C + C3COO• = C2C•COOTB	1.18E+178	−55.6	47179	0.079	*a*
C2C*C + C3COO• = C2C•COOTB	1.44E+228	−70.36	69388	1	*a*
C2C*C + C3COO• = C2C•COOTB	4.67E+286	−87.61	96483	10	*a*
C2C*C + C3COO• = C2CYC2O + C3CO•	8.43E+10	−0.01	19293	0.0001	*a*
C2C*C + C3COO• = C2CYC2O + C3CO•	1.23E+11	−0.06	19369	0.001	*a*
C2C*C + C3COO• = C2CYC2O + C3CO•	3.03E+12	−0.48	20020	0.01	*a*

TABLE 4. (Continued)

reactions	*A*	*n*	E_a	atm	
C2C*C + C3COO• = C2CYC2O + C3CO•	1.31E+12	−0.37	19826	0.079	*a*
C2C*C + C3COO• = C2CYC2O + C3CO•	5.07E+33	−6.89	29535	1	*a*
C2C*C + C3COO• = C2CYC2O + C3CO•	4.06E+82	−21.57	52409	10	*a*
C2C•COOTB = C2CYC2O + C3CO•	6.37E+136	−36.48	103499	0.0001	*a*
C2C•COOTB = C2CYC2O + C3CO•	3.03E−10	4.61	9115	0.001	*a*
C2C•COOTB = C2CYC2O + C3CO•	7.58E−7	3.89	10242	0.01	*a*
C2C•COOTB = C2CYC2O + C3CO•	2.01E+37	−10	23453	0.079	*a*
C2C•COOTB = C2CYC2O + C3CO•	8.85E+55	−14.82	34288	1	*a*
C2C•COOTB = C2CYC2O + C3CO•	2.36E+51	−12.7	36418	10	*a*
C2C*C = CC•*C + CH3	6.22E+52	−11.28	110189	0.0001	*a*
C2C*C = CC•*C + CH3	5.57E+40	−7.39	106603	0.001	*a*
C2C*C = CC•*C + CH3	6.08E+28	−3.6	102620	0.01	*a*
C2C*C = CC•*C + CH3	1.35E+21	−1.2	99935	0.079	*a*
C2C*C = CC•*C + CH3	4.50E+19	−0.74	99409	1	*a*
C2C*C = CC•*C + CH3	4.24E+19	−0.73	99399	10	*a*
C3•COH = C2C*C + OH	7.72E+70	−19.3	43211	0.0001	*a*
C3•COH = C2C*C + OH	3.19E+73	−19.68	45792	0.001	*a*
C3•COH = C2C*C + OH	1.02E+72	−18.77	47303	0.01	*a*
C3•COH = C2C*C + OH	6.95E+64	−16.2	46542	0.079	*a*
C3•COH = C2C*C + OH	2.33E+45	−9.88	40934	1	*a*
C3•COH = C2C*C + OH	8.95E+26	−4.05	34746	10	*a*
C3•COH + O2 = C2COHCQ•	2.01E+127	−38.45	29686	0.0001	*a*
C3•COH + O2 = C2COHCQ•	6.84E+132	−39.52	33535	0.001	*a*
C3•COH + O2 = C2COHCQ•	4.08E+133	−39.02	36892	0.01	*a*
C3•COH + O2 = C2COHCQ•	1.23E+119	−33.89	34762	0.079	*a*
C3•COH + O2 = C2COHCQ•	1.10E+79	−20.94	22911	1	*a*
C3•COH + O2 = C2COHCQ•	1.70E+40	−8.67	9804	10	*a*
C3•COH + O2 = C2CO•CQ	4.69E+105	−33.9	25391	0.0001	*a*
C3•COH + O2 = C2CO•CQ	1.56E+111	−34.96	29236	0.001	*a*
C3•COH + O2 = C2CO•CQ	6.84E+111	−34.43	32528	0.01	*a*
C3•COH + O2 = C2CO•CQ	2.11E+96	−29	29917	0.079	*a*
C3•COH + O2 = C2CO•CQ	2.74E+47	−13.41	13695	1	*a*
C3•COH + O2 = C2CO•CQ	1.57E−17	6.36	−12891	10	*a*
C3•COH + O2 = C2C*O + C•H2OOH	9.03E+27	−5.17	3727	0.0001	*a*
C3•COH + O2 = C2C*O + C•H2OOH	2.44E+31	−6.2	5320	0.001	*a*
C3•COH + O2 = C2C*O + C•H2OOH	1.37E+43	−9.7	11132	0.01	*a*
C3•COH + O2 = C2C*O + C•H2OOH	2.03E+52	−12.31	17167	0.079	*a*
C3•COH + O2 = C2C*O + C•H2OOH	6.75E+38	−7.88	15753	1	*a*
C3•COH + O2 = C2C*O + C•H2OOH	3.73E+09	1.22	7228	10	*a*
C3•COH + O2 = C2•COHCQ	3.76E+102	−32.29	19941	0.0001	*a*
C3•COH + O2 = C2•COHCQ	6.25E+101	−31.54	19819	0.001	*a*
C3•COH + O2 = C2•COHCQ	2.60E+97	−29.67	18536	0.01	*a*
C3•COH + O2 = C2•COHCQ	9.82E+104	−31.5	22615	0.079	*a*
C3•COH + O2 = C2•COHCQ	2.72E+165	−49.2	51407	1	*a*
C3•COH + O2 = C2•COHCQ	1.49E+193	−56.79	69860	10	*a*
C3•COH + O2 = C*C(C)CQ + OH	5.32E+28	−5.09	19402	0.0001	*a*
C3•COH + O2 = C*C(C)CQ + OH	5.67E+28	−5.1	19415	0.001	*a*
C3•COH + O2 = C*C(C)CQ + OH	1.49E+29	−5.23	19610	0.01	*a*
C3•COH + O2 = C*C(C)CQ + OH	1.72E+34	−6.75	21982	0.079	*a*
C3•COH + O2 = C*C(C)CQ + OH	1.89E+59	−14.15	35029	1	*a*
C3•COH + O2 = C*C(C)CQ + OH	7.39E+51	−11.44	38184	10	*a*
C3•COH + O2 = C*C(C)OH + C•H2OOH	4.60E+23	−3.36	14509	0.0001	*a*
C3•COH + O2 = C*C(C)OH + C•H2OOH	5.87E+23	−3.39	14558	0.001	*a*
C3•COH + O2 = C*C(C)OH + C•H2OOH	1.25E+25	−3.79	15179	0.01	*a*
C3•COH + O2 = C*C(C)OH + C•H2OOH	6.31E+33	−6.4	19321	0.079	*a*
C3•COH + O2 = C*C(C)OH + C•H2OOH	2.08E+59	−13.9	33221	1	*a*
C3•COH + O2 = C*C(C)OH + C•H2OOH	4.57E+47	−9.87	34953	10	*a*
C2COHCQ• = C2CO•CQ	5.74E+44	−11.72	24317	0.0001	*a*
C2COHCQ• = C2CO•CQ	6.06E+53	−14.07	29754	0.001	*a*
C2COHCQ• = C2CO•CQ	2.41E+55	−14.15	32686	0.01	*a*
C2COHCQ• = C2CO•CQ	1.37E+44	−10.38	30150	0.079	*a*
C2COHCQ• = C2CO•CQ	4.64E+23	−3.88	23457	1	*a*
C2COHCQ• = C2CO•CQ	8.08E+10	0.12	18939	10	*a*
C2COHCQ• = C2•COHCQ	3.88E+48	−13.27	27073	0.0001	*a*
C2COHCQ• = C2•COHCQ	2.32E+60	−16.32	33905	0.001	*a*
C2COHCQ• = C2•COHCQ	2.73E+65	−17.31	38772	0.01	*a*
C2COHCQ• = C2•COHCQ	1.49E+55	−13.73	37241	0.079	*a*
C2COHCQ• = C2•COHCQ	1.31E+31	−6.04	29697	1	*a*
C2COHCQ• = C2•COHCQ	8.52E+13	−0.64	23692	10	*a*
C2CO•CQ = C2C*O + C•H2OOH	5.60E+37	−8.81	24699	0.0001	*a*
C2CO•CQ = C2C*O + C•H2OOH	6.13E+38	−8.82	24719	0.001	*a*
C2CO•CQ = C2C*O + C•H2OOH	1.53E+40	−8.94	24922	0.01	*a*
C2CO•CQ = C2C*O + C•H2OOH	5.30E+44	−9.99	26753	0.079	*a*
C2CO•CQ = C2C*O + C•H2OOH	9.02E+46	−9.99	29439	1	*a*

TABLE 4. (Continued)

reactions	*A*	*n*	E_a	atm	
C2CO•CQ = C2C*O + C•H2OOH	1.49E−102	34.84	−36998	10	*a*
C2•COHCQ = C*C(C)CQ + OH	2.38E+67	−19.72	60338	0.0001	*a*
C2•COHCQ = C*C(C)CQ + OH	7.57E−101	31.92	−8444	0.001	*a*
C2•COHCQ = C*C(C)CQ + OH	1.64E+18	−5.95	19687	0.01	*a*
C2•COHCQ = C*C(C)CQ + OH	2.76E+53	−15.53	32699	0.079	*a*
C2•COHCQ = C*C(C)CQ + OH	5.73E+75	−20.47	48155	1	*a*
C2•COHCQ = C*C(C)CQ + OH	5.48E+50	−11.59	44722	10	*a*
C2•COHCQ = C*C(C)OH + C•H2OOH	1.92E+67	−19.14	56053	0.0001	*a*
C2•COHCQ = C*C(C)OH + C•H2OOH	1.43E−101	32.74	−12532	0.001	*a*
C2•COHCQ = C*C(C)OH + C•H2OOH	9.60E+21	−6.48	18337	0.01	*a*
C2•COHCQ = C*C(C)OH + C•H2OOH	1.21E+52	−14.55	30329	0.079	*a*
C2•COHCQ = C*C(C)OH + C•H2OOH	1.31E+70	−18.42	43658	1	*a*
C2•COHCQ = C*C(C)OH + C•H2OOH	1.79E+43	−9.12	38836	10	*a*
C•H2OOH = CH2O + OH	4.37E+13	−1.39	2254	0.0001	*a*
C•H2OOH = CH2O + OH	1.70E+16	−1.87	2996	0.001	*a*
C•H2OOH = CH2O + OH	6.28E+18	−2.29	4280	0.01	*a*
C•H2OOH = CH2O + OH	2.65E+30	−5.79	8785	0.079	*a*
C•H2OOH = CH2O + OH	4.24E−58	21.27	−26060	1	*a*
C•H2OOH = CH2O + OH	1.62E+09	0.96	−879	10	*a*
C2C*C + OH = C2C•COH	1.39E+79	−22.16	16482	0.0001	*a*
C2C*C + OH = C2C•COH	1.11E+81	−22.35	18621	0.001	*a*
C2C*C + OH = C2C•COH	2.19E+79	−21.4	19898	0.01	*a*
C2C*C + OH = C2C•COH	5.83E+70	−18.4	18539	0.079	*a*
C2C*C + OH = C2C•COH	9.10E+48	−11.34	12146	1	*a*
C2C*C + OH = C2C•COH	2.39E+27	−4.52	4845	10	*a*
C2C•COH + O2 = C2CQ•COH	9.46E+146	−45.02	34219	0.0001	*a*
C2C•COH + O2 = C2CQ•COH	1.34E+154	−46.36	39998	0.001	*a*
C2C•COH + O2 = C2CQ•COH	2.50E+151	−44.73	42450	0.01	*a*
C2C•COH + O2 = C2CQ•COH	4.53E+137	−39.86	40451	0.079	*a*
C2C•COH + O2 = C2CQ•COH	2.37E+103	−28.66	30908	1	*a*
C2C•COH + O2 = C2CQ•COH	8.98E+62	−15.81	17692	10	*a*
C2C•COH + O2 = C2CQCO•	1.20E+122	−39.23	30142	0.0001	*a*
C2C•COH + O2 = C2CQCO•	2.07E+129	−40.59	35950	0.001	*a*
C2C•COH + O2 = C2CQCO•	3.45E+126	−38.95	38375	0.01	*a*
C2C•COH + O2 = C2CQCO•	2.39E+112	−33.96	36161	0.079	*a*
C2C•COH + O2 = C2CQCO•	9.91E+73	−21.54	24465	1	*a*
C2C•COH + O2 = C2CQCO•	2.83E+17	−3.97	2326	10	*a*
C2C•COH + O2 = C2C•OOH + CH2O	4.59E+33	−7.04	6215	0.0001	*a*
C2C•COH + O2 = C2C•OOH + CH2O	1.22E+37	−8.07	7817	0.001	*a*
C2C•COH + O2 = C2C•OOH + CH2O	2.87E+47	−11.16	12922	0.01	*a*
C2C•COH + O2 = C2C•OOH + CH2O	6.07E+57	−14.16	18979	0.079	*a*
C2C•COH + O2 = C2C•OOH + CH2O	1.28E+55	−13.05	21527	1	*a*
C2C•COH + O2 = C2C•OOH + CH2O	2.54E+33	−6.18	16415	10	*a*
C2C•COH + O2 = C2•CQCOH	5.81E+109	−34.17	22575	0.0001	*a*
C2C•COH + O2 = C2•CQCOH	1.93E+120	−36.72	28835	0.001	*a*
C2C•COH + O2 = C2•CQCOH	4.05E+127	−38.31	34512	0.01	*a*
C2C•COH + O2 = C2•CQCOH	1.45E+134	−39.73	40279	0.079	*a*
C2C•COH + O2 = C2•CQCOH	4.72E+142	−41.56	48845	1	*a*
C2C•COH + O2 = C2•CQCOH	5.11E+135	−38.66	52249	10	*a*
C2C•COH + O2 = C*C(C)Q + C•H2OH	4.87E+29	−5.61	21900	0.0001	*a*
C2C•COH + O2 = C*C(C)Q + C•H2OH	4.90E+29	−5.62	21901	0.001	*a*
C2C•COH + O2 = C*C(C)Q + C•H2OH	5.39E+29	−5.63	21920	0.01	*a*
C2C•COH + O2 = C*C(C)Q + C•H2OH	5.01E+30	−5.92	22367	0.079	*a*
C2C•COH + O2 = C*C(C)Q + C•H2OH	6.96E+42	−9.55	28192	1	*a*
C2C•COH + O2 = C*C(C)Q + C•H2OH	1.72E+63	−15.51	39823	10	*a*
C2C•COH + O2 = C*C(C)COH + HO2	7.29E+12	−0.68	423	0.0001	*a*
C2C•COH + O2 = C*C(C)COH + HO2	2.46E+16	−1.75	2049	0.001	*a*
C2C•COH + O2 = C*C(C)COH + HO2	5.06E+27	−5.13	7452	0.01	*a*
C2C•COH + O2 = C*C(C)COH + HO2	2.86E+43	−9.79	15621	0.079	*a*
C2C•COH + O2 = C*C(C)COH + HO2	8.67E+59	−14.49	26447	1	*a*
C2C•COH + O2 = C*C(C)COH + HO2	2.43E+59	−13.88	32061	10	*a*
C2C•COH + O2 = C2CQC•OH	2.75E+123	−38.6	28196	0.0001	*a*
C2C•COH + O2 = C2CQC•OH	1.80E+130	−39.85	33391	0.001	*a*
C2C•COH + O2 = C2CQC•OH	7.46E+128	−38.68	35795	0.01	*a*
C2C•COH + O2 = C2CQC•OH	3.70E+120	−35.52	35397	0.079	*a*
C2C•COH + O2 = C2CQC•OH	3.35E+106	−30.53	33676	1	*a*
C2C•COH + O2 = C2CQC•OH	3.94E+102	−28.71	36525	10	*a*
C2C•COH + O2 = C2C*COH + HO2	3.78E+17	−2.09	30	0.0001	*a*
C2C•COH + O2 = C2C*COH + HO2	8.19E+22	−3.69	2462	0.001	*a*
C2C•COH + O2 = C2C*COH + HO2	2.23E+36	−7.71	8981	0.01	*a*
C2C•COH + O2 = C2C*COH + HO2	7.12E+48	−11.36	16049	0.079	*a*
C2C•COH + O2 = C2C*COH + HO2	1.16E+52	−12.03	21189	1	*a*
C2C•COH + O2 = C2C*COH + HO2	1.06E+44	−9.24	22606	10	*a*

TABLE 4. (Continued)

reactions	*A*	*n*	E_a	atm	
C2CQ•COH = C2CQCO•	6.42E+43	−11.42	23861	0.0001	*a*
C2CQ•COH = C2CQCO•	1.03E+55	−14.44	30144	0.001	*a*
C2CQ•COH = C2CQCO•	1.64E+58	−15	33741	0.01	*a*
C2CQ•COH = C2CQCO•	1.19E+48	−11.59	31527	0.079	*a*
C2CQ•COH = C2CQCO•	1.45E+30	−5.88	25776	1	*a*
C2CQ•COH = C2CQCO•	3.00E+15	−1.27	20645	10	*a*
C2CQ•COH = C2•CQCOH	5.62E+50	−14.77	29652	0.0001	*a*
C2CQ•COH = C2•CQCOH	7.24E+70	−20.04	39877	0.001	*a*
C2CQ•COH = C2•CQCOH	5.04E+82	−22.84	48201	0.01	*a*
C2CQ•COH = C2•CQCOH	3.91E+77	−20.69	49346	0.079	*a*
C2CQ•COH = C2•CQCOH	7.26E+57	−14.17	44332	1	*a*
C2CQ•COH = C2•CQCOH	2.13E+33	−6.37	36336	10	*a*
C2CQ•COH = C2CQC•OH	1.42E+49	−13.53	27732	0.0001	*a*
C2CQ•COH = C2CQC•OH	4.04E+64	−17.6	36141	0.001	*a*
C2CQ•COH = C2CQC•OH	8.43E+72	−19.51	42561	0.01	*a*
C2CQ•COH = C2CQC•OH	1.01E+65	−16.64	42000	0.079	*a*
C2CQ•COH = C2CQC•OH	4.02E+44	−10.04	36027	1	*a*
C2CQ•COH = C2CQC•OH	4.18E+23	−3.42	28912	10	*a*
C2CQCO• = C2C•OOH + CH2O	1.17E+34	−7.66	24914	0.0001	*a*
C2CQCO• = C2C•OOH + CH2O	1.24E+35	−7.67	24931	0.001	*a*
C2CQCO• = C2C•OOH + CH2O	2.28E+36	−7.74	25110	0.01	*a*
C2CQCO• = C2C•OOH + CH2O	5.59E+39	−8.4	26760	0.079	*a*
C2CQCO• = C2C•OOH + CH2O	3.12E+22	−2.36	22117	1	*a*
C2CQCO• = C2C•OOH + CH2O	8.56E+25	−4.8	12034	10	*a*
C2•CQCOH = C*C(C)Q + C•H2OH	7.76E−155	48.17	−31728	0.0001	*a*
C2•CQCOH = C*C(C)Q + C•H2OH	7.76E−155	48.17	−31728	0.0001	*a*
C2•CQCOH = C*C(C)Q + C•H2OH	1.17E+15	−2.29	28185	0.001	*a*
C2•CQCOH = C*C(C)Q + C•H2OH	2.46E+30	−9.09	27985	0.01	*a*
C2•CQCOH = C*C(C)Q + C•H2OH	3.17E+47	−13.6	33008	0.079	*a*
C2•CQCOH = C*C(C)Q + C•H2OH	1.57E+69	−19.04	43439	1	*a*
C2•CQCOH = C*C(C)Q + C•H2OH	3.98E+76	−20.23	50875	10	*a*
C2•CQCOH = C*C(C)COH + HO2	6.54E−120	39.68	−34602	0.0001	*a*
C2•CQCOH = C*C(C)COH + HO2	2.80E+42	−11.14	17634	0.001	*a*
C2•CQCOH = C*C(C)COH + HO2	5.43E+39	−9.64	20187	0.01	*a*
C2•CQCOH = C*C(C)COH + HO2	4.36E+47	−11.74	24089	0.079	*a*
C2•CQCOH = C*C(C)COH + HO2	9.11E+54	−13.54	28931	1	*a*
C2•CQCOH = C*C(C)COH + HO2	6.93E+49	−11.58	29096	10	*a*
C2CQC•OH = C2C*COH + HO2	9.00E+69	−17.15	46143	0.0001	*a*
C2CQC•OH = C2C*COH + HO2	8.26E+42	−11.38	16606	0.001	*a*
C2CQC•OH = C2C*COH + HO2	2.10E+29	−6.53	14318	0.01	*a*
C2CQC•OH = C2C*COH + HO2	2.06E+36	−8.35	17961	0.079	*a*
C2CQC•OH = C2C*COH + HO2	1.14E+47	−11.22	23992	1	*a*
C2CQC•OH = C2C*COH + HO2	1.32E+48	−11.13	26666	10	*a*
C2C•OOH = C2C*O + OH	5.74E+13	−0.45	4787	0.0001	*a*
C2C•OOH = C2C*O + OH	3.01E+33	−6.37	13083	0.001	*a*
C2C•OOH = C2C*O + OH	3.98E+11	0.05	1392	0.01	*a*
C2C•OOH = C2C*O + OH	1.53E+12	−0.15	982	0.079	*a*
C2C•OOH = C2C*O + OH	5.56E+16	−1.02	6207	1	*a*
C2C•OOH = C2C*O + OH	1.92E−68	24.39	−30338	10	*a*
C2C*C + HO2 = C*C(C)Q + CH3	4.87E+10	0.43	29194	0.0001	*a*
C2C*C + HO2 = C*C(C)Q + CH3	4.87E+10	0.43	29194	0.001	*a*
C2C*C + HO2 = C*C(C)Q + CH3	4.87E+10	0.43	29194	0.01	*a*
C2C*C + HO2 = C*C(C)Q + CH3	4.86E+10	0.43	29193	0.079	*a*
C2C*C + HO2 = C*C(C)Q + CH3	1.46E+11	0.29	29411	1	*a*
C2C*C + HO2 = C*C(C)Q + CH3	4.42E+20	−2.54	34148	10	*a*
C2C*C + HO2 = C2CYC2O + OH (via TS3)	9.19E+02	2.2	7821	0.0001	*a*
C2C*C + HO2 = C2CYC2O + OH (via TS3)	4.80E+03	1.99	8151	0.001	*a*
C2C*C + HO2 = C2CYC2O + OH (via TS3)	7.33E+06	1.03	9634	0.01	*a*
C2C*C + HO2 = C2CYC2O + OH (via TS3)	6.26E+14	−1.34	13441	0.079	*a*
C2C*C + HO2 = C2CYC2O + OH (via TS3)	4.62E+30	−6.02	21899	1	*a*
C2C*C + HO2 = C2CYC2O + OH (via TS3)	1.79E+30	−5.61	25216	10	*a*
C*C(C)Q = C2•C*O + OH	5.56E−118	38.81	−36437	0.0001	*a*
C*C(C)Q = C2•C*O + OH	3.11E−117	38.89	−36523	0.001	*a*
C*C(C)Q = C2•C*O + OH	7.54E−119	39.71	−37410	0.01	*a*
C*C(C)Q = C2•C*O + OH	8.42E−233	75.89	−76671	0.079	*a*
C*C(C)Q = C2•C*O + OH	1.98E−316	101.12	−115250	1	*a*
C*C(C)Q = C2•C*O + OH	2.67E+28	−5.4	13111	10	*a*
C2C*C + HO2 = C2C•COOH	2.24E+93	−27.54	33502	0.0001	*a*
C2C*C + HO2 = C2C•COOH	7.04E+100	−29.37	38284	0.001	*a*
C2C*C + HO2 = C2C•COOH	1.21E+103	−29.52	41850	0.01	*a*
C2C*C + HO2 = C2C•COOH	8.33E+89	−24.99	39507	0.079	*a*
C2C*C + HO2 = C2C•COOH	3.57E+48	−11.82	26159	1	*a*
C2C*C + HO2 = C2C•COOH	9.68E+15	−1.62	14630	10	*a*

TABLE 4. (Continued)

reactions	*A*	*n*	E_a	atm	
C2C*C + HO2 = C2C*CQ + H	1.79E+21	−2.99	37469	0.0001	*a*
C2C*C + HO2 = C2C*CQ + H	1.79E+21	−2.99	37469	0.001	*a*
C2C*C + HO2 = C2C*CQ + H	1.95E+21	−3	37486	0.01	*a*
C2C*C + HO2 = C2C*CQ + H	2.35E+25	−4.23	39371	0.079	*a*
C2C*C + HO2 = C2C*CQ + H	1.00E+40	−8.49	47834	1	*a*
C2C*C + HO2 = C2C*CQ + H	4.04E+18	−1.76	42539	10	*a*
C2C*C + HO2 = C*C(C)CQ + H	1.29E+21	−2.75	36710	0.0001	*a*
C2C*C + HO2 = C*C(C)CQ + H	1.28E+21	−2.75	36710	0.001	*a*
C2C*C + HO2 = C*C(C)CQ + H	1.45E+21	−2.77	36733	0.01	*a*
C2C*C + HO2 = C*C(C)CQ + H	4.66E+25	−4.12	38820	0.079	*a*
C2C*C + HO2 = C*C(C)CQ + H	1.02E+40	−8.28	47241	1	*a*
C2C*C + HO2 = C*C(C)CQ + H	9.43E+17	−1.36	41692	10	*a*
C2C*C + HO2 = C2CYC2O + OH (via TS5)	1.02E+08	0.72	12825	0.0001	*a*
C2C*C + HO2 = C2CYC2O + OH (via TS5)	1.37E+17	−2.01	17187	0.001	*a*
C2C*C + HO2 = C2CYC2O + OH (via TS5)	6.02E+32	−6.64	25288	0.01	*a*
C2C*C + HO2 = C2CYC2O + OH (via TS5)	1.51E+40	−8.66	31180	0.079	*a*
C2C*C + HO2 = C2CYC2O + OH (via TS5)	1.48E+14	−0.41	25014	1	*a*
C2C*C + HO2 = C2CYC2O + OH (via TS5)	2.58E−23	10.88	12862	10	*a*
C2C*C + HO2 = C2CCOO$^{\bullet}$ (via TS7)	1.67E+97	−28.49	39425	0.0001	*a*
C2C*C + HO2 = C2CCOO$^{\bullet}$ (via TS7)	2.87E+99	−28.77	42991	0.001	*a*
C2C*C + HO2 = C2CCOO$^{\bullet}$ (via TS7)	2.26E+98	−27.95	46371	0.01	*a*
C2C*C + HO2 = C2CCOO$^{\bullet}$ (via TS7)	1.36E+85	−23.41	45517	0.079	*a*
C2C*C + HO2 = C2CCOO$^{\bullet}$ (via TS7)	1.38E+40	−9.1	33131	1	*a*
C2C*C + HO2 = C2CCOO$^{\bullet}$ (via TS7)	6.04E−08	5.59	17720	10	*a*
C2C*C + HO2 = C2C*C + HO2	6.17E+13	−2.32	17955	0.0001	*a*
C2C*C + HO2 = C2C*C + HO2	2.23E+25	−5.74	24034	0.001	*a*
C2C*C + HO2 = C2C*C + HO2	5.94E+40	−10.22	33026	0.01	*a*
C2C*C + HO2 = C2C*C + HO2	9.55E+49	−12.71	40928	0.079	*a*
C2C*C + HO2 = C2C*C + HO2	1.50E+33	−7.09	41050	1	*a*
C2C*C + HO2 = C2C*C + HO2	4.48E−06	4.93	31379	10	*a*
C2C*C + HO2 = C3$^{\bullet}$C + O2	1.22E+20	−3.33	17975	0.0001	*a*
C2C*C + HO2 = C3$^{\bullet}$C + O2	4.43E+31	−6.75	24062	0.001	*a*
C2C*C + HO2 = C3$^{\bullet}$C + O2	1.09E+47	−11.22	33047	0.01	*a*
C2C*C + HO2 = C3$^{\bullet}$C + O2	1.57E+56	−13.69	40934	0.079	*a*
C2C*C + HO2 = C3$^{\bullet}$C + O2	2.20E+39	−8.05	41036	1	*a*
C2C*C + HO2 = C3$^{\bullet}$C + O2	6.23E+00	3.97	31354	10	*a*
C2C*C + HO2 = C2$^{\bullet}$CCOOH	6.13E+78	−24.29	33562	0.0001	*a*
C2C*C + HO2 = C2$^{\bullet}$CCOOH	4.31E+77	−23.61	34976	0.001	*a*
C2C*C + HO2 = C2$^{\bullet}$CCOOH	3.34E+70	−21.12	33900	0.01	*a*
C2C*C + HO2 = C2$^{\bullet}$CCOOH	4.33E+60	−17.86	31015	0.079	*a*
C2C*C + HO2 = C2$^{\bullet}$CCOOH	3.85E+94	−27.76	48551	1	*a*
C2C*C + HO2 = C2$^{\bullet}$CCOOH	8.05E+117	−34.19	65872	10	*a*
C2C*C + HO2 = C*CC + C$^{\bullet}$H2OOH	6.42E+18	−2.9	28260	0.0001	*a*
C2C*C + HO2 = C*CC + C$^{\bullet}$H2OOH	6.11E+18	−2.89	28233	0.001	*a*
C2C*C + HO2 = C*CC + C$^{\bullet}$H2OOH	1.48E+26	−5.11	31623	0.01	*a*
C2C*C + HO2 = C*CC + C$^{\bullet}$H2OOH	1.95E+48	−11.65	43132	0.079	*a*
C2C*C + HO2 = C*CC + C$^{\bullet}$H2OOH	4.99E+49	−11.45	51770	1	*a*
C2C*C + HO2 = C*CC + C$^{\bullet}$H2OOH	2.79E−01	4.4	40515	10	*a*
C2C$^{\bullet}$COOH = C2C*CQ + H	6.42E+32	−11.7	38173	0.0001	*a*
C2C$^{\bullet}$COOH = C2C*CQ + H	1.80E+50	−16.46	40395	0.001	*a*
C2C$^{\bullet}$COOH = C2C*CQ + H	3.91E+84	−25.75	52880	0.01	*a*
C2C$^{\bullet}$COOH = C2C*CQ + H	6.40E+101	−29.57	64157	0.079	*a*
C2C$^{\bullet}$COOH = C2C*CQ + H	1.87E+81	−21.82	63259	1	*a*
C2C$^{\bullet}$COOH = C2C*CQ + H	3.13E+33	−6.44	48692	10	*a*
C2C$^{\bullet}$COOH = C*C(C)CQ + H	5.21E+33	−11.71	37701	0.0001	*a*
C2C$^{\bullet}$COOH = C*C(C)CQ + H	2.47E+51	−16.54	40101	0.001	*a*
C2C$^{\bullet}$COOH = C*C(C)CQ + H	2.13E+85	−25.71	52655	0.01	*a*
C2C$^{\bullet}$COOH = C*C(C)CQ + H	5.12E+101	−29.29	63633	0.079	*a*
C2C$^{\bullet}$COOH = C*C(C)CQ + H	5.52E+80	−21.44	62450	1	*a*
C2C$^{\bullet}$COOH = C*C(C)CQ + H	1.52E+33	−6.15	47869	10	*a*
C2C$^{\bullet}$COOH = C2CYC2O + OH	7.02E+46	−12.62	26199	0.0001	*a*
C2C$^{\bullet}$COOH = C2CYC2O + OH	1.10E+54	−14.4	30249	0.001	*a*
C2C$^{\bullet}$COOH = C2CYC2O + OH	5.67E+59	−15.71	34554	0.01	*a*
C2C$^{\bullet}$COOH = C2CYC2O + OH	1.42E+55	−13.91	34937	0.079	*a*
C2C$^{\bullet}$COOH = C2CYC2O + OH	1.30E+32	−6.48	28010	1	*a*
C2C$^{\bullet}$COOH = C2CYC2O + OH	7.28E+12	−0.43	21315	10	*a*
C2C$^{\bullet}$COOH = C2CCOO$^{\bullet}$	1.89E+45	−12.33	26065	0.0001	*a*
C2C$^{\bullet}$COOH = C2CCOO$^{\bullet}$	4.72E+51	−13.91	29722	0.001	*a*
C2C$^{\bullet}$COOH = C2CCOO$^{\bullet}$	3.18E+56	−15	33428	0.01	*a*
C2C$^{\bullet}$COOH = C2CCOO$^{\bullet}$	4.33E+51	−13.18	33382	0.079	*a*
C2C$^{\bullet}$COOH = C2CCOO$^{\bullet}$	6.60E+30	−6.5	26976	1	*a*
C2C$^{\bullet}$COOH = C2CCOO$^{\bullet}$	3.51E+14	−1.39	21287	10	*a*

TABLE 4. (Continued)

reactions	*A*	*n*	E_a	atm	
C2CCOO• = C2C*C + HO2 (via TS9)	2.13E+69	−20.76	43611	0.0001	*a*
C2CCOO• = C2C*C + HO2 (via TS9)	6.77E+81	−23.52	51859	0.001	*a*
C2CCOO• = C2C*C + HO2 (via TS9)	1.19E+78	−21.55	54150	0.01	*a*
C2CCOO• = C2C*C + HO2 (via TS9)	7.81E+67	−17.93	52785	0.079	*a*
C2CCOO• = C2C*C + HO2 (via TS9)	1.01E+47	−11.09	47036	1	*a*
C2CCOO• = C2C*C + HO2 (via TS9)	1.40E+24	−3.85	39463	10	*a*
C2CCOO• = C3•C + O2	3.41E+75	−21.74	43611	0.0001	*a*
C2CCOO• = C3•C + O2	9.80E+87	−24.49	51841	0.001	*a*
C2CCOO• = C3•C + O2	1.66E+84	−22.51	54123	0.01	*a*
C2CCOO• = C3•C + O2	1.04E+74	−18.88	52747	0.079	*a*
C2CCOO• = C3•C + O2	1.31E+53	−12.05	46990	1	*a*
C2CCOO• = C3•C + O2	1.89E+30	−4.81	39420	10	*a*
C2CCOO• = C2•CCOOH	9.36E+58	−15.86	34101	0.0001	*a*
C2CCOO• = C2•CCOOH	3.15E+60	−15.89	37039	0.001	*a*
C2CCOO• = C2•CCOOH	6.69E+48	−11.95	34506	0.01	*a*
C2CCOO• = C2•CCOOH	1.36E+35	−7.57	30222	0.079	*a*
C2CCOO• = C2•CCOOH	1.02E+20	−2.81	25048	1	*a*
C2CCOO• = C2•CCOOH	2.38E+10	0.21	21608	10	*a*
C2•CCOOH = C*CC + C•H2OOH	4.26E−147	46.4	−34596	0.0001	*a*
C2•CCOOH = C*CC + C•H2OOH	4.94E−324	101.83	−99710	0.001	*a*
C2•CCOOH = C*CC + C•H2OOH	1.24E−278	87.32	−91429	0.01	*a*
C2•CCOOH = C*CC + C•H2OOH	1.35E+34	−8.51	24995	0.079	*a*
C2•CCOOH = C*CC + C•H2OOH	2.60E+35	−7.29	31540	1	*a*
C2•CCOOH = C*CC + C•H2OOH	8.66E+29	−5.12	31842	10	*a*
C2C*CQ = C2C•C*O + OH	3.93E−304	96.22	−107080	0.0001	*a*
C2C*CQ = C2C•C*O + OH	1.94E−294	93.55	−103420	0.001	*a*
C2C*CQ = C2C•C*O + OH	9.90E+40	−10.02	21509	0.01	*a*
C2C*CQ = C2C•C*O + OH	2.94E+48	−12	25039	0.079	*a*
C2C*CQ = C2C•C*O + OH	2.11E+57	−14.27	29910	1	*a*
C2C*CQ = C2C•C*O + OH	1.57E+63	−15.64	34168	10	*a*
C3•C + HO2 = C2CCOOH	7.24E+85	−27.89	15621	0.0001	*a*
C3•C + HO2 = C2CCOOH	1.32E+92	−28.84	16332	0.001	*a*
C3•C + HO2 = C2CCOOH	2.17E+99	−29.85	19309	0.01	*a*
C3•C + HO2 = C2CCOOH	9.27E+99	−28.92	22364	0.079	*a*
C3•C + HO2 = C2CCOOH	7.50E+86	−23.74	22289	1	*a*
C3•C + HO2 = C2CCOOH	2.40E+58	−14.28	15050	10	*a*
C3•C + HO2 = C2CCO• + OH	2.04E+13	0	3	0.0001	*a*
C3•C + HO2 = C2CCO• + OH	2.04E+13	0	3	0.001	*a*
C3•C + HO2 = C2CCO• + OH	2.22E+13	−0.01	20	0.01	*a*
C3•C + HO2 = C2CCO• + OH	2.91E+15	−0.65	1003	0.079	*a*
C3•C + HO2 = C2CCO• + OH	1.01E+29	−4.66	8017	1	*a*
C3•C + HO2 = C2CCO• + OH	5.68E+27	−4.03	10757	10	*a*
C2CCOOH = C2CCO• + OH	3.30E+89	−24.07	66102	0.0001	*a*
C2CCOOH = C2CCO• + OH	1.07E+83	−21.66	65742	0.001	*a*
C2CCOOH = C2CCO• + OH	4.10E+71	−17.78	63400	0.01	*a*
C2CCOOH = C2CCO• + OH	2.54E+55	−12.54	58635	0.079	*a*
C2CCOOH = C2CCO• + OH	1.33E+34	−5.8	51565	1	*a*
C2CCOOH = C2CCO• + OH	1.89E+21	−1.77	47038	10	*a*
C2CCO• = CC•C + CH2O	6.58E−120	39.48	−36250	0.0001	*a*
C2CCO• = CC•C + CH2O	2.56E−241	78.06	−77975	0.001	*a*
C2CCO• = CC•C + CH2O	1.28E−148	48.45	−51257	0.01	*a*
C2CCO• = CC•C + CH2O	9.05E+31	−7.09	15946	0.079	*a*
C2CCO• = CC•C + CH2O	1.29E+40	−9.19	20158	1	*a*
C2CCO• = CC•C + CH2O	5.35E+46	−10.81	24491	10	*a*
C2C•COOH + O2 = C2CQ•CQ	6.52E+80	−23.89	12557	0.0001	*a*
C2C•COOH + O2 = C2CQ•CQ	9.94E+90	−26.14	19813	0.001	*a*
C2C•COOH + O2 = C2CQ•CQ	1.51E+90	−25.06	23465	0.01	*a*
C2C•COOH + O2 = C2CQ•CQ	1.43E+73	−19.18	20389	0.079	*a*
C2C•COOH + O2 = C2CQ•CQ	1.39E+30	−5.51	6250	1	*a*
C2C•COOH + O2 = C2CQ•CQ	7.15E+14	−0.72	823	10	*a*
C2C•COOH + O2 = C2CQC•Q	5.00E+30	−13.27	5239	0.0001	*a*
C2C•COOH + O2 = C2CQC•Q	2.18E+45	−16.94	13992	0.001	*a*
C2C•COOH + O2 = C2CQC•Q	1.22E+45	−16.04	17836	0.01	*a*
C2C•COOH + O2 = C2CQC•Q	1.34E+28	−10.17	14779	0.079	*a*
C2C•COOH + O2 = C2CQC•Q	1.22E−15	3.5	619	1	*a*
C2C•COOH + O2 = C2CQC•Q	2.96E−31	8.39	−5047	10	*a*
C2C•COOH + O2 = C2C*CQ + HO2	2.24E+13	−2.11	5561	0.0001	*a*
C2C•COOH + O2 = C2C*CQ + HO2	6.44E+14	−2.55	6262	0.001	*a*
C2C•COOH + O2 = C2C*CQ + HO2	1.46E+21	−4.43	9569	0.01	*a*
C2C•COOH + O2 = C2C*CQ + HO2	1.41E+20	−3.96	11374	0.079	*a*
C2C•COOH + O2 = C2C*CQ + HO2	3.05E−17	7.36	−304	1	*a*

TABLE 4. (Continued)

reactions	*A*	*n*	*E*a	atm	
C2C•COOH + O2 = C2C*CQ + HO2	9.15E−33	11.91	−5472	10	*a*
C2C•COOH + O2 = C2C(Q)C*O + OH	1.57E+08	1.28	−1405	0.0001	*a*
C2C•COOH + O2 = C2C(Q)C*O + OH	3.12E+14	−0.61	1517	0.001	*a*
C2C•COOH + O2 = C2C(Q)C*O + OH	1.01E+27	−4.31	7991	0.01	*a*
C2C•COOH + O2 = C2C(Q)C*O + OH	3.76E+24	−3.36	9716	0.079	*a*
C2C•COOH + O2 = C2C(Q)C*O + OH	1.37E−14	8.53	−2523	1	*a*
C2C•COOH + O2 = C2C(Q)C*O + OH	2.55E−30	13.14	−7760	10	*a*
C2C•COOH + O2 = C2•CQCQ	9.30E+64	−20.03	5837	0.0001	*a*
C2C•COOH + O2 = C2•CQCQ	1.80E+80	−23.99	14331	0.001	*a*
C2C•COOH + O2 = C2•CQCQ	3.74E+92	−27.06	22369	0.01	*a*
C2C•COOH + O2 = C2•CQCQ	5.71E+101	−29.27	29316	0.079	*a*
C2C•COOH + O2 = C2•CQCQ	5.54E+104	−29.57	35187	1	*a*
C2C•COOH + O2 = C2•CQCQ	1.58E+89	−24.35	33867	10	*a*
C2C•COOH + O2 = C*C(C)Q + C•H2OOH	1.35E+15	−4.85	11035	0.0001	*a*
C2C•COOH + O2 = C*C(C)Q + C•H2OOH	1.28E+15	−4.84	11040	0.001	*a*
C2C•COOH + O2 = C*C(C)Q + C•H2OOH	9.86E+16	−5.4	12115	0.01	*a*
C2C•COOH + O2 = C*C(C)Q + C•H2OOH	8.68E+16	−5.24	14154	0.079	*a*
C2C•COOH + O2 = C*C(C)Q + C•H2OOH	9.37E−13	3.9	7563	1	*a*
C2C•COOH + O2 = C*C(C)Q + C•H2OOH	3.11E−39	12.17	2328	10	*a*
C2C•COOH + O2 = C*C(C)CQ + HO2	2.69E+12	−0.16	893	0.0001	*a*
C2C•COOH + O2 = C*C(C)CQ + HO2	1.10E+17	−1.54	3057	0.001	*a*
C2C•COOH + O2 = C*C(C)CQ + HO2	3.00E+28	−4.94	8918	0.01	*a*
C2C•COOH + O2 = C*C(C)CQ + HO2	3.46E+30	−5.35	12559	0.079	*a*
C2C•COOH + O2 = C*C(C)CQ + HO2	1.89E+10	1.15	9622	1	*a*
C2C•COOH + O2 = C*C(C)CQ + HO2	3.10E−13	8.28	5860	10	*a*
C2CQ•CQ = C2•CQCQ	6.59E+58	−16.31	35832	0.0001	*a*
C2CQ•CQ = C2•CQCQ	2.94E+56	−15.56	35068	0.001	*a*
C2CQ•CQ = C2•CQCQ	2.45E+56	−15.53	35046	0.01	*a*
C2CQ•CQ = C2•CQCQ	2.41E+56	−15.53	35044	0.079	*a*
C2CQ•CQ = C2•CQCQ	2.40E+56	−15.53	35044	1	*a*
C2CQ•CQ = C2•CQCQ	2.40E+56	−15.53	35044	10	*a*
C3•COOH + O2 = C2CQCQ•	6.14E+189	−58.4	48784	0.0001	*a*
C3•COOH + O2 = C2CQCQ•	8.13E+206	−62.76	59212	0.001	*a*
C3•COOH + O2 = C2CQCQ•	3.06E+213	−63.92	65831	0.01	*a*
C3•COOH + O2 = C2CQCQ•	8.38E+205	−60.84	67053	0.079	*a*
C3•COOH + O2 = C2CQCQ•	1.50E+150	−42.93	49934	1	*a*
C3•COOH + O2 = C2CQCQ•	1.30E+71	−18.21	21594	10	*a*
C3•COOH + O2 = C2•CQCQ	5.27E+102	−32.47	19372	0.0001	*a*
C3•COOH + O2 = C2•CQCQ	2.30E+95	−29.51	18175	0.001	*a*
C3•COOH + O2 = C2•CQCQ	1.66E+72	−21.86	9959	0.01	*a*
C3•COOH + O2 = C2•CQCQ	1.49E+49	−14.34	1944	0.079	*a*
C3•COOH + O2 = C2•CQCQ	3.25E+23	−5.96	−5859	1	*a*
C3•COOH + O2 = C2•CQCQ	1.61E+27	−6.58	−182	10	*a*
C3•COOH + O2 = C*C(C)Q + C•H2OOH	1.78E+33	−8.37	18035	0.0001	*a*
C3•COOH + O2 = C*C(C)Q + C•H2OOH	1.80E+33	−8.37	18040	0.001	*a*
C3•COOH + O2 = C*C(C)Q + C•H2OOH	4.60E+33	−8.49	18274	0.01	*a*
C3•COOH + O2 = C*C(C)Q + C•H2OOH	9.59E+35	−9.14	20159	0.079	*a*
C3•COOH + O2 = C*C(C)Q + C•H2OOH	1.99E−02	2.76	9725	1	*a*
C3•COOH + O2 = C*C(C)Q + C•H2OOH	7.01E−59	20.58	−5854	10	*a*
C3•COOH + O2 = C*C(C)CQ + HO2	2.05E+11	0.32	−28	0.0001	*a*
C3•COOH + O2 = C*C(C)CQ + HO2	4.30E+16	−1.27	2459	0.001	*a*
C3•COOH + O2 = C*C(C)CQ + HO2	1.87E+29	−5.03	8791	0.01	*a*
C3•COOH + O2 = C*C(C)CQ + HO2	5.05E+36	−7.08	14404	0.079	*a*
C3•COOH + O2 = C*C(C)CQ + HO2	2.29E+04	3.28	7034	1	*a*
C3•COOH + O2 = C*C(C)CQ + HO2	1.38E−28	13.59	631	10	*a*
C3•COOH + O2 = C2CQ•CQ	9.63E+190	−58.81	49068	0.0001	*a*
C3•COOH + O2 = C2CQ•CQ	3.69E+216	−65.8	62744	0.001	*a*
C3•COOH + O2 = C2CQ•CQ	4.98E+243	−73.26	78470	0.01	*a*
C3•COOH + O2 = C2CQ•CQ	8.08E+239	−71.25	83254	0.079	*a*
C3•COOH + O2 = C2CQ•CQ	1.75E+142	−40.33	53011	1	*a*
C3•COOH + O2 = C2CQ•CQ	7.61E−15	8.21	−2882	10	*a*
C3•COOH + O2 = C2CQC•Q	4.41E+73	−26.47	22156	0.0001	*a*
C3•COOH + O2 = C2CQC•Q	3.98E+99	−33.58	35983	0.001	*a*
C3•COOH + O2 = C2CQC•Q	4.72E+125	−40.7	51366	0.01	*a*
C3•COOH + O2 = C2CQC•Q	2.13E+121	−38.52	55948	0.079	*a*
C3•COOH + O2 = C2CQC•Q	2.47E+23	−7.51	25593	1	*a*
C3•COOH + O2 = C2CQC•Q	3.47E−134	41.17	−30601	10	*a*
C3•COOH + O2 = C2C*CQ + HO2	8.94E+27	−7	9267	0.0001	*a*
C3•COOH + O2 = C2C*CQ + HO2	9.60E+30	−7.91	10691	0.001	*a*
C3•COOH + O2 = C2C*CQ + HO2	1.73E+45	−12.15	17759	0.01	*a*
C3•COOH + O2 = C2C*CQ + HO2	5.60E+51	−13.73	24930	0.079	*a*
C3•COOH + O2 = C2C*CQ + HO2	2.06E−57	20.31	−8550	1	*a*
C3•COOH + O2 = C2C*CQ + HO2	4.85E−220	70.51	−66273	10	*a*

TABLE 4. (Continued)

reactions	*A*	*n*	*E*a	atm	
C3•COOH + O2 = C2C(Q)C*O + OH	6.21E+24	−4.48	1692	0.0001	*a*
C3•COOH + O2 = C2C(Q)C*O + OH	9.39E+36	−8.13	7426	0.001	*a*
C3•COOH + O2 = C2C(Q)C*O + OH	3.40E+59	−14.75	19511	0.01	*a*
C3•COOH + O2 = C2C(Q)C*O + OH	2.45E+58	−13.87	24845	0.079	*a*
C3•COOH + O2 = C2C(Q)C*O + OH	2.84E−49	19.67	−8185	1	*a*
C3•COOH + O2 = C2C(Q)C*O + OH	1.37E−210	69.46	−65465	10	*a*
C2CQCQ• = C2•CQCQ	1.58E+39	−9.86	26541	0.0001	*a*
C2CQCQ• = C2•CQCQ	5.14E+59	−15.71	35251	0.001	*a*
C2CQCQ• = C2•CQCQ	7.19E+62	−16.43	37378	0.01	*a*
C2CQCQ• = C2•CQCQ	8.07E+62	−16.44	37411	0.079	*a*
C2CQCQ• = C2•CQCQ	8.20E+62	−16.44	37416	1	*a*
C2CQCQ• = C2•CQCQ	8.21E+62	−16.44	37416	10	*a*
C2CQCQ• = C2CQ•CQ	2.08E+34	−8.78	17023	0.0001	*a*
C2CQCQ• = C2CQ•CQ	6.50E+46	−12.34	22955	0.001	*a*
C2CQCQ• = C2CQ•CQ	2.65E+47	−12.35	24056	0.01	*a*
C2CQCQ• = C2CQ•CQ	2.87E+47	−12.36	24085	0.079	*a*
C2CQCQ• = C2CQ•CQ	2.90E+47	−12.36	24089	1	*a*
C2CQCQ• = C2CQ•CQ	2.90E+47	−12.36	24089	10	*a*
C2•CQCQ = C*C(C)Q + C•H2OOH	9.62E+00	2.02	28991	0.0001	*a*
C2•CQCQ = C*C(C)Q + C•H2OOH	9.98E−03	−1.12	22074	0.001	*a*
C2•CQCQ = C*C(C)Q + C•H2OOH	8.16E+28	−10.02	29002	0.01	*a*
C2•CQCQ = C*C(C)Q + C•H2OOH	4.30E+46	−14.45	33556	0.079	*a*
C2•CQCQ = C*C(C)Q + C•H2OOH	1.67E+68	−19.81	42904	1	*a*
C2•CQCQ = C*C(C)Q + C•H2OOH	6.77E+79	−22.75	49490	10	*a*
C2•CQCQ = C*C(C)CQ + HO2	1.39E+24	−5.43	13844	0.0001	*a*
C2•CQCQ = C*C(C)CQ + HO2	1.30E+16	−3.6	8005	0.001	*a*
C2•CQCQ = C*C(C)CQ + HO2	2.05E+36	−9.13	16427	0.01	*a*
C2•CQCQ = C*C(C)CQ + HO2	2.94E+42	−10.39	20641	0.079	*a*
C2•CQCQ = C*C(C)CQ + HO2	1.25E+52	−12.74	26945	1	*a*
C2•CQCQ = C*C(C)CQ + HO2	7.94E+53	−12.88	29799	10	*a*
C2•CQCQ = C2CQCQ•	9.49E+52	−15.63	14289	0.0001	*a*
C2•CQCQ = C2CQCQ•	8.65E+16	−3.11	7439	0.001	*a*
C2•CQCQ = C2CQCQ•	1.16E+24	−4.94	10984	0.01	*a*
C2•CQCQ = C2CQCQ•	3.70E+27	−5.74	13289	0.079	*a*
C2•CQCQ = C2CQCQ•	7.52E+30	−6.5	15828	1	*a*
C2•CQCQ = C2CQCQ•	8.84E+25	−4.8	14919	10	*a*
C2CQ•CQ = C2CQCQ•	9.15E+59	−17.02	24710	0.0001	*a*
C2CQ•CQ = C2CQCQ•	2.41E+46	−12.35	21811	0.001	*a*
C2CQ•CQ = C2CQCQ•	4.64E+46	−12.44	21915	0.01	*a*
C2CQ•CQ = C2CQCQ•	4.95E+46	−12.45	21925	0.079	*a*
C2CQ•CQ = C2CQCQ•	4.99E+46	−12.45	21927	1	*a*
C2CQ•CQ = C2CQCQ•	5.00E+46	−12.45	21927	10	*a*
C2CQ•CQ = C2CQC•Q	1.70E+60	−18.39	38009	0.0001	*a*
C2CQ•CQ = C2CQC•Q	3.16E+48	−13.01	29936	0.001	*a*
C2CQ•CQ = C2CQC•Q	4.91E+48	−13.07	29971	0.01	*a*
C2CQ•CQ = C2CQC•Q	5.12E+48	−13.07	29974	0.079	*a*
C2CQ•CQ = C2CQC•Q	5.15E+48	−13.07	29975	1	*a*
C2CQ•CQ = C2CQC•Q	5.15E+48	−13.07	29975	10	*a*
C2CQC•Q = C2C*CQ + HO2	2.80E+07	−0.76	21715	0.0001	*a*
C2CQC•Q = C2C*CQ + HO2	2.21E−38	10.46	4880	0.001	*a*
C2CQC•Q = C2C*CQ + HO2	1.18E−39	11.16	3991	0.01	*a*
C2CQC•Q = C2C*CQ + HO2	1.51E−07	1.55	16150	0.079	*a*
C2CQC•Q = C2C*CQ + HO2	2.10E−66	20.13	−6453	1	*a*
C2CQC•Q = C2C*CQ + HO2	3.36E+02	−0.77	18324	10	*a*
C2CQC•Q = C2C(Q)C*O + OH	8.95E+06	−0.46	−292	0.0001	*a*
C2CQC•Q = C2C(Q)C*O + OH	1.05E−25	9.86	−10748	0.001	*a*
C2CQC•Q = C2C(Q)C*O + OH	5.64E−27	10.56	−11637	0.01	*a*
C2CQC•Q = C2C(Q)C*O + OH	7.29E+05	0.95	525	0.079	*a*
C2CQC•Q = C2C(Q)C*O + OH	1.08E−53	19.52	−22060	1	*a*
C2CQC•Q = C2C(Q)C*O + OH	1.40E+15	−1.34	2766	10	*a*
C2CQC•Q = C2CQ•CQ	2.92E−06	0.86	−1216	0.0001	*a*
C2CQC•Q = C2CQ•CQ	1.11E−45	13.53	−2069	0.001	*a*
C2CQC•Q = C2CQ•CQ	5.94E−47	14.23	−2958	0.01	*a*
C2CQC•Q = C2CQ•CQ	7.62E−15	4.62	9202	0.079	*a*
C2CQC•Q = C2CQ•CQ	1.10E−73	23.19	−13393	1	*a*
C2CQC•Q = C2CQ•CQ	1.79E−05	2.3	11416	10	*a*
C2C(Q)C*O = C2C•C*O + HO2	7.34E+88	−27	77425	0.0001	*a*
C2C(Q)C*O = C2C•C*O + HO2	3.78E+94	−27.74	79761	0.001	*a*
C2C(Q)C*O = C2C•C*O + HO2	1.03E+99	−28.06	83840	0.01	*a*
C2C(Q)C*O = C2C•C*O + HO2	2.40E+94	−25.83	85164	0.079	*a*
C2C(Q)C*O = C2C•C*O + HO2	1.55E+76	−19.47	82069	1	*a*
C2C(Q)C*O = C2C•C*O + HO2	7.12E+47	−10.31	73630	10	*a*
C2C(Q)C*O = C2C(O•)CO + OH	4.80E+92	−25.08	66140	0.0001	*a*

TABLE 4. (Continued)

reactions	*A*	*n*	E_a	atm	
C2C(Q)C*O = C2C(O•)CO + OH	2.34E+86	−22.72	65836	0.001	*a*
C2C(Q)C*O = C2C(O•)CO + OH	1.41E+75	−18.9	63569	0.01	*a*
C2C(Q)C*O═C2C(O•)CO + OH	3.81E+58	−13.54	58685	0.079	*a*
C2C(Q)C*O═C2C(O•)CO + OH	3.51E+36	−6.56	51377	1	*a*
C2C(Q)C*O═C2C(O•)CO + OH	3.81E+22	−2.18	46469	10	*a*
C2•C*C + O2 = C*C(C)CQ•	1.21E+77	−22.53	16717	0.0001	*a*
C2•C*C + O2 = C*C(C)CQ•	5.72E+80	−23.27	18927	0.001	*a*
C2•C*C + O2 = C*C(C)CQ•	1.80E+84	−23.92	21669	0.01	*a*
C2•C*C + O2 = C*C(C)CQ•	5.51E+84	−23.66	23674	0.079	*a*
C2•C*C + O2 = C*C(C)CQ•	2.59E+75	−20.28	22772	1	*a*
C2•C*C + O2 = C*C(C)CQ•	9.21E+52	−13	16307	10	*a*
C2•C*C + O2 = C*CICC*O + OH	4.60E+08	0.6	18544	0.0001	*a*
C2•C*C + O2 = C*CICC*O + OH	4.64E+08	0.59	18545	0.001	*a*
C2•C*C + O2 = C*CICC*O + OH	4.57E+08	0.6	18544	0.01	*a*
C2•C*C + O2 = C*CICC*O + OH	4.41E+08	0.6	18538	0.079	*a*
C2•C*C + O2 = C*CICC*O + OH	2.64E+10	0.07	19362	1	*a*
C2•C*C + O2 = C*CICC*O + OH	7.48E+21	−3.32	25354	10	*a*
C2•C*C + O2 = C*C(C)CO• + O	7.41E+18	−2.16	42073	0.0001	*a*
C2•C*C + O2 = C*C(C)CO• + O	7.41E+18	−2.16	42073	0.001	*a*
C2•C*C + O2 = C*C(C)CO• + O	7.41E+18	−2.16	42073	0.01	*a*
C2•C*C + O2 = C*C(C)CO• + O	7.44E+18	−2.16	42074	0.079	*a*
C2•C*C + O2 = C*C(C)CO• + O	7.28E+18	−2.15	42070	1	*a*
C2•C*C + O2 = C*C(C)CO• + O	9.88E+18	−2.19	42130	10	*a*
C2•C*C + O2 = C*C(C•)CQ	1.71E+75	−21.25	22090	0.0001	*a*
C2•C*C + O2 = C*C(C•)CQ	3.27E+66	−18.11	21430	0.001	*a*
C2•C*C + O2 = C*C(C•)CQ	3.15E+48	−12.18	17164	0.01	*a*
C2•C*C + O2 = C*C(C•)CQ	1.73E+38	−8.76	15477	0.079	*a*
C2•C*C + O2 = C*C(C•)CQ	3.11E+37	−8.25	18388	1	*a*
C2•C*C + O2 = C*C(C•)CQ	9.38E+26	−4.79	17594	10	*a*
C2•C*C + O2 = C*CYCCOC + OH	2.18E+17	−2.28	12131	0.0001	*a*
C2•C*C + O2 = C*CYCCOC + OH	1.27E+29	−5.73	18560	0.001	*a*
C2•C*C + O2 = C*CYCCOC + OH	1.11E+24	−3.94	19820	0.01	*a*
C2•C*C + O2 = C*CYCCOC + OH	3.49E+01	3.06	13623	0.079	*a*
C2•C*C + O2 = C*CYCCOC + OH	5.91E−12	6.9	11097	1	*a*
C2•C*C + O2 = C*CYCCOC + OH	9.94E−08	5.52	15771	10	*a*
C2•C*C + O2 = C*C*C + C•H2OOH	3.16E+10	0.55	34689	0.0001	*a*
C2•C*C + O2 = C*C*C + C•H2OOH	1.99E+10	0.6	34579	0.001	*a*
C2•C*C + O2 = C*C*C + C•H2OOH	2.31E+12	−0.03	35363	0.01	*a*
C2•C*C + O2 = C*C*C + C•H2OOH	8.59E+20	−2.5	40518	0.079	*a*
C2•C*C + O2 = C*C*C + C•H2OOH	2.26E+00	3.95	35441	1	*a*
C2•C*C + O2 = C*C*C + C•H2OOH	1.17E−08	6.32	33558	10	*a*
C2•C*C + O2 = CCYC•COOC	1.46E+61	−19.49	20035	0.0001	*a*
C2•C*C + O2 = CCYC•COOC	3.69E+67	−20.92	21541	0.001	*a*
C2•C*C + O2 = CCYC•COOC	3.51E+75	−22.69	25420	0.01	*a*
C2•C*C + O2 = CCYC•COOC	3.75E+81	−23.89	30154	0.079	*a*
C2•C*C + O2 = CCYC•COOC	7.92E+80	−22.85	34796	1	*a*
C2•C*C + O2 = CCYC•COOC	3.62E+61	−16.21	32730	10	*a*
C2•C*C + O2 = CC•C*O + CH2O	1.74E+04	1.41	23216	0.0001	*a*
C2•C*C + O2 = CC•C*O + CH2O	1.75E+04	1.41	23217	0.001	*a*
C2•C*C + O2 = CC•C*O + CH2O	1.82E+04	1.41	23227	0.01	*a*
C2•C*C + O2 = CC•C*O + CH2O	2.31E+04	1.38	23282	0.079	*a*
C2•C*C + O2 = CC•C*O + CH2O	2.27E+07	0.48	24757	1	*a*
C2•C*C + O2 = CC•C*O + CH2O	2.14E+22	−3.9	33165	10	*a*
C2•C*C + O2 = CCYC•CO + CH2O (via CCYC•COOC)	1.22E+08	0.14	8990	0.0001	*a*
C2•C*C + O2 = CCYC•CO + CH2O (via CCYC•COOC)	1.34E+08	0.13	9010	0.001	*a*
C2•C*C + O2 = CCYC•CO + CH2O (via CCYC•COOC)	4.06E+09	−0.32	9705	0.01	*a*
C2•C*C + O2 = CCYC•CO + CH2O (via CCYC•COOC)	1.02E+18	−2.83	13789	0.079	*a*
C2•C*C + O2 = CCYC•CO + CH2O (via CCYC•COOC)	2.83E+36	−8.22	24211	1	*a*
C2•C*C + O2 = CCYC•CO + CH2O (via CCYC•COOC)	2.80E+37	−8.14	29857	10	*a*
C2•C*C + O2 = C2•CYCCOO	2.38E+60	−20.36	20827	0.0001	*a*
C2•C*C + O2 = C2•CYCCOO	2.25E+61	−20.35	20817	0.001	*a*
C2•C*C + O2 = C2•CYCCOO	8.56E+62	−20.52	21097	0.01	*a*
C2•C*C + O2 = C2•CYCCOO	9.33E+66	−21.43	23010	0.079	*a*
C2•C*C + O2 = C2•CYCCOO	7.20E+65	−20.59	24079	1	*a*
C2•C*C + O2 = C2•CYCCOO	3.21E+54	−16.61	21107	10	*a*
C2•C*C + O2 = C2•C*O + CH2O	8.84E+09	−0.43	10055	0.0001	*a*
C2•C*C + O2 = C2•C*O + CH2O	8.88E+09	−0.43	10057	0.001	*a*
C2•C*C + O2 = C2•C*O + CH2O	9.80E+09	−0.44	10079	0.01	*a*
C2•C*C + O2 = C2•C*O + CH2O	6.34E+11	−0.98	10922	0.079	*a*
C2•C*C + O2 = C2•C*O + CH2O	1.31E+23	−4.35	16591	1	*a*
C2•C*C + O2 = C2•C*O + CH2O	2.73E+30	−6.37	22269	10	*a*
C2•C*C + O2 = CCYC•CO + CH2O (via C2•CYCCOO)	4.98E+05	0.51	15697	0.0001	*a*
C2•C*C + O2 = CCYC•CO + CH2O (via C2•CYCCOO)	5.04E+05	0.51	15700	0.001	*a*

TABLE 4. (Continued)

reactions	*A*	*n*	E_a	atm	
C2•C*C + O2 = CCYC•CO + CH2O (via C2•CYCCOO)	4.88E+05	0.51	15695	0.01	*a*
C2•C*C + O2 = CCYC•CO + CH2O (via C2•CYCCOO)	5.34E+05	0.5	15713	0.079	*a*
C2•C*C + O2 = CCYC•CO + CH2O (via C2•CYCCOO)	4.49E+09	−0.68	17557	1	*a*
C2•C*C + O2 = CCYC•CO + CH2O (via C2•CYCCOO)	7.42E+21	−4.26	24257	10	*a*
C*C(C)CQ• = C*CICC*O + OH	1.33E+31	−11.02	40679	0.0001	*a*
C*C(C)CQ• = C*CICC*O + OH	6.63E+37	−12.6	41406	0.001	*a*
C*C(C)CQ• = C*CICC*O + OH	5.56E+48	−15.32	43263	0.01	*a*
C*C(C)CQ• = C*CICC*O + OH	6.47E+62	−18.81	47329	0.079	*a*
C*C(C)CQ• = C*CICC*O + OH	5.43E+75	−21.5	54454	1	*a*
C*C(C)CQ• = C*CICC*O + OH	6.97E+70	−18.94	56896	10	*a*
C*C(C)CQ• = C*C(C)CO• + O	3.97E+24	−11.82	62162	0.0001	*a*
C*C(C)CQ• = C*C(C)CO• + O	1.66E+31	−13.39	62822	0.001	*a*
C*C(C)CQ• = C*C(C)CO• + O	3.10E+41	−15.92	64065	0.01	*a*
C*C(C)CQ• = C*C(C)CO• + O	2.31E+53	−18.8	65171	0.079	*a*
C*C(C)CQ• = C*C(C)CO• + O	4.50E+75	−24.23	68674	1	*a*
C*C(C)CQ• = C*C(C)CO• + O	2.10E+98	−29.07	79246	10	*a*
C*C(C)CQ• = C*C(C•)CQ	2.98E+39	−10.35	25259	0.0001	*a*
C*C(C)CQ• = C*C(C•)CQ	4.62E+43	−11.4	27606	0.001	*a*
C*C(C)CQ• = C*C(C•)CQ	1.97E+48	−12.53	30601	0.01	*a*
C*C(C)CQ• = C*C(C•)CQ	6.60E+49	−12.69	32692	0.079	*a*
C*C(C)CQ• = C*C(C•)CQ	5.62E+43	−10.47	32297	1	*a*
C*C(C)CQ• = C*C(C•)CQ	2.65E+29	−5.82	28195	10	*a*
C*C(C)CQ• = CCYC•COOC	3.74E+36	−11.65	31220	0.0001	*a*
C*C(C)CQ• = CCYC•COOC	1.12E+44	−13.45	32691	0.001	*a*
C*C(C)CQ• = CCYC•COOC	4.28E+55	−16.33	36986	0.01	*a*
C*C(C)CQ• = CCYC•COOC	2.10E+63	−18	41557	0.079	*a*
C*C(C)CQ• = CCYC•COOC	4.93E+64	−17.67	45139	1	*a*
C*C(C)CQ• = CCYC•COOC	1.33E+52	−13.24	43300	10	*a*
C*C(C)CQ• = C2•CYCCOO	1.17E+38	−12.35	32270	0.0001	*a*
C*C(C)CQ• = C2•CYCCOO	2.16E+45	−14.1	33510	0.001	*a*
C*C(C)CQ• = C2•CYCCOO	2.85E+57	−17.13	37542	0.01	*a*
C*C(C)CQ• = C2•CYCCOO	3.26E+66	−19.18	42440	0.079	*a*
C*C(C)CQ• = C2•CYCCOO	1.03E+69	−19.13	46516	1	*a*
C*C(C)CQ• = C2•CYCCOO	1.48E+57	−14.86	45146	10	*a*
C*C(C•)CQ = C*CYCCOC + OH	3.57E+64	−18.12	40551	0.0001	*a*
C*C(C•)CQ = C*CYCCOC + OH	8.13E+64	−17.49	43962	0.001	*a*
C*C(C•)CQ = C*CYCCOC + OH	6.36E+47	−11.67	40384	0.01	*a*
C*C(C•)CQ = C*CYCCOC + OH	2.70E+26	−4.85	33561	0.079	*a*
C*C(C•)CQ = C*CYCCOC + OH	1.17E+13	−0.64	28917	1	*a*
C*C(C•)CQ = C*CYCCOC + OH	9.62E+12	−0.62	28887	10	*a*
C*C(C•)CQ = C*C*C + C•H2OOH	8.33E+58	−19.21	59434	0.0001	*a*
C*C(C•)CQ = C*C*C + C•H2OOH	3.75E+79	−23.85	66536	0.001	*a*
C*C(C•)CQ = C*C*C + C•H2OOH	3.50E+82	−22.94	72301	0.01	*a*
C*C(C•)CQ = C*C*C + C•H2OOH	4.06E+60	−15.05	68875	0.079	*a*
C*C(C•)CQ = C*C*C + C•H2OOH	1.16E+23	−2.87	57736	1	*a*
C*C(C•)CQ = C*C*C + C•H2OOH	6.80E+22	−2.8	57670	10	*a*
CCYC•COOC = CC•C*O + CH2O	5.93E+31	−11.05	43772	0.0001	*a*
CCYC•COOC = CC•C*O + CH2O	5.51E+39	−12.96	44826	0.001	*a*
CCYC•COOC = CC•C*O + CH2O	1.44E+52	−16.01	46921	0.01	*a*
CCYC•COOC = CC•C*O + CH2O	6.85E+66	−19.54	51004	0.079	*a*
CCYC•COOC = CC•C*O + CH2O	3.41E+77	−21.36	57585	1	*a*
CCYC•COOC = CC•C*O + CH2O	2.21E+66	−16.84	57842	10	*a*
CCYC•COOC = CCYC•CO + CH2O	4.00E+44	−11.68	25160	0.0001	*a*
CCYC•COOC = CCYC•CO + CH2O	7.76E+49	−12.93	27935	0.001	*a*
CCYC•COOC = CCYC•CO + CH2O	5.17E+55	−14.32	31537	0.01	*a*
CCYC•COOC = CCYC•CO + CH2O	5.13E+57	−14.56	34019	0.079	*a*
CCYC•COOC = CCYC•CO + CH2O	3.78E+49	−11.64	33152	1	*a*
CCYC•COOC = CCYC•CO + CH2O	5.82E+31	−5.91	27775	10	*a*
C2•CYCCOO = C2•C*O + CH2O	9.94E+51	−13.87	29395	0.0001	*a*
C2•CYCCOO = C2•C*O + CH2O	9.94E+52	−13.87	29395	0.001	*a*
C2•CYCCOO = C2•C*O + CH2O	9.94E+53	−13.87	29395	0.01	*a*
C2•CYCCOO = C2•C*O + CH2O	7.86E+54	−13.87	29395	0.079	*a*
C2•CYCCOO = C2•C*O + CH2O	2.48E+56	−13.99	29574	1	*a*
C2•CYCCOO = C2•C*O + CH2O	4.83E+56	−13.77	29294	10	*a*
C2•CYCCOO = CCYC•CO + CH2O	7.18E+46	−13.25	29391	0.0001	*a*
C2•CYCCOO = CCYC•CO + CH2O	7.18E+47	−13.25	29391	0.001	*a*
C2•CYCCOO = CCYC•CO + CH2O	7.18E+48	−13.25	29391	0.01	*a*
C2•CYCCOO = CCYC•CO + CH2O	5.68E+49	−13.25	29392	0.079	*a*
C2•CYCCOO = CCYC•CO + CH2O	1.80E+51	−13.37	29571	1	*a*
C2•CYCCOO = CCYC•CO + CH2O	3.56E+51	−13.16	29293	10	*a*
CCYC•CO = C2•C*O	6.20E+54	−13.83	16122	0.0001	*a*
CCYC•CO = C2•C*O	2.52E+54	−13.36	17241	0.001	*a*
CCYC•CO = C2•C*O	8.92E+49	−11.67	17104	0.01	*a*
CCYC•CO = C2•C*O	4.90E+40	−8.57	14883	0.079	*a*

TABLE 4. (Continued)

reactions	*A*	*n*	E_a	atm	
CCYC•CO = C2•C*O	3.51E+25	−3.72	10121	1	*a*
CCYC•CO = C2•C*O	4.77E+16	−0.93	7062	10	*a*
CCYC•CO = C*C*O + CH3	6.62E+17	−1.28	8420	0.0001	*a*
CCYC•CO = C*C*O + CH3	4.03E+23	−2.98	11638	0.001	*a*
CCYC•CO = C*C*O + CH3	1.94E+29	−4.58	15680	0.01	*a*
CCYC•CO = C*C*O + CH3	1.41E+29	−4.39	17943	0.079	*a*
CCYC•CO = C*C*O + CH3	2.08E+15	−0.02	15504	1	*a*
CCYC•CO = C*C*O + CH3	2.42E−05	6.04	9517	10	*a*
C2•C*O = C*C*O + CH3	3.31E+54	−13.99	49310	0.0001	*a*
C2•C*O = C*C*O + CH3	1.54E+53	−13.2	50149	0.001	*a*
C2•C*O = C*C*O + CH3	8.15E+47	−11.22	49797	0.01	*a*
C2•C*O = C*C*O + CH3	4.12E+38	−8.1	47640	0.079	*a*
C2•C*O = C*C*O + CH3	1.51E+24	−3.47	43161	1	*a*
C2•C*O = C*C*O + CH3	4.18E+15	−0.77	40227	10	*a*
C2CYC2O = CCYC•CO + CH3	3.15E+28	−3.2	92312	0.0001	*a*
C2CYC2O = CCYC•CO + CH3	7.95E+20	−0.82	89614	0.001	*a*
C2CYC2O = CCYC•CO + CH3	7.88E+18	−0.2	88890	0.01	*a*
C2CYC2O = CCYC•CO + CH3	7.32E+18	−0.19	88879	0.079	*a*
C2CYC2O = CCYC•CO + CH3	7.25E+18	−0.19	88877	1	*a*
C2CYC2O = CCYC•CO + CH3	7.24E+18	−0.19	88877	10	*a*
C2CYCC•O = C2C•C*O	7.94E+70	−18.99	20888	0.0001	*a*
C2CYCC•O = C2C•C*O	1.63E+70	−18.38	22353	0.001	*a*
C2CYCC•O = C2C•C*O	2.75E+63	−15.9	21779	0.01	*a*
C2CYCC•O = C2C•C*O	3.51E+49	−11.33	18094	0.079	*a*
C2CYCC•O = C2C•C*O	2.04E+28	−4.58	11158	1	*a*
C2CYCC•O = C2C•C*O	1.38E+17	−1.07	7237	10	*a*
C2CYCC•O = C2C*C*O + H	4.27E+16	−0.65	17334	0.0001	*a*
C2CYCC•O = C2C*C*O + H	8.27E+16	−0.74	17467	0.001	*a*
C2CYCC•O = C2C*C*O + H	3.74E+21	−2.13	19735	0.01	*a*
C2CYCC•O = C2C*C*O + H	1.55E+30	−4.64	24755	0.079	*a*
C2CYCC•O = C2C*C*O + H	2.79E+23	−2.34	25420	1	*a*
C2CYCC•O = C2C*C*O + H	5.14E−01	4.97	18457	10	*a*
C2CYCC•O = C*CICC*O + H	4.90E+16	−0.65	17900	0.0001	*a*
C2CYCC•O = C*CICC*O + H	7.67E+16	−0.71	17990	0.001	*a*
C2CYCC•O = C*CICC*O + H	8.69E+20	−1.92	19952	0.01	*a*
C2CYCC•O = C*CICC*O + H	4.60E+29	−4.47	24921	0.079	*a*
C2CYCC•O = C*CICC*O + H	8.68E+23	−2.49	25964	1	*a*
C2CYCC•O = C*CICC*O + H	2.34E+00	4.78	19102	10	*a*
C2C•C*O = C2C*C*O + H	2.93E+62	−18.18	49748	0.0001	*a*
C2C•C*O = C2C*C*O + H	2.97E+68	−19.18	52339	0.001	*a*
C2C•C*O = C2C*C*O + H	1.62E+69	−18.53	55042	0.01	*a*
C2C•C*O = C2C*C*O + H	1.23E+63	−15.99	55563	0.079	*a*
C2C•C*O = C2C*C*O + H	3.05E+41	−8.8	50112	1	*a*
C2C•C*O = C2C*C*O + H	1.91E+22	−2.69	43841	10	*a*
C2C•C*O = C*CICC*O + H	1.01E+62	−18.13	50101	0.0001	*a*
C2C•C*O = C*CICC*O + H	1.96E+68	−19.2	52638	0.001	*a*
C2C•C*O = C*CICC*O + H	3.74E+69	−18.69	55498	0.01	*a*
C2C•C*O = C*CICC*O + H	8.21E+63	−16.26	56241	0.079	*a*
C2C•C*O = C*CICC*O + H	2.92E+42	−9.1	50956	1	*a*
C2C•C*O = C*CICC*O + H	5.80E+22	−2.83	44555	10	*a*
C2•C*O + O2 = CC*OCOO•	2.12E+72	−20.82	13434	0.0001	*a*
C2•C*O + O2 = CC*OCOO•	1.61E+75	−21.33	15119	0.001	*a*
C2•C*O + O2 = CC*OCOO•	7.87E+77	−21.76	17277	0.01	*a*
C2•C*O + O2 = CC*OCOO•	9.25E+77	−21.39	18776	0.079	*a*
C2•C*O + O2 = CC*OCOO•	1.43E+70	−18.51	18001	1	*a*
C2•C*O + O2 = CC*OCOO•	9.49E+53	−13.15	13830	10	*a*
C2•C*O + O2 = C•C*OCOOH	1.70E+72	−21.28	12929	0.0001	*a*
C2•C*O + O2 = C•C*OCOOH	1.08E+76	−22.09	14661	0.001	*a*
C2•C*O + O2 = C•C*OCOOH	2.30E+82	−23.63	17905	0.01	*a*
C2•C*O + O2 = C•C*OCOOH	1.49E+92	−26.23	23375	0.079	*a*
C2•C*O + O2 = C•C*OCOOH	3.57+103	−29.05	32033	1	*a*
C2•C*O + O2 = C•C*OCOOH	7.29E+82	−22.01	29528	10	*a*
C2•C*O + O2 = C*C*O + C•H2OOH	6.37E+14	−0.62	23583	0.0001	*a*
C2•C*O + O2 = C*C*O + C•H2OOH	6.37E+14	−0.62	23583	0.001	*a*
C2•C*O + O2 = C*C*O + C•H2OOH	6.34E+14	−0.62	23581	0.01	*a*
C2•C*O + O2 = C*C*O + C•H2OOH	6.13E+14	−0.61	23573	0.079	*a*
C2•C*O + O2 = C*C*O + C•H2OOH	1.24E+15	−0.7	23686	1	*a*
C2•C*O + O2 = C*C*O + C•H2OOH	7.96E+25	−3.88	29561	10	*a*
CC*OCOO• = C•C*OCOOH	5.49E+36	−9.36	20726	0.0001	*a*
CC*OCOO• = C•C*OCOOH	1.93E+42	−10.7	23648	0.001	*a*
CC*OCOO• = C•C*OCOOH	4.15E+47	−11.98	26956	0.01	*a*
CC*OCOO• = C•C*OCOOH	8.22E+49	−12.39	29168	0.079	*a*
CC*OCOO• = C•C*OCOOH	1.75E+46	−10.94	29459	1	*a*

TABLE 4. (Continued)

reactions	*A*	*n*	E_a	atm	
CC*OCOO• = C•C*OCOOH	3.07E+34	−7.1	26235	10	*a*
C•C*OCOOH = C*C*O + C•H2OOH	1.04E−296	91.58	−67927	0.0001	*a*
C•C*OCOOH = C*C*O + C•H2OOH	3.40E−121	36.5	−10149	0.001	*a*
C•C*OCOOH = C*C*O + C•H2OOH	4.66E+09	−3.99	30712	0.01	*a*
C•C*OCOOH = C*C*O + C•H2OOH	2.47E+27	−8.59	33224	0.079	*a*
C•C*OCOOH = C*C*O + C•H2OOH	1.45E+56	−15.58	44304	1	*a*
C•C*OCOOH = C*C*O + C•H2OOH	1.98E+56	−14	50137	10	*a*
C2•C*C + HO2 = C*C(C)CQ	9.44E+83	−24.89	15628	0.0001	*a*
C2•C*C + HO2 = C*C(C)CQ	5.62E+86	−24.93	18428	0.001	*a*
C2•C*C + HO2 = C*C(C)CQ	3.55E+84	−23.52	20303	0.01	*a*
C2•C*C + HO2 = C*C(C)CQ	6.98E+75	−20.28	19643	0.079	*a*
C2•C*C + HO2 = C*C(C)CQ	6.34E+53	−13	13900	1	*a*
C2•C*C + HO2 = C*C(C)CQ	4.39E+30	−5.64	6340	10	*a*
C2•C*C + HO2 = C*C(C)CO• + OH	5.62E+12	−0.03	41	0.0001	*a*
C2•C*C + HO2 = C*C(C)CO• + OH	2.54E+14	−0.53	814	0.001	*a*
C2•C*C + HO2 = C*C(C)CO• + OH	3.42E+22	−2.95	4826	0.01	*a*
C2•C*C + HO2 = C*C(C)CO• + OH	4.53E+32	−5.9	10685	0.079	*a*
C2•C*C + HO2 = C*C(C)CO• + OH	6.79E+31	−5.39	13855	1	*a*
C2•C*C + HO2 = C*C(C)CO• + OH	4.16E+10	1.27	8562	10	*a*
C*C(C)CQ = C*C(C)CO• + OH	4.74E+81	−21.6	65577	0.0001	*a*
C*C(C)CQ = C*C(C)CO• + OH	5.10E+76	−19.67	65613	0.001	*a*
C*C(C)CQ = C*C(C)CO• + OH	3.05E+66	−16.17	63617	0.01	*a*
C*C(C)CQ = C*C(C)CO• + OH	1.25E+52	−11.51	59459	0.079	*a*
C*C(C)CQ = C*C(C)CO• + OH	4.28E+32	−5.33	53014	1	*a*
C*C(C)CQ = C*C(C)CO• + OH	9.68E+20	−1.68	48922	10	*a*
C*C(C)CO• = CC•*C + CH2O	1.34E−143	44.54	−29531	0.0001	*a*
C*C(C)CO• = CC•*C + CH2O	1.07−312	98.3	−86962	0.001	*a*
C*C(C)CO• = CC•*C + CH2O	3.81E−135	41.94	−33059	0.01	*a*
CC*OCOO• = C•C*OCOOH	3.07E+34	−7.1	26235	10	*a*
C*C(C)CO• = CC•*C + CH2O	2.86E+21	−6	22931	0.079	*a*
C*C(C)CO• = CC•*C + CH2O	7.26E+36	−9.9	26770	1	*a*
C*C(C)CO• = CC•*C + CH2O	3.19E+51	−13.38	33873	10	*a*
C*C(C)CO• = C*CICC*O + H	2.13E−126	41.46	−39454	0.0001	*a*
C*C(C)CO• = C*CICC*O + H	3.35E−241	78.01	−78482	0.001	*a*
C*C(C)CO• = C*CICC*O + H	3.40E−128	42.05	−44402	0.01	*a*
C*C(C)CO• = C*CICC*O + H	2.54E+28	−6.04	14033	0.079	*a*
C*C(C)CO• = C*CICC*O + H	4.78E+35	−7.88	17976	1	*a*
C*C(C)CO• = C*CICC*O + H	1.65E+40	−8.88	21480	10	*a*
C*CICC•*O = CC•*C + CO	1.36E+34	−6.68	40490	0.0001	*a*
C*CICC•*O = CC•*C + CO	3.67E+20	−2.39	35948	0.001	*a*
C*CICC•*O = CC•*C + CO	2.17E+14	−0.43	33756	0.01	*a*
C*CICC•*O = CC•*C + CO	1.10E+13	−0.03	33293	0.079	*a*
C*CICC•*O = CC•*C + CO	6.94E+12	0.04	33220	1	*a*
C*CICC•*O = CC•*C + CO	6.93E+12	0.04	33220	10	*a*
C*C(C)COH = C2•C*C + OH	1.11E+15	−0.02	79554	0.0001	*a*
C*C(C)COH = C2•C*C + OH	1.07E+15	−0.01	79548	0.001	*a*
C*C(C)COH = C2•C*C + OH	1.07E+15	−0.01	79547	0.01	*a*
C*C(C)COH = C2•C*C + OH	1.06E+15	−0.01	79547	0.079	*a*
C*C(C)COH = C2•C*C + OH	1.06E+15	−0.01	79547	1	*a*
C*C(C)COH = C2•C*C + OH	1.06E+15	−0.01	79547	10	*a*
C3CCC3+OH = H2O + C3•CCC3	9.99E+06	2	179		*b*
C3CCC3+HO2 = H2O2+C3•CCC3	1.00E+12	0	17300		*c*
C3CCC3 + O = OH + C3•CCC3	3.90E+14	0	7681		*d*
C3•CCC3 + C*CC = C*CC• + C3CCC3	2.23	3.5	6637		*e*
C3•CCC3 + C2C*C = C2•C*C + C3CCC3	4.46	3.5	6637		*f*
C3C• + C3CCC3 = C3C + C3•CCC3	1.12E−05	5.17	9068		*g*
C3C• + HO2 = C3C + O2	3.01E+11	0	0		*h*
C3C• + C2C*C = C3C + C2•C*C	84.4	3.3	17169		*i*
C3C + H = C3C• + H2	2.40E+08	1.5	4280		*d*
C3C + OH = C3C• + H2O	1.20E+06	1.5	−1540		*d*
C3C + HO2 = C3C• + H2O2	3.61E+03	2.55	10532		*j*
C3C + O = C3C• + OH	1.70E+08	1.5	2270		*d*
C3C + CH3 = C3C• + CH4	8.10E+05	1.87	17480		*d*
CH3 + C*C*C = C2•C*C	4.57E+13	0	54190		*k*
C2C*C + O = C2•C*C + OH	7.54E+10	0.7	7633		*l*
C2C*C + OH = C2•C*C + H2O	3.90E+06	2	−298		*m*
C2C*C + OH = C2C*C•+H2O	1.61E+06	2	2778		*n*
C2C*C + HO2 = C2•C*C + H2O2	1.21E+04	2.6	13910		*o*
C2C*C + O2 = C2•C*C + HO2	2.40E+13	0	39600		*p*
C2CYC2O + OH = C2CYCC•O + H2O	2.40E+06	2	−2190		*d*
C2CYC2O + C2•C*C = C2CYCC•O + C2C*C	7.80E+01	3.3	18171		*q*
C2CYC2O + C*CC• = C2CYCC•O + C*CC	7.80E+01	3.3	18171		*q*
C2CYC2O + C3COO• = C2CYCC•O + C3COOH	7.20E+03	2.55	12450		*r*

TABLE 4. (Continued)

reactions	*A*	*n*	E_a	atm	
C2CYC2O + CH3OO = C2CYCC•O + CH3OOH	7.20E+03	2.55	12450		*r*
C2CYC2O + CH3 = C2CYCC•O + CH4	1.62E+06	1.87	6635		*d*
C2C*O + O2 = C2•C*O + HO2	8.00E+13	0	46800		*s*
C2C*O = CH3 + CC•*O	2.70E+16	0	81741		*t*
CC•*O = CH3 + CO	2.50E+13	0	16382		*u*
C2C*O + OH = C2•C*O + H2O	1.02E+12	0	1192		*v*
C2C*O + O = C2•C*O + OH	1.00E+13	0	5962		*w*
C2C*O + H = C2•C*O + H2	1.86E+13	0	6357		*x*
C2C*O + CH3 = CH4 + C2•C*O	3.29E+11	0	9600		*y*
C2•C*O + H = C2C*O	1.00E+13	0	0		*a*
C2•C*O + C2C*C = C2•C*C + C2C*O	2.23	3.5	6637		*z*
CCYC•COC + C2C*C = CCYCOCC + C2•C*C	6.02E−05	4.98	8362		*aa*
C3C• + C2C*C = C3C + C2•C*C	84.4	3.3	17169		*i*
CCYC•COC + C*CC = C*CC• + CCYCOCC	3.01E−05	4.98	8362		*ab*
CCYC•COOC + C2C*C = CCYCCOOC + C2•C*C	1.34E−01	4	8066		*aa*
CCYC•COOC + C*CC = CCYCCOOC + C*CC•	6.62E−02	4	8066		*ab*
C2•C*C + C2•C*C = DIC2•C*C	2.00E+13	0	0		*ac*
C2•C*C + C*CC• = C2*CCCC*C	1.00E+13	0	0		*ac*
C*C(C)CO•+C2C*C = C2•C*C + C*C(C)COH	1.80E+02	2.95	11978		*ad*
C*C(C)CO•+C*CC = C*C(C)COH + C*CC•	9.00E+01	2.95	11978		*ae*
C*CICC*O + CH3 = CH4 + C*CICC•*O	8.10E+05	1.87	−1165		*d*
C*CICC*O + OH = H2O + C*CICC•*O	1.20E+06	2	1310		*d*
C*CICC*O + HO2 = H2O2+C*CICC•*O	3.01E+12	0	11923		*af*
C*CICC*O + C*CC• = C*CC + C*CICC•*O	3.08E+11	0	7218		*ag*
C*CICC*O + C2•C*C = C2C*C + C*CICC•*O	3.08E+11	0	7218		*ag*
C*CICC•*O = CC•*C + CO	1.50E+11	0	4809		*ah*
C3•CCC3 + C*C(C)COH = C*C(C)CO• + C3CCC3	10.5	3.1	8962		*ai*
C*C(C)COH = C2•C*C + OH	3.69E+12	0.09	32934		*a*
C*C(C)COH + HO2 = C*C(C)CO• + H2O2	3.34E+03	2.55	18860		*aj*
C*C(C)OH + HO2 = C2•C*O + H2O2	1.93E+04	2.6	13910		*ak*
C2C*COH + HO2 = C2C•C*O + H2O2	9.64E+03	2.6	13910		*al*
C*CC + O = C*CC•+OH	6.03E+10	0.7	7633		*i*
CC•*C + C2C*C = C*CC + C2•C*C	4.42	3.5	4682		*am*
CC•*C + C3CCC3 = C3•CCC3 + C*CC	2.72	3.65	5167		*an*
C*CC• + C*CC• = C*CCCC*C	1.03E+13	0	−262		*i*
C*C*C + C*CC• = C#CC• + C*CC	1.26E+08	1.9	18191		*ao*
C*C*C + C2•C*C = C#CC• + C2C*C	1.26E+08	1.9	18191		*ao*
C#CC• + C#CC• = CYC6H6	3.4E+13	0	0		*ap*
O + CH4 = CH3 + OH	6.92E+08	1.56	8485		*aq*
CH3 + C2C*C = CH4 + C2•C*C	1.86E+06	1.87	1219		*d*
CH3 + C3CCC3 = C3•CCC3 + CH4	1.46E+07	1.87	10600		*d*
CH3 + O2 = CH3OO	1.99E+31	−6.72	4212		*a*
CH3 + O2 = CH2O + OH	2.61E+08	1.01	12487		*a*
CH3 + CH2O = HCO + CH4	5.54E+03	2.81	5862		*ar*
CH3 + HO2 = CH3O• + OH	1.81E+13	0	0		*aq*
CH3O• = CH2O + H	6.13E+28	−5.65	31351		*a*
CH3O• + HO2 = CH2O + H2O2	3.01E+11	0	0		*ar*
CH2O + O = OH + HCO	1.81E+13	0	3080		*ar*
CH2O + H = H2 + HCO	2.29E+10	1.05	3279		*aq*
CH2O + OH = H2O + HCO	3.44E+09	1.18	−447		*aq*
HCO + O2 = CO + HO2	6.25E+15	−1.15	2018		*as*
HCO + O2 = CO2 + OH	5.45E+14	−1.15	2018		*as*
CO + O = CO2	6.17E+14	0	3001		*ar*
CO + H + M = HCO + M	6.31E+20	−1.82	3688		*aq*
CO + OH = CO2 + H	6.32E+06	1.5	−497		*ar*
CO + HO2 = CO2 + OH	1.51E+14	0	23650		*ar*
CO + O2 = CO2 + O	2.53E+12	0	47693		*ar*
H + O2 = OH + O	1.99E+14	0	16802		*aq*
H + O2 + M = HO2 + M	1.41E+18	−0.8	0		*aq*
	H2/3.41/N2/1.0/H2O/2.53/				
OH + HO2 = H2O + O2	1.45E+16	−1	0		*ar*
H + HO2 = OH + OH	1.69E+14	0	874		*ar*
H + HO2 = H2 + O2	6.62E+13	0	2126		*ar*
O + HO2 = O2 + OH	1.75E+13	0	−397		*at*
OH + OH = O + H2O	1.51E+09	1.14	99		*aq*
O + H2 = OH + H	5.12E+04	2.67	6285		*aq*
O + O + M = O2 + M	1.89E+13	0	−1788		*ar*
H + H + M = H2 + M	5.44E+18	−1.3	0		*ar*
	N2/1.0/				
H + OH + M = H2O + M	2.21E+22	−2	0		*aq*
	N2/1.0/ H2O/16.96/				
HO2 + HO2 = H2O2 + O2	1.87E+12	0	1540		*aq*
H2O2 + M = OH + OH + M	1.21E+17	0	45507		*aq*

TABLE 4. (Continued)

reactions	*A*	*n*	E_a	atm	
		N2/1.0/			
H2O2 + H = H2 + HO2	4.82E+13	0	7949		*ar*
H2O2 + OH = HO2 + H2O	1.75E+12	0	318		*at*
CH4 + HO2 = H2O2 + CH3	9.04E+12	0	24641		*aq*
HO2 + C*CC = C*CC• + H2O2	9.64E+03	2.6	13910		*i*
H2 + OH = H2O + H	1.02E+08	1.6	3300		*aq*
2HO2 = 2OH + O2	1.00E+12	0	11500		*as*
HO2 ⇒ X + Y	1	0	0		*au*
H2O2 ⇒ H2O + X	1	0	0		*au*
X + X ⇒ O2	1.00E+15	0	0		*au*
X + Y + Y ⇒ H2O + O2	1.00E+19	0	0		*au*
H + O + M = OH + M	4.71E+18	−1	0		*ar*
HO2 + H = H2O + O	3.01E+13	0	1721		*aq*
H2O2 + H = H2O + OH	2.41E+13	0	3974		*ar*
H2O2 + O = OH + HO2	9.63E+06	2	3974		*ar*

[a] From QRRK calculations. [b] Reference 63. [c] Reference 68. [d] Reference 69. [e] C*CC + C3.C = C*CC• + C3C (ref 65). [f] 2 × C*CC + C3•C = C*CC• + C3C (ref 65). [g] 2 × C3C• + C3C = C3C + C3•C (ref 45). [h] C2H5 + HO2 = C2H6 + O2 (ref 62). [i] Reference 65. [j] Reference 45. [k] Reference 69. [l] 1.25 × C*CC + O = C*CC•. + OH (ref 65). [m] 1.25 × C*CC + OH = C*CC• + H2O (ref 65). [n] 0.75 × C*CC + OH = CC*C• + H2O (ref 65). [o] 1.25 × C*CC + OH = C*CC• + H2O (ref 65). [p] Best fit in isobutene oxidation. [q] *A* factor from C*CC• + CCC = C*CC + CC•C, $E_a = \Delta U + 8.066$ (ref 65). [r] *A* factor from 2 × C3C + CH3OO = C3C• + CH3OOH; $E_a = \Delta U + 0.5$ (ref 45). [s] Estimate $A = 8e13$, $E_a = \Delta U + 1.0$. [t] Reference 72. [u] Reference 62. [v] Reference 66. [w] Reference 67. [x] Reference 73. [y] Reference 63. [z] C2H5 + C*CC = C2H6 + C*CC• (ref 65). [aa] 2 × CC•C + C*CC = CCC + C*CC• (ref 65). [ab] CC.C + C*CCBullet= CCC + C*CC• (ref 65). [ac] C*CC•+ C*CC• = C*CCCC*C (ref 65). [ad] 2 × CH3O• + C*CC = CH3OH + C*CC• (ref 65). [ae] CH3O• + C*CC = CH3OH + C*CC• (ref 65). [af] CC*O + HO2 = CC•*O + H2O2 (ref 64). [ag] C*CC•+ CC*O = C*CC + CC•*O (ref 70). [ah] C2H3 + CO = CH2CHC•*O (ref 62) and ⟨*MR*⟩. [ai] C3•C + CH3OH = C3C + CH3O• (ref 45). [aj] *A* factor from $^1/_9$(C3C + HO2 = C3•C + H2O2) and $E_a = \Delta U + 3$ (ref 45). [ak] 2 × C*CC + HO2 = C*CC• + H2O2 (ref 65). [al] C*CC + HO2 = C*CC• + H2O2 (ref 65). [am] 2 × C2H3 + C*CC = C2H4 + C*CC• (ref 65). [an] 2 × C2H3 + C3C = C2H4 + C3•C (ref 65). [ao] C*CC• + CH2O = C*CC + HCO (ref 65). [ap] Reference 71. [aq] Reference 64. [ar] Reference 62. [as] Estimate in this study. [at] Reference 72. [au] Wall reaction; see text and ref 11. [av] Rate constants in the form $AT^n \exp(-E_a/RT)$. Units, *A* factor: bimolecular, $cm^3\ mol^{-1}\ s^{-1}$; unimolecular, s^{-1}; E_a, cal/mol.

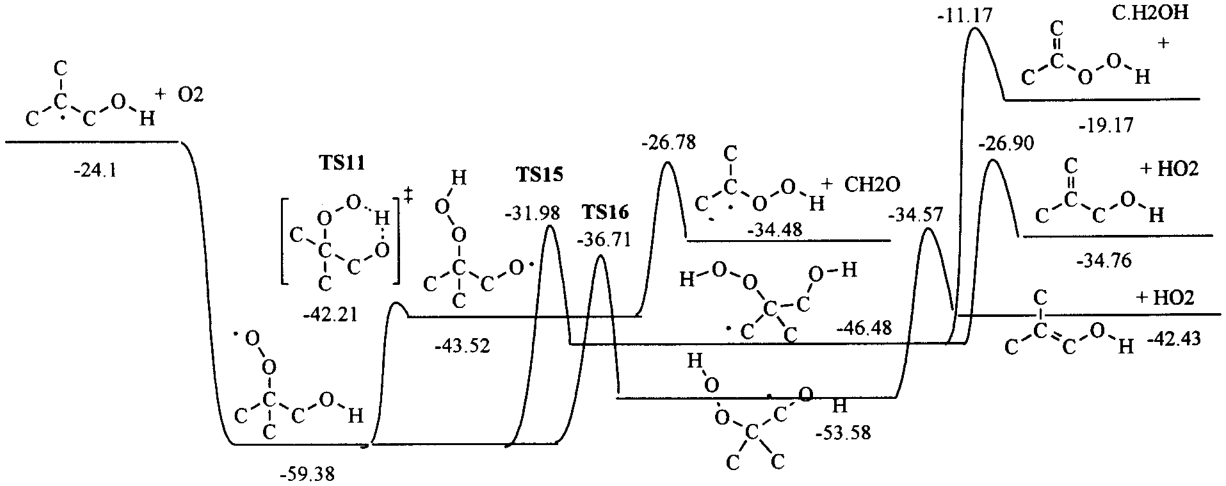


Figure 2. Potential energy diagram for $C_2C^{\bullet}COH + O_2 \Rightarrow$ products.

based on molar volumes and compressibility.[37] When necessary, estimation is done in a consistent and uniform manner via use of generic reaction rate constants with reference to literature, experiment, or theoretical calculation in each case. The QRRK calculation input parameters and their references are listed in the table associated with the respective reaction system.

Recent Modifications to the Quantum RRK Calculation. Recent modifications to the quantum RRK calculation include the following.

(a) A manifold of three frequencies is now used plus one external rotation is now included for the density of states, $\rho(E)/Q$, and in the calculation of $k(E)$.

(b) The Leonard-Jones collision frequency Z_{LJ} is now calculated by $Z_{LJ} = Z\Omega$ (2,2) integral[36,37] obtained from the fit of Reid et al.[37]

The QRRK analysis for $k(E)$ with modified strong collision and a constant F_E for falloff has been used previously to analyze a variety of chemical activation reaction systems by Westmoreland et al.,[38,39] Dean et al.,[40] and Bozzelli et al.[41,42] There are a number of recent publications by other researchers that utilize the QRRK formalism with a more exact calculation of F_E in modified strong collision analysis[75−80] or utilize just a QRRK formalism.[81,82] It is shown to yield reasonable results in these applications and provides a framework by which the effects of both temperature and pressure can be estimated for complex chemical activation or unimolecular dissociation reaction systems. The reaction channels resulting from O_2 addition to $C_2C^{\bullet}COH$ adducts illustrated in Figure 2 serve as an example of such complexity. The system incorporates 15 reactions: 8 forward, 4 reverse, 3 stabilizations, with 3 adducts in steady state and most barriers below $\Delta H_f°_{298}$ of the reactants. We feel that QRRK analysis combined with either modified strong collision or master equation for falloff is a reasonable method to estimate the rate constants as a function of temperature and pressure for these complex systems.

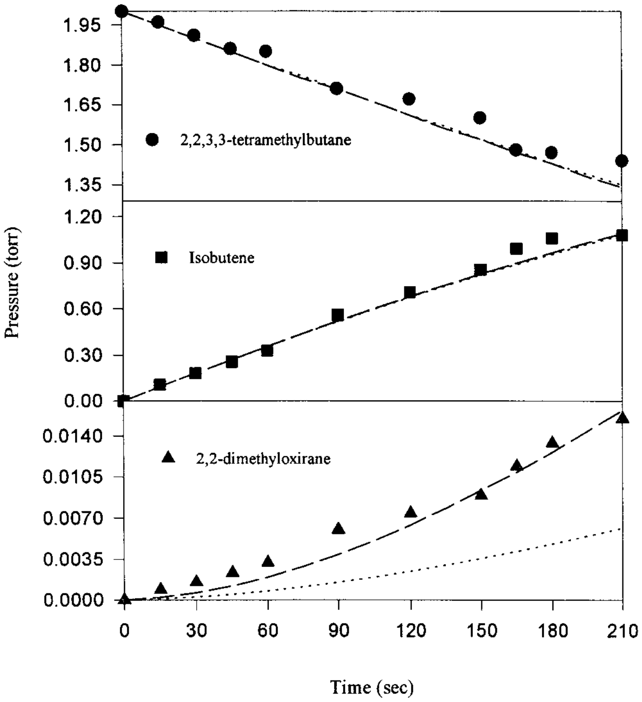


Figure 3. Comparison of model prediction and experimental data. Symbols are experimental data from Arti et al.,[11] 773 K and 60 Torr. Dash lines are model prediction using of barrier 16.13 kcal/mol for $C_3{}^{\bullet}COOH \rightarrow$ 2,2-dimethyloxirane + OH. Dot lines are model prediction using of barrier 17.98 kcal/mol for $C_3{}^{\bullet}COOH \rightarrow$ 2,2-dimethyloxirane + OH.

Experimental Data and Reactor Modeling

We use experimental data published by Atri et al.[11] for decomposition of 2,2,3,3-tetramethylbutane (C_3CCC_3) in the presence of oxygen. This experimental study was carried out in a Pyrex flow reactor coated with potassium chloride and conditioned: at slow flow, up to several minutes reaction time, 773 K and 60 Torr.

In previous studies,[12,13,43] Walker showed the $C_3CCC_3 + O_2 \Rightarrow$ isobutene + HO_2 reaction gives higher rate constants in KCl-coated vessels than in aged boric acid-coated vessels at temperatures greater than 723 K. He postulated that HO_2 radicals and H_2O_2 are efficiently destroyed at the KCl-coated vessel surface at these temperatures. The basic mechanism postulated by Atri et al. involves the overall reactions listed in (1−4) for conversion to stable molecules.

$$C_3C{-}CC_3 \rightarrow 2C_3C^{\bullet} \tag{1}$$

$$C_3C^{\bullet} + O_2 \rightarrow C_2C{=}C + HO_2 \tag{2}$$

$$HO_2 \xrightarrow{\text{surface}} {}^{1}/_{2}H_2O + {}^{3}/_{4}O_2 \tag{3}$$

$$H_2O_2 \xrightarrow{\text{surface}} H_2O + {}^{1}/_{2}O_2 \tag{4}$$

For reactor modeling, two dummy molecules, X and Y, and four unidirectional reactions are added to our mechanism to simulate surface effects in the KCl-coated reactor (reaction 3 and 4 above). The points in Figure 3 illustrate experimental data of the Walker and Baldwin research group.

Results and Discussion

Formation of *tert*-Butyl Radical ($C_3C^{\bullet}$). The *tert*-butyl radical is generated in our mechanism by the homogeneous decomposition of 2,2,3,3-tetramethylbutane in the presence of O_2. Previous experiments[11−13,43] on the oxidation C_3CCC_3 in a KCl-coated vessel have shown that homolysis of the central C−C bond (reaction 1) is the dominant reaction path over alternative initiation reactions, which include other CH3−C scission reactions, C−H scissions, and abstraction of a primary H atom by O_2, even at high pressures of O_2. The $C_3C{\cdots}CC_3$ bond is 77.32 kcal/mol, weaker by 6.6 kcal/mol at 298 K than other C−C bonds in the 2,2,3,3-tetramethylbutane molecule due to steric effects (repulsion of *tert*-butyl methyls, gauche interactions). Cleavage of the $C_3CCC_3{\cdots}H$ bond requires 101.1 kcal/mol and has a lower *A* factor than $C_3C{\cdots}CC_3$ bond cleavage.

$$(CH_3)_3C{-}C(CH_3)_3 \rightarrow 2C_3C^{\bullet} \tag{1}$$

We use the high-pressure limit $A_\infty = 6.0 \times 10^{16}\ s^{-1}$, $E_{a,\infty} = 69.47$ kcal/mol for $C_3C{\cdots}CC_3$ fission from analysis of both Tsang's[44] and Arti's results.[11]

Unimolecular Decay *tert*-Butyl Radical ($C_3C^{\bullet}$). The unimolecular decomposition of reaction 5 has been studied by Knyazev et al.[17] over a temperature range 712−779 K in He bath gas (2.35−17.36 Torr).

$$C_3C^{\bullet} \xrightarrow{(TS13)} C_2C{=}C + H \tag{5}$$

Knyazev et al. used a heated tubular flow reactor and photoionization mass spectrometer for radical species detection. They create a transition-state model and calculate rate constants using master equation/RRKM calculation to determine a high-pressure limit rate constant for the decomposition reaction ($k_{5,\infty} = (2.18 \times 10^9)T^{1.48} \exp(-36004/RT)\ s^{-1}$) and the reverse reaction ($k_{-5,\infty} = (1.03 \times 10^{11})T^{0.25} \exp(-1464/RT)\ cm^3\ molecule^{-1}\ s^{-1}$). Parts a and b of Figure 4 compare the decomposition rate constants from experimental data of Knyazev et al. with our QRRK calculations using collision parameters of Knyazev et al. The high-pressure limit rate constants are from Knyazev et al. ($(2.18 \times 10^9)T^{1.48} \exp(-36004/RT)\ s^{-1}$) and Tsang et al.[45] ($8.3 \times 10^{13} \exp(-38145/RT)\ s^{-1}$), respectively. The agreement of our QRRK calculations using the rate constant parameters of Tsang with the experimental data is excellent; use of rate constant parameters of Knyazev in our calculations yield predictions that are ca. 10% high.

Figure 4c illustrates results from use of ab initio determined values for the reactant *tert*-butyl radical and the transition state structure, CBS-q//MP2(full)/6-31g(d) for energy with structure and frequencies determined at the MP2(full)/6-31g(d) level. We use canonical transition state theory and obtain a high-pressure limit $A_{5,\infty}$ of $(2.5 \times 10^{16})T^{-0.91873}\ s^{-1}$. Tunneling is taken into account using the Erwin−Henry computer code[74] (Eckart formalism) to determine high-pressure limit rate constants. The reaction barrier of H atom addition to isobutene is calculated to be 0.52 kcal/mol at the CBS-q//MP2(full)/6-31g(d) level. MP2-calculated frequencies and moment of inertia for transition state (TS13) are described in Table 5. A comparison of rate constants from QRRK calculation using the high-pressure limit rate constant $(2.5 \times 10^{16})T^{-0.91873} \exp(-37500/RT)\ s^{-1}$ with experimental data of Knyazev et al. is illustrated in Figure 4c. Arrhenius pre-exponential factors for MP2 combined with the calculated β scission reaction barrier, $\Delta H_{rxn} + E_a$ for H addition at CBS-q//MP2(full)/6-31g(d) level, tunneling for the hydrogen atom elimination, and QRRK analysis yield good estimates of rate constants, in the falloff. These results from our QRRK analysis, canonical TST, tunneling, and ab initio calculated

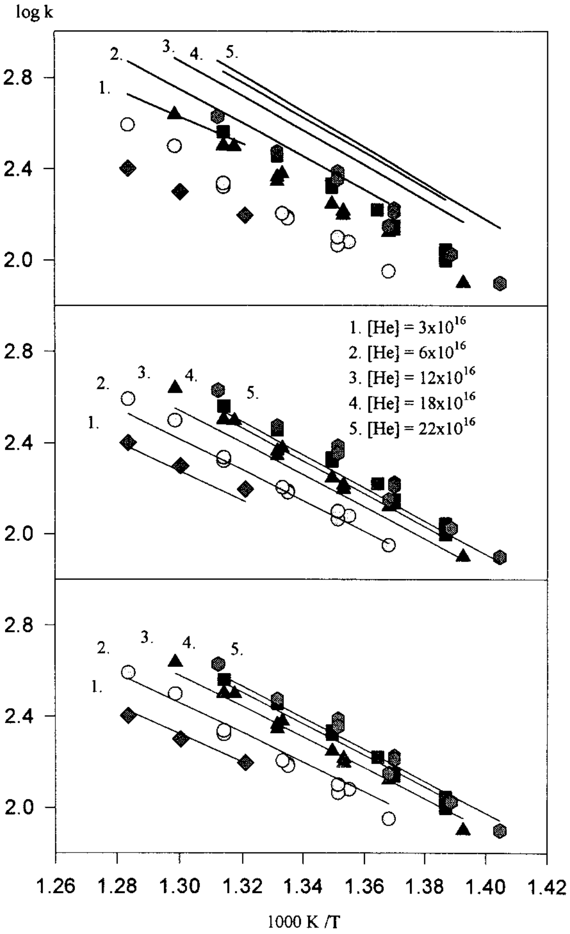


Figure 4. Plot of the *tert*-butyl radical unimolecular rate constants (log *k* vs 1000 K/*T*) for different He densities (atom cm^{-3}). Symbols are experimental data from Knyazev et al.[17] (a) Lines represent the results of QRRK calculation using the high-pressure limit rate constants from Knyazev et al.[17] ((2.18 × 10^9)$T^{1.48}$ exp(−36004/*RT*)). (b) Lines represent the results of QRRK calculation using the high-pressure limit rate constants from Tsang et al.[45] ((8.3 × 10^{13}) exp(−38145/*RT*)). (c) Lines represent the results of QRRK calculation using the high-pressure limit rate constants from ab initio calculation of transition state structure, canonical TST, and tunneling ((2.5 × 10^{16})$T^{-0.92}$ exp(−37500/*RT*)).

TABLE 5: Frequencies and Moments of Inertia for Transition State (TS13) Calculated at the MP2(full)/6-31g(d) Level

molecule	frequencies	moments of inertia[a]
TS13	(−1209.96), 160.71, 187.62, 310.47, 351.78, 389.62, 456.41, 566.92, 849.08, 880.50, 1000.67, 1024.42, 1075.10, 1082.60, 1118.11, 1150.19, 1359.67, 1465.27, 1471.77, 1493.69, 1532.27, 1548.17, 1549.51, 1563.43, 1718.82, 3086.30, 3089.62, 3157.77, 3159.55, 3203.61, 3204.92, 3216.43, 3307.31	220.62451, 224.58246, 401.49206

[a] Units, amu bohr^2.

thermodynamic parameters are very similar, 1.1% higher, than data in Figure 4b that use Tsang's parameters.

Overall kinetic analysis shows this unimolecular H atom elimination reaction is important, although it is slow on a scale relative to O_2 addition, $C_3C^\bullet + O_2 \leftrightarrow C_3COO^\bullet$. The reverse of oxygen addition, where $C_3C^\bullet$ radical is regenerated, is however also important.

***tert*-Butyl Radical ($C_3C^\bullet$) + O_2.** The *tert*-butyl radical combines with O_2 to form the chemically activated $C_3COO^{\bullet *}$ adduct. The major reaction channels of $C_3COO^{\bullet *}$ include dissociation back to reactants, stabilization to $C_3COO^\bullet$, molecular elimination to $C_2C{=}C + HO_2$, and isomerization (H shift) to $C_3^\bullet COOH^*$. The $C_3^\bullet COOH^*$ isomer can undergo β-scission to $C_2C{=}C + HO_2$, cyclize to $C_2CYC_2O + OH$, undergo β-scission to $C{=}C(C)OOH + CH_3$, be stabilized to $C_3^\bullet COOH$, or isomerize back to $C_3COO^{\bullet *}$. Reaction of $C_3COO^{\bullet *}$ adduct to $C_3CO^\bullet + O$ is included for completeness, but it is only important at higher temperature (above 1500 K). The potential energy level diagram for reaction paths is shown in Figure 5.

$\Delta H_f°_{298}(C_3COO^\bullet)$ (−25.16 kcal/mol) is calculated by Lay et al.[46] using isodesmic reactions and ab initio calculations (MP4SDTQ/6-31g(d)//MP2/6-31g(d) and G2). Bond energy $DH°_{298}$(HOOCC−H) is determined to be 101.1 + 1.77 = 102.87 kcal/mol, using $DH°_{298}(C_2H_5{-}H)$ = 101.1 kcal/mol and reaction enthalpy ΔH_{rxn} = −1.77 kcal/mol at the G2 level for the isodesmic reaction 6.

$$CC + C^\bullet COOH \rightarrow C^\bullet C + CCOOH \qquad (6)$$

$DH°_{298}(C_2C(OOH)C{-}H)$ (103.69 kcal/mol) is determined to be 102.87 − (−0.82) = 103.69 kcal/mol, using $DH°_{298}$(HOOCC−H) = 102.87 kcal/mol and the calculated reaction enthalpy ΔH_{rxn} = −0.82 kcal/mol at CBS-q//MP2(full)/6-31g(d) and CBS-q//B3LYP/6-31g(d) levels for the isodesmic reaction 7.

$$C_3^\bullet COOH + CCOOH \rightarrow C_3COOH + C^\bullet COOH \qquad (7)$$

$\Delta H_f°_{298}(C_3^\bullet COOH)$(−7.81 kcal/mol) is derived from $\Delta H_f°_{298}(C_3COOH)$ and $DH°_{298}(C_2C(OOH)C{-}H)$ using the following equation:

$$\Delta H_f°_{298}(C_3^\bullet COOH) = DH°_{298}(C_2C(OOH)C{-}H) + \Delta H_f°_{298}(C_3COOH) - \Delta H_f°_{298}(H)$$

$$-7.81\ \text{kcal/mol} = (103.69\ \text{kcal/mol}) + (-59.4\ \text{kcal/mol}) - (52.1\ \text{kcal/mol})$$

Enthalpies of formation for transition states are calculated from reaction enthalpies (enthalpy differences between TS and reactants) in the exothermic direction plus enthalpies of formation of the reactants. $\Delta H_f°_{298}$(TS1) (2.29 kcal/mol) is determined from ($\Delta H_f°_{298}(C_2C{=}C) + \Delta H_f°_{298}(HO_2)$) (−0.3 kcal/mol) plus reaction enthalpy ($\Delta H^\ddagger_{TS1-(C2C=C+HO2)}$) (2.59 kcal/mol). $\Delta H_f°_{298}$(TS2) (7.68 kcal/mol) is determined from $\Delta H_f°_{298}(C_3^\bullet COOH)$ (−7.81 kcal/mol) plus reaction enthalpy ($\Delta H^\ddagger_{TS2-C3^\bullet COOH}$) (15.49 kcal/mol). $\Delta H_f°_{298}$(TS3)(7.44 kcal/mol) is from ($\Delta H_f°_{298}(C_2C{=}C) + \Delta H_f°_{298}(HO_2)$) (−0.3 kcal/mol) plus reaction enthalpy ($\Delta H^\ddagger_{TS3-(C2C=C+HO_2)}$)(7.74 kcal/mol). All reaction enthalpies above are calculated at the CBS-q//MP2(full)/6-31g(d) level. $\Delta H_f°_{298}$ (TS4)(7.77 kcal/mol) is obtained from fitting experimental data, which results in downward adjustment of the calculated barrier of ca. 2.4 kcal/mol. This is the only barrier adjusted in this study.

High-pressure limit pre-exponential factors (A_∞) for *tert*-butyl peroxy ($C_3COO^\bullet$) molecular elimination to isobutene + HO_2 (reaction 8), isomerization to *tert*-butyl hydroperoxide ($C_3^\bullet COOH$) (reaction 9), hydroperoxide alkyl radical β-scission to isobutene + HO_2 (reaction 10), and hydroperoxide alkyl radical cyclization to 2,2-dimethyloxirane + OH (reaction 11) are calculated using canonical TST along with MP2-determined entropies. High-pressure limit rate constants, k_∞ , are fit to a three-parameter modified Arrhenius equation (A, n, E_a) over the temperature range 300−2000 K. Input parameters for the chemical activation analysis of *tert*-butyl radical + O_2 reaction system are shown

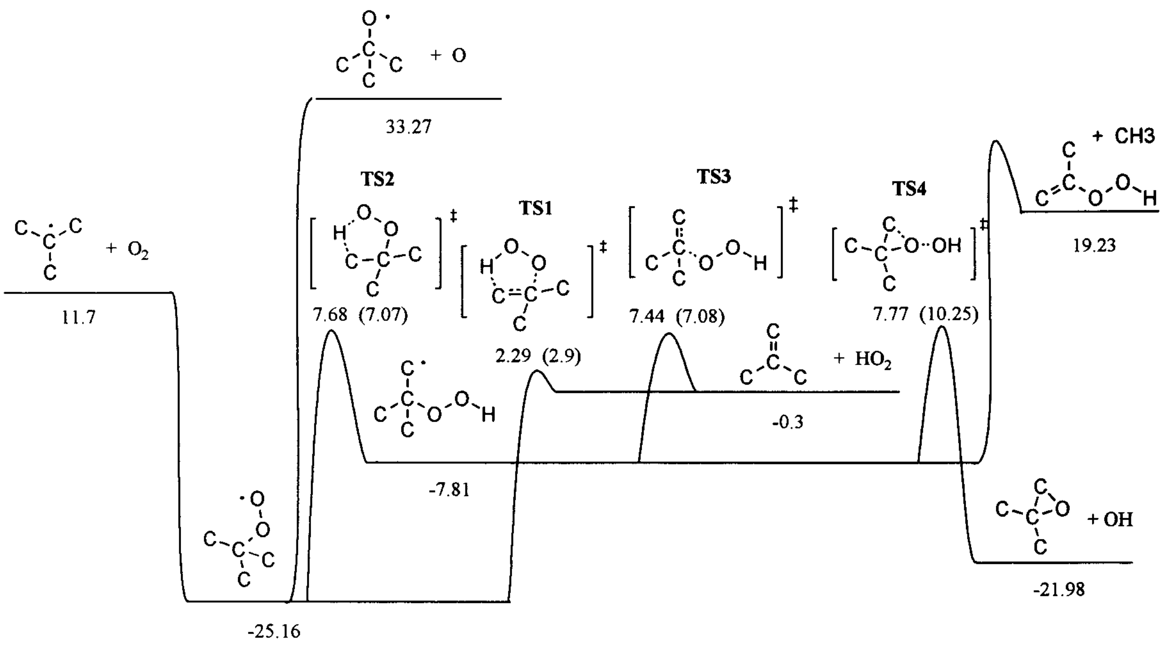


Figure 5. Potential energy diagram of *tert*-butyl radical addition with O_2 reaction based on CBS-q//MP2(full)/6-31g*. Data in parentheses are from CBS-q//B3LYP/6-31g* calculation.

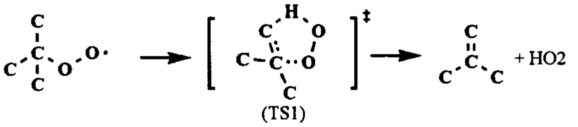
TABLE 6: Input Parameters and High-Pressure Limit Rate Constants (k_∞) for QRRK Calculation: $C_3C^\bullet + O_2 \rightarrow$ Products[e]

	reaction	A (s^{-1} or cm^3/mol s)	n	E_a (kcal/mol)	ref
k_1	$C_3C^\bullet + O_2 \rightarrow C_3COO^\bullet$	6.62×10^{12}	0.0	0.0	61
k_{-1}	$C_3COO^\bullet \rightarrow C_3C^\bullet + O_2$	6.83×10^{15}	0.0	33.50	*a*
k_2	$C_3COO^\bullet \rightarrow C_3CO^\bullet + O$	1.70×10^{15}	0.0	59.01	85
k_3	$C_3COO^\bullet \rightarrow C_2C{*}C + HO_2$	3.70×10^{10} (4.93×10^{10})	0.82385 (0.8481)	27.43 (28.04)	*b*
k_4	$C_3COO^\bullet \rightarrow C_3{}^\bullet COOH^\bullet$	1.44×10^{10} (3.97×10^{9})	0.80848 (1.04314)	32.76 (32.06)	*b*
k_{-4}	$C_3{}^\bullet COOH \rightarrow C_3COO^\bullet$	7.21×10^{9} (3.33×10^{9})	0.24214 (0.39273)	15.65 (14.80)	*c*
k_5	$C_3{}^\bullet COOH \rightarrow C_2C{*}C + HO_2$	1.21×10^{13} (2.63×10^{14})	−0.12331 (−0.63326)	15.89 (15.81)	*b*
k_6	$C_3{}^\bullet COOH \rightarrow C_2CYC2O + OH$	5.89×10^{11} (4.11×10^{9})	0.04910 (0.7975)	16.13 (17.96)	*d*
k_7	$C_3{}^\bullet COOH \rightarrow C{*}C(C)Q{+}CH_3$	9.21×10^{13}	0.0	35.49	62

[a] Via k_{-1} and $\langle MR \rangle$, $E_{a-1} = \Delta U_{rxn}$. [b] Fitting with three-parameter modified Arrhenius equation; A estimated using TST and MP2-determined entropies, E_a evaluated from CBS-q//MP2(full)/6-31G* calculation plus endothermicity of reaction enthalpy. [c] Fitting with three-parameter modified Arrhenius equation; A estimated using TST and MP2-determined entropies, E_a evaluated from CBS-q//MP2(full)/6-31G* calculation. [d] Fitting with three-parameter modified Arrhenius equation; A estimated using TST and MP2-determined entropies, E_a best fit experimental data in this study. [e] LJ parameters: $\sigma = 5.55A$; $e/k = 585$ K. Geometric mean frequency (from CPFIT ref 34). $C_3{}^\bullet COOH$: 250.1 cm^{-1} (10.789), 1090.9 cm^{-1} (16.285), 2881.2 cm^{-1} (9.417). $C_3COO^\bullet$: 368 cm^{-1} (12.104), 1230.1 cm^{-1} (16.899), 3157.5 cm^{-1} (7.998). Data in parentheses are from B3LYP-determined entropies and CBS-q//B3LYP/6-31g* calculation.

in Table 6. Parameters in Table 6 are referenced to the ground (stabilized) level of the complex, as this is the formalism used in QRRK theory. References to specific high-pressure rate constants and falloff parameters are also listed in Table 6. The MP2-determined frequencies and moment of inertia for transition states, TS1−TS4, *tert*-butyl peroxy ($C_3COO^\bullet$), and *tert*-butyl hydroperoxide ($C_3{}^\bullet COOH$) are listed in Table 7.

The rate constant for isomerization of $C3COO^\bullet \leftrightarrow TS2 \leftrightarrow C3^\bullet COOH$, reaction 9, includes Eckart calculation of H tunneling, as described in Schwartz et al.[74] The imaginary frequency of TS2, 1266 cm^{-1}, used in the Eckart tunneling calculation is adjusted (down) from the MP2(full)/6-31g(d) determined imaginary frequency of 2876 cm^{-1} as recommended by Schwartz et al. This imaginary frequency (1266 cm^{-1}) yields tunneling factors of $\Gamma = 1.3$ for reaction 9 at 773 K. Other tunneling factors (Γs) at 500, 600, and 1000 K are 1.8, 1.5, and 1.2 for reaction 9, respectively. Schwartz et al. applied tunneling corrections with adjustment of the imaginary frequency and lowered barrier heights, to fit G2 calculated transition state parameters with experimental rate constants. The reactions were OH abstraction of hydrogen from CH_4, CH_3F, CH_2F_2, and CHF_3. An average decrease in barrier height of 1.12 kcal/mol from data obtained at the G2 level was used and the frequency was reduced by factors of 0.44 and 0.4 for MP2(full)/6-311g(d,p) and HF/6-31g(d) determined imaginary frequencies, respectively.



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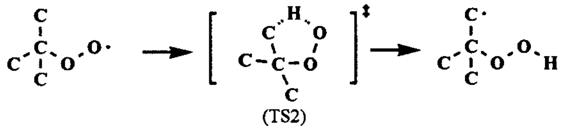

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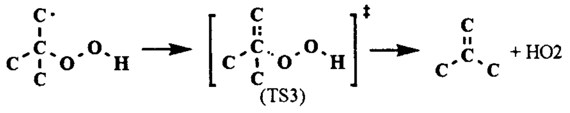

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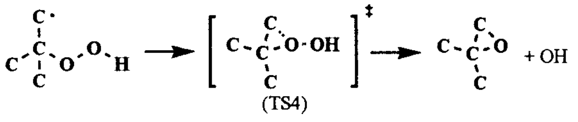


(11)

TABLE 7: Frequencies and Moments of Inertia for Intermediates and Transition States of C3C· + O_2 Reaction System Calculated at MP2(full)/6-31g(d) Level

molecule	frequencies	moments of inertia[a]
C3COO$^•$	129.64, 217.46, 268.16, 273.05, 286.26, 346.92, 376.52, 415.53, 455.19, 565.71, 763.56, 870.63, 970.60, 973.12, 998.18, 1080.04, 1089.89, 1245.28, 1309.86, 1326.36, 1352.84, 1453.60, 1457.53, 1479.70, 1533.11, 1548.05, 1548.93, 1559.77, 1559.88, 1581.36, 3112.08, 3114.13, 3117.49, 3203.72, 3205.34, 3210.33, 3211.69, 3225.47, 3228.10	398.87628, 616.98629, 617.41482
TS1	(−1261.40), 134.30, 179.70, 219.72, 223.72, 241.76, 387.53, 441.56, 526.71, 558.48, 593.16, 695.08, 849.14, 983.21, 1011.75, 1045.85, 1061.96, 1108.40, 1146.51, 1252.23, 1364.17, 1462.48, 1469.71, 1489.72, 1533.33, 1542.86, 1543.72, 1552.50, 1564.24, 1658.17, 1714.68, 3092.18, 3095.40, 3176.79, 3178.48, 3184.52, 3208.74, 3211.02, 3276.42	410.73702, 711.77631, 714.82995
TS2	(−2876.70), 217.20, 227.15, 265.66, 313.11, 357.38, 407.36, 421.95, 524.03, 625.78, 681.05, 817.15, 902.73, 955.77, 979.79, 1015.81, 1069.36, 1103.91, 1233.33, 1245.49, 1304.27, 1319.61, 1345.61, 1453.88, 1467.02, 1505.61, 1539.47, 1549.05, 1555.60, 1570.87, 1827.28, 3109.60, 3113.34, 3171.19, 3200.77, 3205.41, 3213.61, 3223.94, 3270.48	378.17489, 589.09898, 613.33608
C3$^•$COOH	74.77, 151.87, 247.28, 258.62, 270.51, 285.52, 354.23, 361.16, 397.82, 470.20, 537.23, 569.03, 777.74, 916.46, 950.41, 985.38, 1036.53, 1062.73, 1215.97, 1315.91, 1340.47, 1360.49, 1397.58, 1447.16, 1461.52, 1519.40, 1540.58, 1556.29, 1560.93, 1575.49, 3110.12, 3115.33, 3199.99, 3206.33, 3218.34, 3224.71, 3233.46, 3349.63, 3718.98	395.14592, 624.04899, 633.96915
TS3	(−775.53), 96.01, 163.16, 189.74, 219.70, 239.37, 308.20, 396.81, 403.49, 449.38, 479.88, 663.38, 836.26, 891.92, 994.48, 1012.61, 1046.61, 1062.66, 1117.39, 1168.90, 1362.65, 1418.99, 1452.66, 1467.74, 1494.20, 1533.91, 1545.87, 1547.47, 1563.70, 1640.61, 3108.35, 3113.14, 3195.40, 3201.12, 3219.70, 3225.07, 3231.87, 3326.24, 3681.71	404.16563, 708.21527, 734.08415
TS4	(−1325.33), 151.04, 211.92, 218.36, 234.31, 265.59, 365.52, 370.62, 426.77, 435.40, 509.57, 644.44, 789.84, 792.74, 925.43, 958.60, 991.17, 1066.23, 1072.66, 1129.12, 1210.86, 1331.97, 1408.74, 1457.99, 1468.67, 1526.72, 1535.88, 1551.63, 1563.20, 1571.37, 3111.27, 3114.77, 3203.59, 3208.15, 3218.90, 3221.32, 3256.00, 3379.64, 3770.68	430.34696, 605.93921, 628.62574

[a] Units, amu bohr^2.

An overall analysis of the reaction system indicates that the initial reaction of $C_3C^• + O_2 \rightarrow C_3COO^•$ has $\Delta H_{rxn,800K} = 35.09$ kcal/mol and $\Delta U_{rxn,800K} = 33.50$ kcal/mol with a reasonable high *A* factor for reverse reaction of 6.83×10^{15} s^{-1}, i.e., a moderately high *A*, thus, a loose transition state. Molecular (HO_2) elimination from $C_3COO^•$ to isobutene + HO_2 (via TS1) has an E_a of 27.43 kcal/mol with an *A* factor of 8.86×10^{12} s^{-1} at 773 K. This elimination transition state is slightly looser than $C_3COO^•$ H shift isomerization (via TS2) to $C_3{}^•COOH$. The H shift isomerization has an E_a of 32.76 kcal/mol, which is higher than HO_2 molecular elimination and lower than reverse reaction to $C_3C^• + O_2$ from the stabilized adduct. The H shift has a slightly lower *A* factor 3.11×10^{12} s^{-1} at 773 K than HO_2 molecular elimination. Both HO_2 molecular and H shift isomerization through five-member ring TS's have barriers lower than dissociation to $C_3C^• + O_2$, but tight TS's. $C_3{}^•COOH$ decomposition to isobutene + HO_2 (via TS3) has an *A* of 5.33×10^{12} s^{-1} at 773 K, which is lower than that for the elimination to C=C(C)Q + CH_3, 9.21×10^{13} s^{-1} (Q represents OOH group), but higher than that for reverse isomerization, 3.61×10^{10} s^{-1}, or 2,2-dimethyloxirane formation, 8.17×10^{11} s^{-1}. Dissociation to isobutene + HO_2 has only a slightly higher E_a of 15.89 kcal/mol than reverse isomerization of $C_3COO^•$, 15.65 kcal/mol, but lower than E_a's for 2,2-dimethyloxirane formation, 16.13 kcal/mol, and C=C(C)Q + CH3 elimination, 35.49 kcal/mol. The rate constants listed above refer to 773 K at high-pressure limits and are used for the QRRK input. The products isobutene + HO_2 are both relatively stable and build up in concentration so that reverse and further reactions of these species are important. The OH from the 2,2-dimethyloxirane formation reacts rapidly with other species; there is, effectively, no reverse reaction; OH addition to isobutene is, however, important.

Figure 6 illustrates the predicted effect of temperature at 760 Torr and at 60 Torr on *tert*-butyl radical + O_2 reaction. The data illustrate that at low pressure and high temperature more of the energized complex reacts to $C_2C{=}C + HO_2$ than is stabilized (most reacts back to $C_3C^• + O_2$). At lower temperatures, stabilization of the adduct is an important channel. The HO_2 molecular elimination reaction channel is faster than the

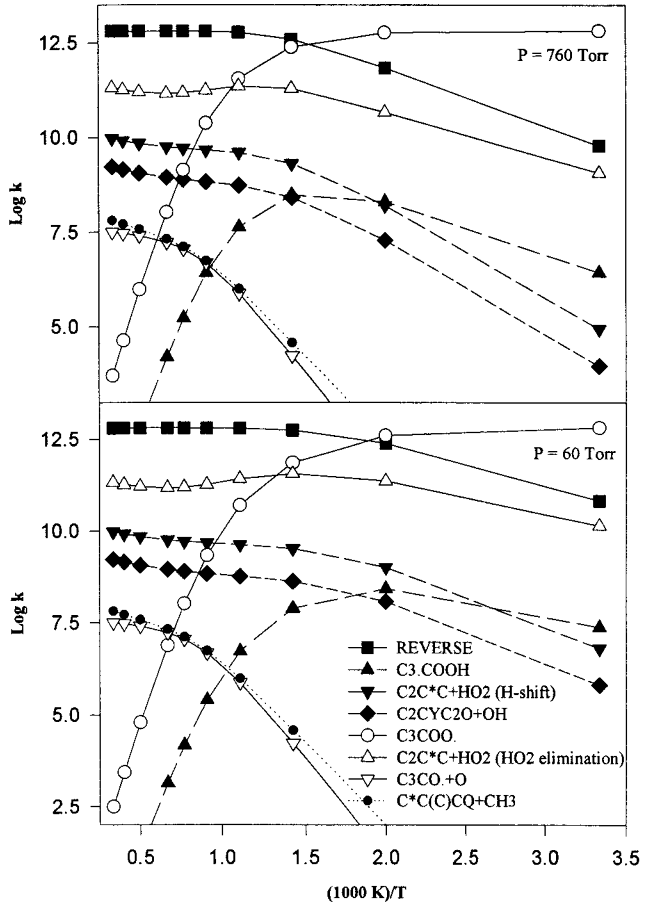


Figure 6. Calculated rate constants at different temperatures for chemically activated reactions *tert*-butyl radical + $O_2 \Rightarrow [C_3COO^•]^* \Rightarrow$ products: (a) pressure at 760 Torr; (b) pressure at 60 Torr. On the basis of CBS-q//MP2(full)/6-31g* calculation.

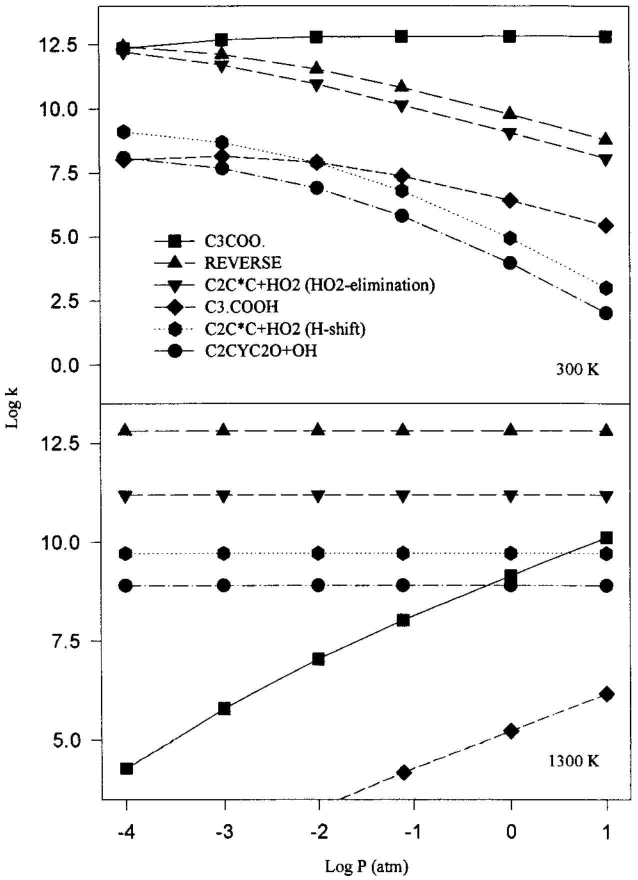


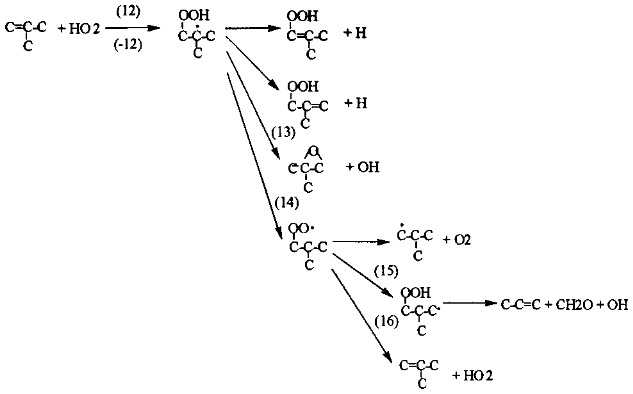
Figure 7. Calculated rate constants at different pressure for chemically activated reactions *tert*-butyl radical + $O_2 \Rightarrow [C_3COO^•]^* \Rightarrow$ products: (a) 300 K; (b) 1300 K. On the basis of CBS-q//MP2(full)/6-31g* calculation.

H shift isomerization channel due to the lower barrier and similar *A* factor. The effects of pressure on rate constants are illustrated in Figure 7 for temperatures of 300 and 1300 K. At 300 K, stabilization of the complex, $C_3COO^•$, is the dominant reaction channel above 0.0001 Torr. At 1300 K, dissociation of the complex to reactants (reverse reaction) is the primary reaction of the energized adduct below 10 atm.

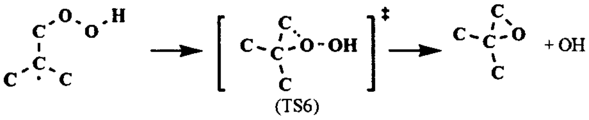
The rate of *tert*-butyl radical loss by reaction with O_2 increases with a decease in temperature and increase in pressure, as expected for reversible formation of the *tert*-butyl peroxy adduct. A significant fraction of this adduct, $C_3COO^•$, dissociates back to reactants at high temperature. This is a result of the high *A* for reverse reaction relative to the tight TST for isomerization or HO_2 molecular elimination where the reaction barriers are within 5.4 kcal/mol of dissociation. The rate constants to stabilization decrease with decease in pressure and increase in temperature above 700 K, due to the higher rate for dissociation of $C_3COO^•$ back to $C_3C^• + O_2$. Rate constants for direct (chemical activation) formation of 2,2-dimethyloxirane + OH and C=C(C)Q + CH_3 channels increase with increase in temperature and pressure.

The energized hydroperoxy radical $C_3^•COOH^*$, if formed, dissociates to $C_2C{=}C + HO_2$ almost completely at low pressures and high temperature due to the higher *A* factor and similar barrier for this β-scission channel, relative to reverse isomerization. At higher pressures, larger fractions of $C_3^•COOH$ are stabilized. Increased pressure, therefore, amplifies the importance of subsequent reactions of this hydroperoxide alkyl radical with O_2. At high temperature (above 1500 K), the C_3-$CO^• + O$ channel becomes important.

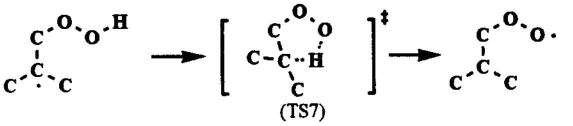
Isobutene ($C_2C{=}C$) + HO_2. Isobutene is formed by H atom elimination from $C_3C^•$ by HO_2 molecular elimination from C_3-$COO^•$ and by HO_2 elimination from $C_3^•COOH$. The isobutene + HO_2 reaction system becomes important as a result of the relatively high yields of isobutene and high concentration of HO_2 in this intermediate temperature oxidation of *tert*-butyl radical. The addition of HO_2 radical to isobutene (addition at the isobutene CD/H2 carbon atom, CD = carbon double bond) proceeds through the sequence described below. Addition to the isobutene CD/C2 carbon atom is treated by reverse of reaction in the *tert*-butyl radical + O_2 system, as discussed above.



The reaction channels of the stabilized $C_2C^•COOH$ adduct include dissociation back to isobutene + HO_2 (reaction −12, via TS5), H atom elimination (β-scission) to olefin hydroperoxides, cyclization to form 2,2-dimethyloxirane product with OH radical (reaction 13, via TS6), and isomerization via five-member ring transition state (hydrogen shift) to form isobutyl peroxy radical (reaction 14, via TS7). The isobutyl peroxy radical can undergo β-scission to isobutyl radical + O_2, HO_2 molecular elimination to isobutene (reaction 16, via TS9), and H shift isomerization via a six-member ring transition state to hydroperoxide radical (reaction 15, via TS8) with subsequent β-scission to propene, formaldehyde, and OH radical. The potential energy diagram for $C_2C{=}C + HO_2$ (HO_2 addition at the CD/H2 carbon) reaction system is illustrated in Figure 8.



(13)



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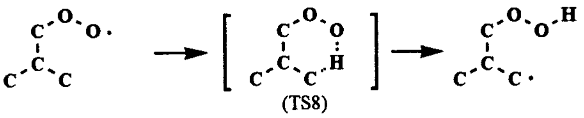

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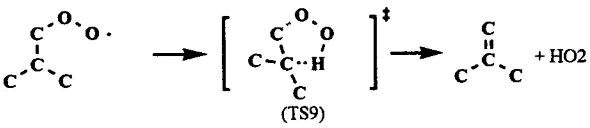


(16)

Enthalpies of formation of $C_2^•CCOOH$, $C_2C^•COOH$, and C_2-$CCOO^•$ radicals are determined as −2.18, −8.37, and −19.07

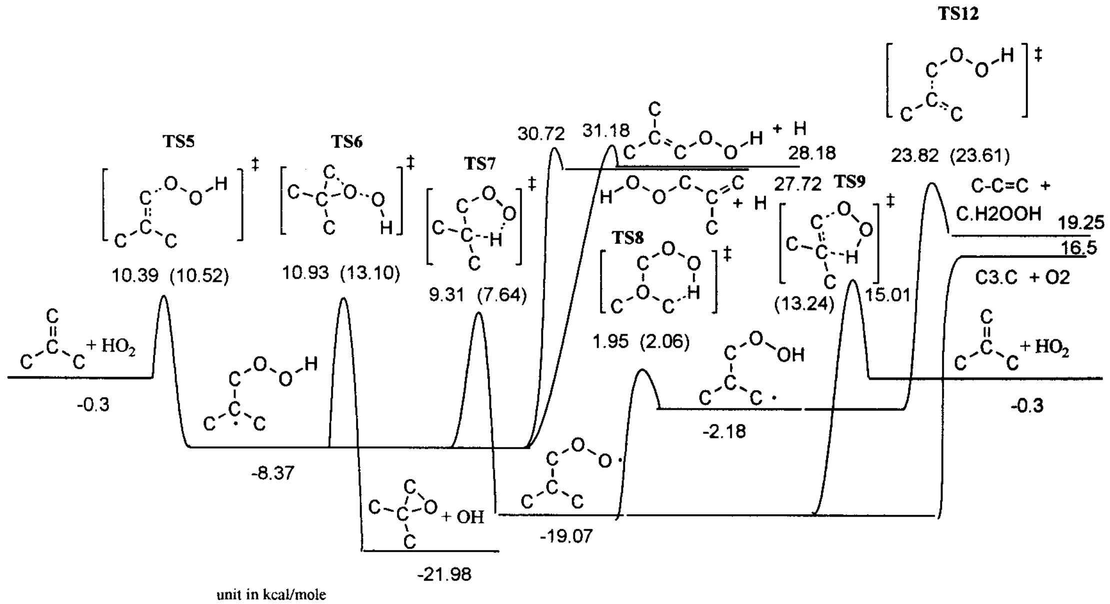


Figure 8. Potential energy diagram for $C_2C{*}C + HO_2 \Rightarrow [C_2C^{\bullet}COOH]^{*} \Rightarrow$ products based on CBS-q//MP2(full)/6-31g*. Data in parentheses are from CBS-q//B3LYP/6-31g* calculation.

kcal/mol, respectively, using calculated bond enthalpies (HOOCC(C)C−H, C_2(COOH)C−H, and C_2CCOO−H) and $\Delta H_f{}^{\circ}{}_{298}$ (C_2CCOOH) (−52.71 kcal/mol). Bond enthalpies of HOOCC(C)C−H, C_2(COOH)C−H, and C_2CCOO−H are calculated from the following isodesmic reactions plus bond enthalpies of HOOCC−H (102.87 kcal/mol) and COO−H (86.65 kcal/mol).[46]

$$C_2^{\bullet}CCOOH + CCOOH \rightarrow C_2CCOOH + C^{\bullet}COOH$$

$$C_2C^{\bullet}COOH + CCOOH \rightarrow C_2CCOOH + C^{\bullet}COOH$$

$$C_2CCOO^{\bullet} + COOH \rightarrow C_2CCOOH + COO^{\bullet}$$

$\Delta H_{rxn,298K}$ of these isodesmic reactions are determined to be 0.24, 6.43, and 0.56 kcal/mol, respectively, using the average value of two calculations: CBS-q//MP2(full)/6-31g(d) and CBS-q//B3LYP/6-31g(d).

$\Delta H_f{}^{\circ}{}_{298}$(TS5) (10.39 kcal/mol) is determined from ($\Delta H_f{}^{\circ}{}_{298}$($C_2C{=}C$) + $\Delta H_f{}^{\circ}{}_{298}$($HO_2$)) (−0.3 kcal/mol) plus reaction enthalpy ($\Delta H^{\ddagger}_{TS5-(C_2C=C+HO_2)}$) (10.69 kcal/mol). $\Delta H_f{}^{\circ}{}_{298}$(TS6) (10.93 kcal/mol) is determined from ($\Delta H_f{}^{\circ}{}_{298}$($C_2C{=}C$) + $\Delta H_f{}^{\circ}{}_{298}$($HO_2$))(−0.3 kcal/mol) plus reaction enthalpy ($\Delta H^{\ddagger}_{TS6-(C_2C=C+HO_2)}$) (11.23 kcal/mol). $\Delta H_f{}^{\circ}{}_{298}$(TS7) (9.31 kcal/mol) is from $\Delta H_f{}^{\circ}{}_{298}$($C_2C^{\bullet}COOH$) (−8.37 kcal/mol) plus reaction enthalpy ($\Delta H^{\ddagger}_{TS7-C_2C^{\bullet}COOH}$) (17.68 kcal/mol). $\Delta H_f{}^{\circ}{}_{298}$(TS8) (1.95 kcal/mol) is from $\Delta H_f{}^{\circ}{}_{298}$($C_2^{\bullet}CCOOH$) (−2.18 kcal/mol) plus reaction enthalpy ($\Delta H^{\ddagger}_{TS8-C_2^{\bullet}CCOOH}$)(4.13 kcal/mol). All reaction enthalpies above are calculated at CBS-q//MP2(full)/6-31g(d) level.

High-pressure limit pre-exponential factors (A_{∞}) for reactions 12−16 are calculated using canonical TST along with MP2-determined entropies. High-pressure limit rate constants, k_{∞}, are fit to a three-parameter modified Arrhenius equation (A, n, E_a) over the temperature range 300−2000 K. The rate constants for isomerization of C2C•COOH ↔ TS7 ↔ C2CCOO•, reaction 14, and C2CCOO• ↔ TS8 ↔ C2•CCOOH, reaction 15, include an Eckart calculation of H tunneling. The imaginary frequency of TS7 and TS8, 1193 and 953 cm^{-1}, used in the Eckart tunneling calculation are adjusted (down) from MP2(full)/6-31g(d) determined imaginary frequency of 2710 and 2167 cm^{-1}. These reduced imaginary frequencies yield tunneling factors of $\Gamma = 1.25$ and 1.15 for reactions 14 and 15, respectively, at 773 K. The MP2-determined frequencies and moments of inertia for transition states, peroxy radicals, and hydroperoxide radicals are listed in Table 8. Input data for QRRK calculations, references to specific high-pressure limit rate constants, and falloff parameters are listed in Tables 9 and 10 (HO_2 addition at the CD/C2 and CD/H2 carbon atoms, respectively).

Reaction barriers (reaction enthalpy difference between TS and reactants) for addition of HO_2 radical to isobutene at the CD/H2 and CD/C2 carbon atoms are calculated to be 7.74 and 10.69 kcal/mol, respectively, at CBS-q//MP2(full)/6-31g(d) level. The high-pressure limit rate constants are determined to be ((1.31 × 10^4)$T^{2.10}$ cm^3/mol s) exp(−7.54 kcal mol^{-1}/RT) and ((5.6 × 10^4)$T^{1.89}$ cm^3/mol s) exp(−10.56 kcal mol^{-1}/RT) for $C_2C{=}C + HO_2 \Rightarrow [C_3^{\bullet}COOH]^{*}$ and $C_2C{=}C + HO_2 \Rightarrow [C_2C^{\bullet}COOH]^{*}$, respectively. HO_2 electrophilic, radical addition to the CD/C2 carbon atom of isobutene has a lower activation energy than addition to the CD/H2 atom, resulting from partial electron donation from two $-CH_3$ groups. In the transition state, CH_3 groups donate electrons (ca. 0.22−0.26 Mulliken charge per CH_3, at MP2(full)/6-31g(d) level) to the olefinic carbon, which is undergoing bond formation with HO_2. Activation energies obtained from ab initio calculation show the same trend as experimental data of Gulati et al.[47] The Walker group[47] reports rate constants for the addition of HO_2 radicals to 2,3-dimethylbut-2-ene and hex-1-ene to be (4.79 × 10^{11}) exp(−8390/RT) (cm^3 mol^{-1} s^{-1}) and (7.94 × 10^{11}) exp(−13930/RT) (cm^3 mol^{-1} s^{-1}) at 673−703 K, respectively.

The calculated rate constants between 300 and 2000 K at 760 Torr from the QRRK/falloff analyses are illustrated in Figure 9. The effects of pressure on rate constants are illustrated in Figure 10 for temperature of 700 K. Figures 9 and 10 illustrate that stabilization of $C_2C^{\bullet}COOH$ adduct is the dominant reaction channel at low temperature and high pressure. At high temperature and low pressure energized complex dissociation back to reactants becomes more important. This reverse reaction (back

TABLE 8: Frequencies and Moments of Inertia for Intermediates and Transition States of C2C*C + HO_2 Reaction System Calculated at the MP2(full)/6-31g(d) Level

molecule	frequencies	moments of inertia[a]
$C2C^{\bullet}COOH$	54.16, 112.67, 145.54, 165.79, 190.59, 265.22, 313.30, 367.31, 410.95, 573.06, 812.86, 867.16, 963.93, 976.30, 1010.90, 1040.97, 1068.46, 1121.40, 1281.29, 1327.47, 1360.54, 1382.34, 1428.06, 1463.00, 1474.71, 1523.72, 1538.09, 1545.33, 1553.98, 1563.03, 3045.98, 3047.52, 3050.83, 3138.54, 3140.57, 3142.38, 3188.03, 3198.07, 3700.57	318.82942, 807.06745, 903.69160
TS5	(−782.49), 53.48, 133.55, 136.83, 153.89, 187.04, 302.56, 390.14, 450.19, 462.72, 485.10, 848.65, 903.55, 992.14, 1003.08, 1031.10, 1071.85, 1119.88, 1135.23, 1182.05, 1366.39, 1417.35, 1462.56, 1469.71, 1484.15, 1531.13, 1540.90, 1548.20, 1560.27, 1692.60, 3089.15, 3093.27, 3165.24, 3167.89, 3203.79, 3209.97, 3219.66, 3312.89, 3666.89	380.31285, 762.51238, 878.64915
TS6	(−1369.21), 113.32, 131.51, 138.47, 162.95, 219.41, 278.79, 325.38, 403.28, 419.28, 491.55, 788.57, 975.60, 1006.54, 1013.10, 1057.56, 1094.56, 1115.71, 1161.45, 1199.28, 1300.27, 1370.07, 1434.50, 1471.11, 1473.56, 1528.97, 1542.99, 1543.66, 1564.90, 1595.45, 3078.58, 3081.06, 3112.69, 3159.34, 3160.89, 3186.07, 3212.61, 3217.28, 3772.37	296.28913, 825.73071, 947.98193
TS7	(−2710.41), 141.63, 213.25, 249.26, 277.02, 310.90, 372.95, 425.20, 574.73, 688.46, 851.99, 965.42, 982.12, 1007.18, 1007.68, 1058.32, 1186.23, 1200.10, 1227.86, 1296.86, 1322.53, 1344.43, 1392.47, 1455.88, 1470.03, 1537.43, 1543.40, 1551.41, 1556.49, 1563.09, 1847.04, 3083.72, 3086.47, 3094.77, 3167.71, 3169.32, 3175.44, 3202.24, 3213.34	342.49651, 689.30912, 764.77772
$C2CCOO^{\bullet}$	81.45, 95.76, 233.29, 254.80, 269.59, 353.72, 422.97, 448.35, 561.76, 850.59, 945.68, 955.56, 968.78, 1013.25, 1016.79, 1187.25, 1219.23, 1243.23, 1285.26, 1326.80, 1364.14, 1421.40, 1438.38, 1463.23, 1481.75, 1533.80, 1551.64, 1558.38, 1568.80, 1574.86, 3099.47, 3103.00, 3107.32, 3126.74, 3186.03, 3190.46, 3198.22, 3205.87, 3216.72	268.22031, 810.52556, 977.48312
TS9	(−1354.46), 127.47, 188.28, 206.02, 217.18, 243.12, 369.74, 432.99, 570.60, 649.47, 713.36, 856.13, 878.30, 990.66, 1007.61, 1076.21, 1079.97, 1120.73, 1187.41, 1225.14, 1338.14, 1466.34, 1473.79, 1495.17, 1541.59, 1553.90, 1563.81, 1571.97, 1589.76, 1740.15, 1894.37, 3092.39, 3094.32, 3171.45, 3171.70, 3192.02, 3192.92, 3217.16, 3305.93	371.65782, 796.94415, 839.07288
TS8	(−2166.99), 129.66, 250.39, 303.38, 323.59, 438.15, 453.57, 489.91, 560.17, 703.74, 869.47, 957.77, 985.79, 993.22, 1021.88, 1064.72, 1171.39, 1208.60, 1209.36, 1244.44, 1305.30, 1321.56, 1352.93, 1413.99, 1416.09, 1462.95, 1514.10, 1535.27, 1559.39, 1564.55, 1616.79, 3099.97, 3102.94, 3126.44, 3158.28, 3182.70, 3191.81, 3202.37, 3253.87	276.71800, 696.43767, 882.06318
$C2^{\bullet}CCOOH$	96.62, 115.52, 133.07, 168.77, 201.03, 247.34, 346.74, 385.37, 402.61, 454.92, 626.06, 859.28, 911.59, 977.78, 1004.88, 1013.33, 1042.51, 1113.93, 1207.26, 1220.27, 1279.39, 1368.56, 1383.57, 1397.07, 1428.99, 1466.37, 1525.55, 1558.70, 1566.86, 1586.31, 3008.25, 3081.39, 3110.15, 3141.29, 3193.38, 3222.02, 3231.18, 3341.56, 3721.14	280.46147, 859.03050, 966.76821
TS12	(−652.21), 57.76, 135.73, 172.72, 196.11, 251.24, 390.20, 432.22, 446.31, 503.10, 601.77, 631.09, 874.59, 878.88, 924.61, 972.56, 1001.29, 1083.07, 1098.90, 1166.39, 1227.12, 1238.02, 1326.49, 1444.96, 461.35, 1490.91, 1494.54, 1550.80, 1561.28, 1636.71, 3113.56, 3166.87, 3196.51, 3205.41, 3211.77, 3223.73, 3301.18, 3308.67, 3569.12	371.83682, 759.37160, 918.60184

[a] Units, amu bohr^2.

to $C_2C{=}C + HO_2$) is faster than the 2,2-dimethyloxirane + OH formation channel by factors of ~4−6 over temperature ranging from 300 to 3000 K at 760 Torr.

OH Addition to Isobutene and Isobutene−OH + O_2. The reactive hydroxy radical is formed mainly through reactions 17−19.

$$C_3C^{\bullet} + O_2 \rightarrow C_2C{=}C + HO_2 \tag{2}$$

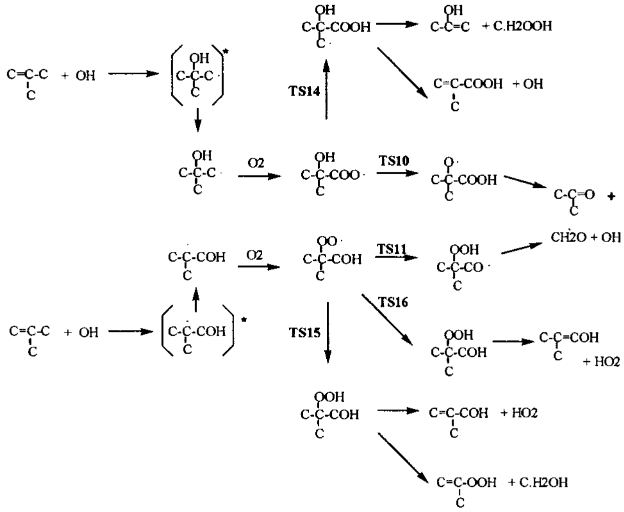
$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{17}$$

$$H_2O_2 + M \rightarrow 2OH + M \tag{18}$$

$$R^{\bullet} + HO_2 \rightarrow RO^{\bullet} + OH \tag{19}$$

OH will add to isobutene that is present at a relatively high concentration. Isobutene−OH adducts will then react with O_2. OH radicals add to isobutene at either the CD/H2 or CD/C2 carbon atom. We use the high-pressure limit rate constant for OH addition to isobutene as 8.5×10^{12} cm^3 mol^{-1} s^{-1} exp($+0.3$ kcal mol$^{-1}/RT$).[63]

In the presence of O_2, the isobutene−OH adducts will react with oxygen to form corresponding peroxy adducts and undergo further reactions (as below).



Where [ ]* indicates a energized intermediate.

The peroxy adducts undergo hydrogen transfer from hydroxyl group, −OH, to the peroxy group, $-OO^{\bullet}$ (via TS10 and TS11),

TABLE 9: Input Parameters and High-Pressure Limit Rate Constants (k_∞) for QRRK Calculations[a]

$C_2C{*}C + HO_2 \leftrightarrow [C_3{}^{\bullet}COOH]{*}$ and $C_2C{*}C + HO_2 \leftrightarrow [C_3COO^{\bullet}]{*}$

	reaction	A (s^{-1} or cc/mol s)	n	E_a (kcal/mol)	ref
k_1	$C_2C{*}C + HO_2 \rightarrow C_3{}^{\bullet}COOH$	1.31×10^4 (2.20×10^3)	2.10058 (2.38948)	7.54 (7.00)	*b*
k_{-1}	$C_3{}^{\bullet}COOH \rightarrow C_2C{*}C + HO_2$	1.21×10^{13}(2.63×10^{14})	−0.12331(−0.63326)	15.89(15.81)	*b*
k_2	$C_2C{*}C + HO_2 \rightarrow C_3COO^{\bullet}$	2.01×10^1 (3.45×10^{-1})	2.48142 (3.22043)	19.60 (21.47)	*b*
k_{-2}	$C_3COO^{\bullet} \rightarrow C_2C{*}C + HO_2$	3.70×10^{10} (4.93×10^{10})	0.82385 (0.8481)	27.43 (28.04)	*b*

geometric mean frequency (from CPFIT ref 34)
$C_3{}^{\bullet}COOH$ 250.1 cm^{-1} (10.789), 1090.9 cm^{-1} (16.285), 2881.2 cm^{-1} (9.417)
$C_3COO^{\bullet}$ 368 cm^{-1} (12.104), 1230.1 cm^{-1} (16.899), 3157.5 cm^{-1} (7.998)
Lennard-Jones parameters: $\sigma = 5.55$A°, $\epsilon/k = 585$ K (ref 37)

$C{*}C(C)Q \rightarrow C_2{}^{\bullet}C{*}O + OH$

	reaction	A (s^{-1} or cc/mol s)	E_a (kcal/mol)
k_1	$C{*}C(C)Q \rightarrow C_2{}^{\bullet}C{*}O + OH$	4.05E15	14.47

geometric mean frequency (from CPFIT ref 34)
$C{*}C(C)Q$ 526.0 cm^{-1} (12.851), 1827.0 cm^{-1} (10.334), 2881.2 cm^{-1} (2.315)
Lennard-Jones parameters: $\sigma = 5.1983$A°, $\epsilon/k = 533.08$ K (ref 37)

k_1 $A_1 = 4.05E{+}15$, from $CCOOH \rightarrow CCO^{\bullet}{+}OH$ (ref 64); $E_{a1} = \Delta U_{rxn} - RTm$

$C2{}^{\bullet}C{*}O \rightarrow C{*}C{*}O + CH_3$

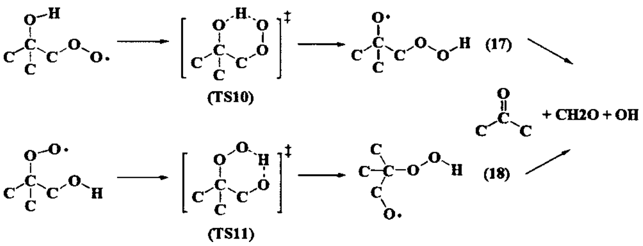
	reaction	A (s^{-1} or cc/mol s)	E_a (kcal/mol)
k_1	$C_2{}^{\bullet}C{*}O \rightarrow C{*}C{*}O + CH_3$	1.11E13	39.44

geometric mean frequency (from CPFIT ref 34)
$C_2{}^{\bullet}C{*}O$ 372.4 cm^{-1} (5.286), 1158.0 cm^{-1} (9.242), 2500.5 cm^{-1} (5.471)
Lennard-Jones parameters: $\sigma = 4.8034$ Å, $\epsilon/k = 481.73$ K (ref 37)

k_1 A_1 via A_{-1} and MR, $E_{a1} = \Delta U_{rxn} + E_{a-1}$
k_{-1} based on $C{=}C{-}C + CH_3$, $A_{-1} = 1.19E11$, $E_{aa-1} = 8.191$ (ref 63)

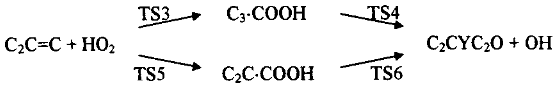
[a] Data in parentheses are from B3LYP-determined entropies and CBS-q//B3LYP/6-31g* calculation. [b] Fitting with two parameter modified Arrhenius equation; *A* estimated using TST- and MP2-determined entropies, E_a evaluated from CBS-q//MP2(full)/6-31G* calculation.

leading to formation of hydroperoxy adducts with a 17.1 kcal/mol barrier that is mostly due to endothermicity. Cleavage of the RO−H bond requires ca. 104 kcal/mol and the formation of the OO···H bond returns only 88.5 kcal/mol. Hydrogen bonding in the ROO···H···OR′ transition state reduces the barrier for this H shift isomerization by ca. 7 cal/mol. β-scission of the resulting oxy radicals form strong carbonyl bonds, C=O. The alkoxy radicals rapidly decompose to final products, formaldehyde, acetone, and OH radicals, after the isomerization. This detailed pathway explains the "Waddington mechanism"[47] for $C_2C{=}C + OH + O_2 \rightarrow$ acetone + CH_2O + OH.



The high-pressure limit rate constants for intramolecular isomerizations−hydrogen transfer are calculated by canonical TST using PM3-determined entropies and fitting a three-parameter (A, n, E_a) modified Arrhenius equation between 300 and 2000 K. The PM3-calculated frequencies and moment of inertia for intermediates and transition states are listed in Table 11. Potential energy diagrams for the isobutene−OH + O_2 reaction systems are illustrated in Figures 2 and 11. High-pressure limit rate constants and references for the QRRK calculation input and falloff parameters are listed in Tables12 and 13. Calculated rate constants for isobutene−OH + $O_2 \rightarrow$ products over the range 300−2000 K at 760 Torr are illustrated in Figures 12 and 13. Rate constant parameters, in the form of $k = AT^n \exp(-E_a/RT)$ for each reaction channel, are reported for the temperature range 500−900 K in Table 4. The isobutene−OH stabilization channel is dominant below 1000 K and above 0.1 atm due to the relatively deep well (31.8 kcal/mol) and large (14-atom) molecule size. The stabilized isobutene−OH adduct rapidly combines with O_2, with the well depth of isobutene−OH + $O_2 \Rightarrow$ isobutene−OH−$OO^{\bullet}$ of ca. 35 kcal/mol.[19] This well depth indicates there is sufficient energy in the energized adduct for isomerization to the oxy radical with subsequent reaction (β-scission) to carbonyl products. These isomerization reactions compete with stabilization.

2,2-Dimethyloxirane (C_2CYC_2O) Formation. 2,2-Dimethyloxirane is formed via three paths: isomerization of $C_3COO^{\bullet}$ to $C_3{}^{\bullet}COOH$, which undergoes cyclization as discussed above, and from the two addition channels of HO_2 to isobutene. The 2,2-dimethyloxirane formation paths via the HO_2 addition to isobutene are



The $C_2C^{\bullet}COOH$ path is less important because TS3 is 3 kcal/mol lower than TS5. We calculate the barrier for 2,2-dimethyloxirane + OH formation from $C_2C^{\bullet}COOH$ to be 19.3 kcal/mol, which is obtained from the enthalpy difference between $C_2C^{\bullet}COOH$ and TS6. The calculated barrier for $C_3{}^{\bullet}COOH \rightarrow$ 2,2-dimethyloxirane + OH reaction is 17.98 kcal/mol (enthalpy difference between $C_3{}^{\bullet}COOH$ and TS4). The calculated enthalpy of TS4 (10.17 kcal/mol) is determined from ($\Delta H_f{}^{\circ}{}_{298}(C_2C{=}C)$ + $\Delta H_f{}^{\circ}{}_{298}(HO_2)$) (−0.3 kcal/mol) plus reaction enthalpy ($\Delta H^{\ddagger}_{TS4-(C2C=C+HO_2)}$) (10.47 kcal/mol) at CBS-q//MP2(full)/6-31g(d). We need to adjust (reduce) the enthalpy of TS4 from 10.17 to 7.77 kcal/mol (barrier from 17.98 to 15.58 kcal/mol) in order to obtain agreement with experimental data of Atri et al.[11] We discuss accuracy of these calculations for barrier

TABLE 10: Input Parameters and High-Pressure Limit Rate Constants (k_∞) for QRRK Calculation[a]

$C_2C^*C + HO_2 \leftrightarrow [C_2C^\bullet COOH]^* \leftrightarrow$ Products

	reaction	A (s^{-1} or cc/mol s)	n	E_a (kcal/mol)
k_1	$C_2C^*C + HO_2 \rightarrow C_2C^\bullet COOH$	5.60×10^4 (6.46×10^2)	1.88925 (2.63530)	10.56 (10.26)
k_{-1}	$C_2C^\bullet COOH \rightarrow C_2C^*C + HO_2$	6.50×10^8 (3.80×10^8)	0.95922 (1.07625)	18.83 (18.91)
k_2	$C_2C^\bullet COOH \rightarrow C_2C^*CQ + H$	7.51×10^{12}		41.26
k_3	$C_2C^\bullet COOH \rightarrow C^*C(C)CQ + H$	3.14×10^{13}		40.77
k_4	$C_2C^\bullet COOH \rightarrow C_2CyC_2O + OH$	1.92×10^8 (2.32×10^7)	0.96504 (1.56530)	19.37 (21.05)
k_5	$C_2C^\bullet COOH \rightarrow C_2CCOO^\bullet$	1.02×10^6 (2.54×10^5)	1.18442 (1.45978)	17.33 (15.54)
k_{-5}	$C_2CCOO^\bullet \rightarrow C_2C^\bullet COOH$	3.67×10^8 (1.44×10^8)	0.90791 (1.10822)	28.18 (26.46)
k_6	$C_2CCOO^\bullet \rightarrow C_2C^*C + HO_2$	5.47×10^8 (1.30×10^8)	0.97272 (1.29753)	33.97 (32.06)
k_7	$C_2CCOO^\bullet \rightarrow C_2^\bullet CCOOH$	8.23×10^7 (3.63×10^7)	0.97453 (1.14529)	20.71 (20.77)
k_{-7}	$C_2^\bullet CCOOH \rightarrow C_2CCOO\cdot$	5.98×10^8 (1.28×10^8)	0.13262 (0.41599)	4.16 (4.15)
k_8	$C_2CCOO^\bullet \rightarrow C_3^\bullet C + O_2$	8.21×10^{14}		33.94
k_9	$C_2^\bullet CCOOH \rightarrow C^*CC + C^\bullet H_2OOH$	3.10×10^{12} (1.43×10^{13})	0.14876 (−0.08714)	26.42 (26.37)

geometric mean frequency (from CPFIT ref 34)
$C_2C^\bullet COOH$ 250.1 cm^{-1} (11.469), 1329.2 cm^{-1} (17.070), 2792.5 cm^{-1} (7.961)
$C_2CCOO^\bullet$ 250.2 cm^{-1} (9.560), 1119.2 cm^{-1} (16.494), 2788.5 cm^{-1} (10.946)
$C_2^\bullet CCOOH$ 250.6 cm^{-1} (10.626), 1179.9 cm^{-1} (17.723), 3081.5 cm^{-1} (9.151)
Lennard-Jones parameters: $\sigma = 5.5471$ Å, $\epsilon/k = 584.86$ K (ref 37)

k_1	fitting with three-parameter modified Arrhenius equation; A_1 estimated using TST and MP2-determined entropies, E_{a1} evaluated from CBS-q// MP2(full)/6-31G* calculation.
k_{-1}	fitting with three-parameter modified Arrhenius equation; A_{-1} estimated using TST and MP2-determined entropies, $E_{a-1} = E_{a1} + \Delta U_{rxn}$
k_2	via k_{-2} and $\langle MR \rangle$
k_{-2}	estimated $A_{-2} = 1.0e13$, $E_{a-2} = 3$
k_3	via k_{-3} and $\langle MR \rangle$
k_{-3}	estimated $A_{-3} = 1.0e13$, $E_{a-3} = 3$
k_4	fitting with three-parameter modified Arrhenius equation, A_4 estimated using TST and MP2-determined entropies, E_{a4} best fit experimental data in this study
k_5	fitting with three-parameter modified Arrhenius equation; A_5 estimated using TST and MP2-determined entropies, E_{a5} evaluated from CBS-q// MP2(full)/6-31G* calculation.
k_{-5}	fitting with three-parameter modified Arrhenius equation; A_4 estimated using TST and MP2-determined entropies, $E_{a-5} = E_{a5} + \Delta U_{rxn}$
k_6	fitting with three-parameter modified Arrhenius equation; A_6 estimated using TST and MP2-determined entropies, E_{a6} evaluated from CBS-q// MP2(full)/6-31G* calculation
k_7	fitting with three parameter modified Arrhenius equation; A_7 estimated using TST and MP2-determined entropies, E_{a7} evaluated from CBS-q// MP2(full)/6-31G* calculation.
k_{-7}	fitting with three parameter modified Arrhenius equation; A_4 estimated using TST and MP2-determined entropies, $E_{a-7} = E_{a7} - \Delta U_{rxn}$
k_8	via k_{-8} and $\langle MR \rangle$
k_{-8}	$A_{-8} = 3.60E12$, $E_{a-8} = 0$, from $C^*CC^\bullet + O_2$ (ref 61)
k_9	fitting with three parameter modified Arrhenius equation; A_1 estimated using TST and MP2-determined entropies, E_{a1} evaluated from CBS-q// MP2(full)/6-31G* calculation.

$C_2C^*CQ \rightarrow$ Products

	reaction	A (s^{-1} or cc/mol-s)	E_a (kcal/mol)
k_1	$C_2C^*CQ \rightarrow C_2C^*C^*O + OH$	4.05E15	21.40

geometic mean frequency (from CPFIT ref 34)
C_2C^*CQ 337.9 cm^{-1} (11.813), 1223.0 cm^{-1} (14.753), 2824.6 cm^{-1} (7.434)
Lennard-Jones parameters: $\sigma = 5.5471$ Å, $\epsilon/k = 584.86$ K (ref 37)

k_1	$A_1 = 4.05E15$, from $CCOOH \rightarrow CCO^\bullet + OH$ (ref 64)

$C2C^*CO^\bullet \rightarrow$ Products

	reaction	A (s^{-1} or cc/mol s)	E_a (kcal/mol)
k_1	$C_2C^*CO^\bullet \rightarrow C_2C^*C^*O + H$	5.14E13	37.39

geometric mean frequency (from CPFIT ref 34)
$C_2C^*CO^\bullet$ 419.1 cm^{-1} (10.253), 1349.8 cm^{-1} (11.776), 3014.7 cm^{-1} (6.971)
Lennard-Jones parameters: $\sigma = 5.1983$ Å, $\epsilon/k = 533.08$ K (ref 37)

k_1	via k_1 and $\langle MR \rangle$, estimated $A_{-1} = 1.0E13$, $E_{a-1} = 3$

[a] Data in parentheses are from B3LYP-determined entropies and CBS-q// B3LYP/6-31g* calculation.

estimates below, and we consider this reduction of 2.4 kcal/mol in one barrier reasonable. We further note that the mechanism results increase by only 0.2% and 1.07% in absolute concentration for isobutene and 2,2-dimethyloxirane formations, respectively, when this barrier is changed from 17.98 to 15.58 kcal/mol. The *tert*-butyl precursor, 2,2,3,3-tetramethylbutane is decreased by 0.8% in absolute concentration.

Figure 3 shows a comparison of our calculation with experimental data at 770 K and 60 Torr. Use of 15.58 and 17.98 kcal/mol barriers for the 2,2-dimethyloxirane + OH radical channel from $C_3^\bullet COOH$ result in 1.62% and 0.55% yields of 2,2-dimethyloxirane at 210 s reaction, respectively. The corre-

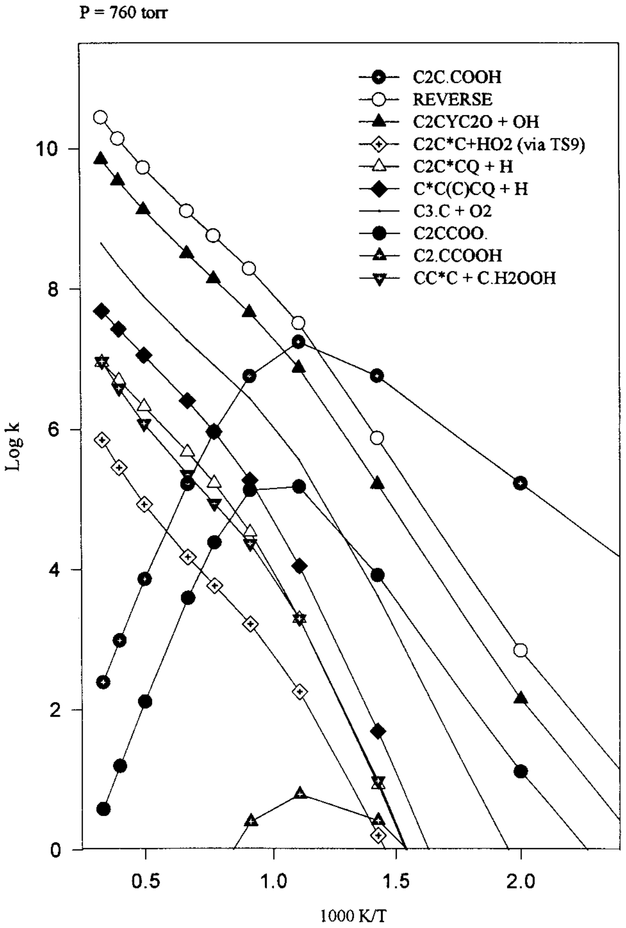


Figure 9. Calculated rate constants at different temperature and 760 Torr for chemically activated reactions $C_2C{*}C + HO_2 \Rightarrow [C_2C^\bullet COOH]^* \Rightarrow$ products. On the basis of CBS-q//MP2(full)/6-31g* calculation.

sponding data are illustrated via dash and dot lines in Figure 3, and the Δ symbols are data of Atri et al.[11] which show a 1.6% yield at 210 s.

Sensitivity analysis shows that an increase in the *A* factor of $C_3COO^\bullet \leftrightarrow TS1 \leftrightarrow C_2C{=}C + HO_2$ by 10 (direct HO_2 molecular elimination from $C_3COO^\bullet$), both forward and reverse directions, results in a decrease of 2,2-dimethyloxirane formation by 47.67% at 15 s and 8.04% at 210 s. If the *A* factor of $C_3COO^\bullet \leftrightarrow$ TS2 is increased by 10 (H-shift isomerization to $C_3^\bullet COOH$ which dissociates to $C_2C{=}C + HO_2$), the 2,2-dimethyloxirane formation is almost unchanged; it increases by only 2.43% at 15 s and 0.44% at 210 s. When the *A* factor for $C_2C{=}C + HO_2 \leftrightarrow [C_2C^\bullet COOH]^* \leftrightarrow C_2C^\bullet COOH$ is increased by 10, the 2,2-dimethyloxirane formation is again not changed significantly; it increases by 1.75% at 15 s and 3.93% at 210 s. Those results are at 60 Torr and 773 K. Figure 14 shows the relative contribution of specific reaction paths to 2,2-dimethyloxirane formation at 773 K and 60 Torr. At early times, the primary path is via the $[C_3COO^\bullet]^*$ adduct isomerization (H-shift) to $[C_3^\bullet COOH]^*$ adduct then reaction to the 2,2-dimethyloxirane plus OH. This path decreases in importance as HO_2 radical and stable isobutene build up in concentration. After several seconds of reaction, the primary path for 2,2-dimethyloxirane formation is from HO_2 addition to isobutene to form $[C_3^\bullet COOH]^*$ (lower barrier addition) then reaction to 2,2-dimethyloxirane + OH. The addition reactions of HO_2 + olefins in these moderate temperature hydrocarbon oxidation systems are clearly important. The O_2 and HO_2 addition reaction and isomerization reaction all have important reverse reaction paths, but due to the high reactivity of OH, the oxirane + OH channel does not.

Decomposition of 2,2-Dimethyloxirane (C_2CYC_2O). C_2CYC_2O reacts with radicals, such as OH, $C_2{}^\bullet C{=}C$, $C_3COO^\bullet$, CH_3, $CH_3OO^\bullet$, and $C{=}CC^\bullet$ to lose a H atom via abstraction.

$$C_2CYC_2O + OH \rightarrow C_2CYCC^\bullet O + H_2O$$

$$C_2CYC_2O + C_2{}^\bullet C{=}C \rightarrow C_2CYCC^\bullet O + C_2C{=}C$$

$$C_2CYC_2O + C{=}CC^\bullet \rightarrow C_2CYCC^\bullet O + C{=}CC$$

$$C_2CYC_2O + CH_3COO^\bullet \rightarrow C_2CYCC^\bullet O + C_3COOH$$

$$C_2CYC_2O + CH_3OO^\bullet \rightarrow C_2CYCC^\bullet O + CH_3OOH$$

$$C_2CYC_2O + CH_3 \rightarrow C_2CYCC^\bullet O + CH_4$$

The $C_2CYCC^\bullet O$ once formed will rapidly break one of the C−O single bonds, releasing the relatively high ring strain (three-member ring) and forming a strong carbonyl (C=O) bond. Subsequent elimination of a H atom to form methacrolein and

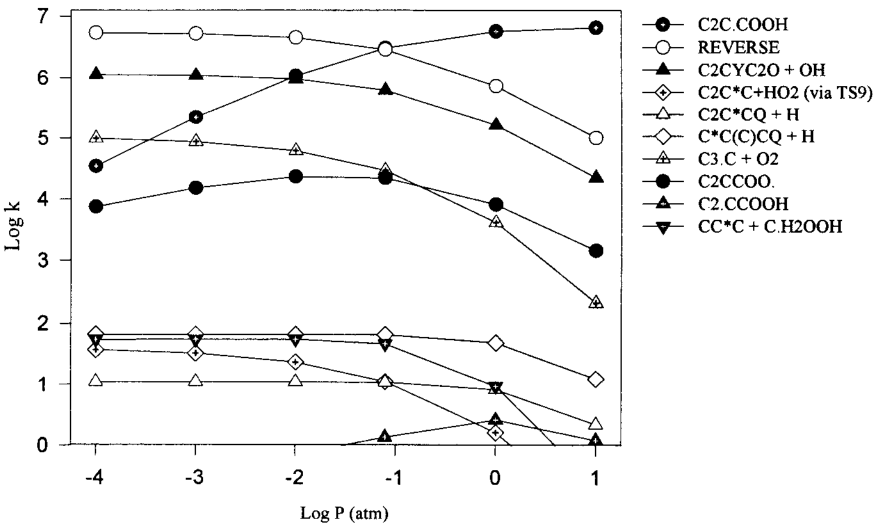


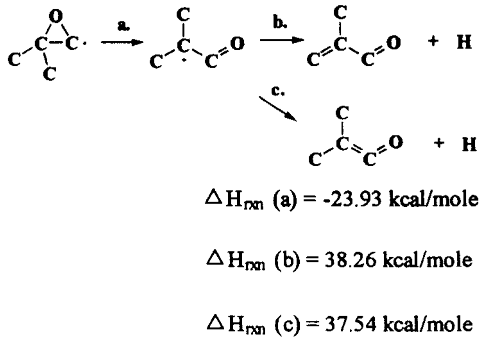
Figure 10. Calculated rate constants at different pressure and 700 K for chemically activated reactions $C_2C{*}C + HO_2 \Rightarrow [C_2C^\bullet COOH]^* \Rightarrow$ products. On the basis of CBS-q//MP2(full)/6-31g* calculation.

TABLE 11: PM3-Determined Frequencies and Moments of Inertia for Intermediates and Transition States of Isobutene−OH + O_2 Reaction System

molecule	frequencies	moments of inertia[a]
C2CQ$^{\bullet}$COH	60.86, 103.69, 158.53, 183.01, 230.69, 296.93, 321.99, 338.98, 377.67, 419.30, 558.70, 605.58, 804.94, 892.16, 912.64, 963.78, 979.97, 995.75, 1049.09, 1133.33, 1215.58, 1245.41, 1312.80, 1339.81, 1371.14, 1383.77, 1397.78, 1398.46, 1399.68, 1406.14, 1407.08, 1408.85, 1443.12, 2936.80, 3020.89, 3082.73, 3083.73, 3084.26, 3085.13, 3177.23, 3178.80, 3887.40	291.233533, 338.436954, 436.864864
TS11	(−870.22), 122.88, 145.99, 173.57, 221.05, 302.57, 349.92, 421.59, 439.56, 504.40, 570.32, 635.27, 855.92, 886.16, 922.66, 933.43, 962.62, 980.44, 989.31, 1018.70, 1105.31, 1190.50, 1218.27, 1271.67, 1311.30, 1328.82, 1382.78, 1395.51, 1397.16, 1399.46, 1403.39, 1406.40, 1407.82, 1776.33, 2957.14, 3020.26, 3084.76, 3086.99, 3087.50, 3088.52, 3179.70, 3180.55	230.297465, 355.352881, 397.562299
C2CQCO$^{\bullet}$	54.47, 97.29, 129.86, 158.54, 189.09, 240.47, 263.69, 340.85, 386.70, 422.76, 487.77, 578.44, 631.62, 815.34, 849.08, 939.24, 955.82, 964.23, 995.88, 1036.87, 1186.38, 1236.21, 1256.68, 1272.55, 1325.83, 1394.38, 1398.83, 1401.63, 1405.58, 1412.77, 1413.23, 1440.19, 1518.69, 2994.59, 3015.48, 3085.29, 3086.26, 3087.24, 3087.58, 3180.59, 3181.66, 3988.34	304.681126, 325.430673, 440.567673
C2COHCQ$^{\bullet}$	36.08, 91.57, 156.17, 185.65, 240.81, 311.90, 339.68, 357.74, 429.62, 481.13, 515.13, 586.82, 866.24, 920.04, 960.03, 965.31, 988.35, 989.68, 1011.51, 1093.82, 1160.90, 1255.92, 1289.90, 1336.94, 1346.73, 1384.22, 1398.84, 1400.74, 1407.78, 1408.69, 1409.29, 1415.55, 1433.80, 2973.53, 3025.28, 3084.46, 3086.98, 3088.75, 3089.47, 3181.50, 3183.73, 3895.54	196.005571, 480.429104, 489.709306
TS15	(−2699.96), 83.12, 113.77, 166.77, 261.04, 325.90, 339.30, 372.53, 415.87, 428.74, 534.43, 563.65, 579.07, 699.49, 883.28, 899.63, 950.74, 968.44, 990.09, 1036.01, 1060.54, 1114.18, 1137.37, 1235.03, 1265.49, 1314.17, 1332.82, 1372.93, 1388.84, 1395.80, 1399.89, 1407.07, 1452.82, 1547.68, 2937.18, 3027.79, 3085.43, 3087.35, 3088.69, 3135.66, 3181.51,3836.21	252.014028, 378.006671, 458.428245
C2$^{\bullet}$CQCOH	77.96, 107.91, 125.09, 146.08, 174.05, 252.13, 267.58, 284.74, 344.79,384.55, 422.48, 486.95, 574.14, 630.94, 741.62, 853.82, 911.53, 918.94,979.38, 993.96, 1062.11, 1126.20, 1194.53, 1250.03, 1307.41, 1316.46, 1360.40, 1389.27, 1392.65, 1401.02, 1412.60, 1412.92, 1432.07, 2921.81, 2971.71, 3089.22, 3092.06, 3153.12, 3184.81, 3201.21, 3909.39, 3968.50	301.509221, 319.436628, 435.630709
TS16	(−2758.61), 100.58, 146.50, 188.97, 197.93, 269.13, 284.43, 307.43, 357.69, 457.29, 477.74, 516.96, 585.68, 655.65, 844.61, 856.07, 924.92, 958.80, 978.47, 988.17, 1023.13, 1080.86, 1231.85, 1250.57, 1275.71, 1325.66, 1388.94, 1394.25, 1398.06, 1402.21, 1404.98, 1410.68, 1413.95, 1445.47, 2947.24, 3085.15, 3086.06, 3088.93, 3090.62, 3180.94, 3181.85, 3901.61	292.899823, 331.689037, 434.464659
C2CQC$^{\bullet}$OH	59.34, 87.46, 125.99, 175.54, 190.05, 206.86, 238.31, 288.86, 309.44, 367.02, 380.12, 432.66, 495.69, 585.83, 808.82, 872.52, 946.25, 958.06, 989.41, 1001.08, 1119.06, 1231.77, 1271.73, 1299.54, 1380.57, 1388.28, 1399.78, 1404.43, 1407.78, 1410.03, 1411.12, 1520.49, 1550.43, 3059.09, 3086.21, 3087.66, 3090.52, 3092.04, 3182.66, 3183.67, 3910.57, 3988.73	187.656693, 492.738857, 499.571646
TS10	(−700.41), 90.74, 148.25, 173.19, 261.74, 325.20, 336.43, 425.65, 465.66, 490.94, 562.46, 651.24, 872.72, 881.67, 943.12, 956.38, 974.11, 983.14, 1007.53, 1035.84, 1108.00, 1153.78, 1251.65, 1270.83, 1304.00, 1349.97, 1364.17, 1394.55, 1397.65, 1398.02, 1403.60, 1407.46, 1411.64, 1722.69, 2971.84, 3045.88, 3086.95, 3088.74, 3089.65, 3090.03, 3181.43, 3183.70	202.977381, 399.814918, 419.935328
C2CO$^{\bullet}$CQ	11.85, 84.46, 159.34, 169.02, 177.65, 192.94, 271.86, 340.54, 358.98, 468.82, 493.17, 547.30, 796.54, 882.81, 915.16, 962.28, 964.11, 989.82, 998.32, 1090.04, 1141.33, 1243.22, 1300.61, 1353.74, 1367.08, 1380.11, 1401.22, 1405.51, 1410.87, 1411.26, 1417.46, 1489.81, 2282.70, 2937.54, 2991.52, 3087.46, 3087.82, 3089.55, 3091.30, 3182.50, 3184.55, 3987.46	183.451362, 560.883182, 564.527788
TS14	(−2791.09), 75.29, 175.28, 259.62, 287.05, 312.80, 346.26, 424.64, 455.67, 480.99, 519.85, 557.56, 681.00, 717.80, 873.68, 953.99, 960.47, 975.89, 995.65, 1058.17, 1092.98, 1122.80, 1129.32, 1162.99, 1232.23, 1324.36, 1334.85, 1355.01, 1363.29, 1392.75, 1396.42, 1403.59, 1412.82, 1418.98, 2960.87, 3038.66, 3083.71, 3088.47, 3114.66, 3137.46, 3182.17, 3898.15	202.873387, 429.133131, 454.272972
C2$^{\bullet}$COHCQ	24.96, 83.47, 117.67, 159.19, 169.76, 183.42, 285.55, 328.97, 347.86, 364.18, 441.14, 503.07, 553.85, 646.46, 795.63, 916.00, 922.30, 934.47, 976.84, 988.25, 1087.09, 1140.73, 1162.62, 1229.96, 1312.11, 1331.87, 1347.02, 1376.73, 1395.64, 1405.07, 1408.16, 1474.32, 1490.67, 2926.68, 2982.85, 3086.49, 3091.84, 3154.06, 3184.32, 3205.03,3897.33, 3989.37	181.191039, 556.802137, 569.411493

[a] Units, 10E−40 g cm^2.

dimethylketene products then occurs.



Reactions Important to $C_2C{=}C$ Formation. The research group of Walker[11−13,43] has suggested that isobutene is a major and a primary product in the decomposition of 2,2,3,3-tetramethylbutane (C_3CCC_3) in the presence of O_2 in KCl-coated vessels. Our analysis indicates that it is formed mainly from $C_3C^{\bullet}$ radicals with O_2 (described above).

The unimolecular decomposition reaction of $C_3C^{\bullet}$ radicals is, on a relative base, slow at 773 K, and isobutene formation by this path is slow. We use the high-pressure limit rate constant for $C_3C^{\bullet} \rightarrow C_2C{=}C + H$ to be $((2.5 \times 10^{16})T^{-0.92}\ s^{-1})\ \exp(-37500/RT)$; rate constants of Knyazev or of Tsang result in little or no change in relative rates.

Isobutene Reaction. Isobutene is consumed by slower reactions, such HO_2 addition then further reaction to 2,2-dimethyloxirane + OH, or addition with OH then reaction of this hydroxyl adduct with O_2. These reaction systems are discussed in the previous sections. Isobutene also reacts by abstraction (loss) of its allylic H atoms (allylic C−H bond

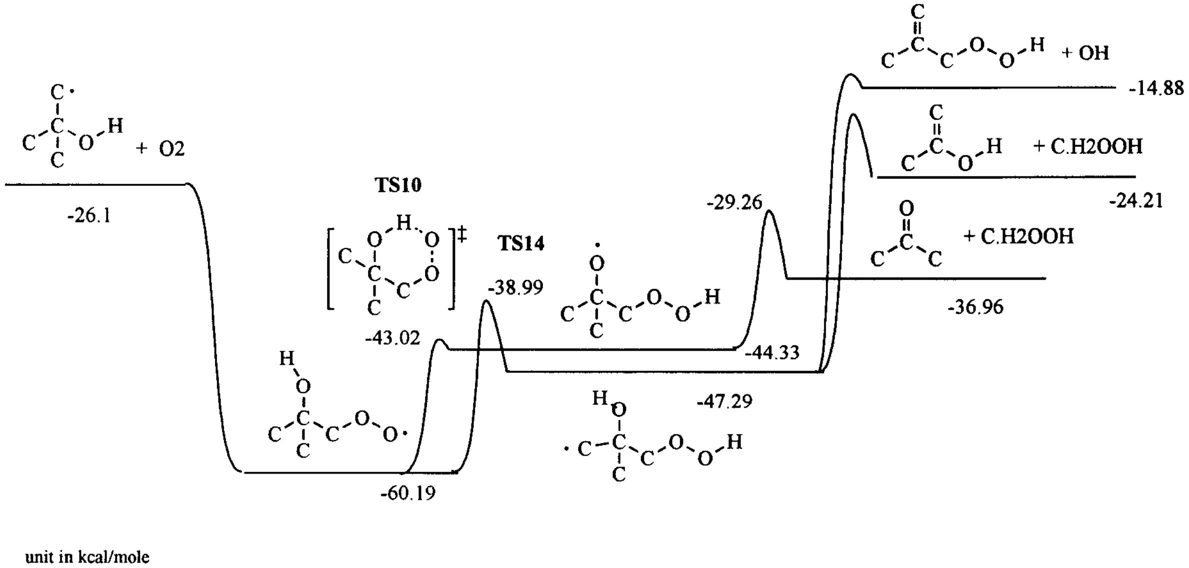


Figure 11. Potential energy diagram for $C_3{}^{\bullet}COH + O_2 \Rightarrow$ products.

energy only 88 kcal/mol) by HO_2, OH, O, O_2, and $CC^{\bullet}{=}C$ radicals.

$$C_2C{=}C + HO_2 \rightarrow C_2{}^{\bullet}C{=}C + H_2O_2$$

$$C_2C{=}C + OH \rightarrow C_2{}^{\bullet}C{=}C + H_2O$$

$$C_2C{=}C + O_2 \rightarrow C_2{}^{\bullet}C{=}C + HO_2$$

$$C_2C{=}C + O \rightarrow C_2{}^{\bullet}C{=}C + OH$$

$$C_2C{=}C + CC^{\bullet}{=}C \rightarrow C_2{}^{\bullet}C{=}C + C{=}CC$$

Loss of 2,2,3,3-Tetramethylbutane (C_3CCC_3). The *tert*-butyl radical is generated by the homogeneous decomposition of 2,2,3,3 tetramethylbutane in the presence of O_2.

$$(CH_3)_3C{-}C(CH_3)_3 \rightarrow 2C_3C^{\bullet} \qquad (1)$$

C_3CCC_3 can also undergo abstraction of H atom by HO_2, OH, C3C$^{\bullet}$, and $CC^{\bullet}{=}C$ radicals.

$$C_3CCC3 + HO_2 \rightarrow C_3{}^{\bullet}CCC_3 + H_2O_2$$

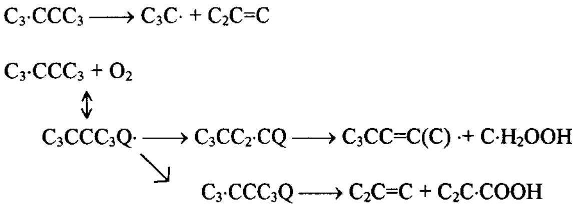
$$C_3CCC3 + OH \rightarrow C_3{}^{\bullet}CCC3 + H_2O$$

$$C_3CCC3 + O \rightarrow C_3{}^{\bullet}CCC_3 + OH$$

$$C_3CCC_3 + C3C^{\bullet} \rightarrow C_3{}^{\bullet}CCC_3 + C3C$$

$$C_3CCC_3 + CC^{\bullet}{=}C \rightarrow C_3{}^{\bullet}CCC_3 + C{=}CC$$

The $C_3{}^{\bullet}CCC_3$ radical undergoes a β-scission or further reacts with O_2. The β-scission reaction is more important above 1000 K and is an added source of isobutene.



Model and Comparison to Experimental Data. A reaction mechanism including the subreaction systems discussed above is assembled as Table 4. The CHEMKIN II interpreter and integrator, version 3.1, is used to model the reaction conditions of Atri et al.[11] for reaction time range 0−210 s, 773 K, and 60 torr. Wall loss reactions of Atri et al.[11] are included in the mechanism. Abstraction reactions are not considered pressure dependent and therefore do not require any falloff analysis. Abstraction reactions of O, OH, HO_2, and R$^{\bullet}$ radicals are taken from evaluated literature wherever possible. A procedure from Dean and Bozzelli[49] is used to estimate abstraction rate constants by H, O, OH, and CH_3 radicals when no literature data are available. A generic rate constant is utilized and adjusted for steric effects and reaction enthalpy for hydrogen abstractions by $C{=}CC^{\bullet}$ and HO_2 radicals.

The comparison of model calculations to experiments for loss of *tert*-butyl precursor, 2,2,3,3-tetramethylbutane, production of isobutene and 2,2-dimethyloxirane over the reaction time range (0−210 s), 773 K and 60 Torr is illustrated in Figure 3. The model shows good agreement with experimental data of Atri et al.[11]

Rate constants at pressures of 0.076, 0.76, 7.6, 60, 760, and 7600 Torr for the chemical activation and unimolecular reactions described above are listed in Table 4.

Accuracy of ab Initio and Density Functional CBS Calculations. The CBS-q calculation method suggests use of the HF/3-21g basis set optimized parameters. We optimize our geometries at a more accurate calculation level (B3LYP/6-31g(d) and MP2(full)/6-31g(d)). We select B3LYP/6-31g(d) and MP2(full)/6-31g(d) calculations for geometry optimization and frequency calculation in the composite CBS-q calculations for analysis of energies of activation and Arrhenius pre-exponential factors.

Curtiss et al.[50] report that B3LYP/6-31g(d,p) provides highly accurate structures for compounds with elements up to atomic number 10. Curtiss et al.[50] further report average errors on a test set of 148 molecules of 1.58 kcal/mol for G2 energy calculation results with a maximum error of 8.4 kcal/mol.

J. Durant[51,52] has compared density functional calculations BHandH and B3LYP with MP2 and Hartree−Fock methods for geometry and vibration frequencies. Durant[51,52] reports that these density functional methods provide excellent (improved)

TABLE 12: Input Parameters and High-Pressure Limit Rate Constants (k_∞) for QRRK Calculations

$C_2C*C + OH \rightarrow C_3{^\bullet}COH$

	reaction	A (s^{-1} or cc/mol s)	E_a (kcal/mol)
k_1	$C_2C*C + OH \rightarrow C_3{^\bullet}COH$	8.5×10^{12}	−0.3
k_{-1}	$C_3{^\bullet}COH \rightarrow C_2C*C + OH$	1.02×10^{14}	30.16

geometric mean frequency (from CPFIT ref 34)
$C_3{^\bullet}COH$ 439.7 cm^{-1} (11.660), 1274.0 cm^{-1} (13.717), 3014.7 cm^{-1} (8.624)
Lennard-Jones parameters: $\sigma = 5.1983$ Å, $\epsilon/k = 553.08$ K (ref 37)

k_1 ref 63; k_{-1} via k_1 and $\langle MR \rangle$

$C_3{^\bullet}COH + O_2 \rightarrow$ Products

	reaction	A (s^{-1} or cc/mol s)	n	E_a (kcal/mol)
k_1	$C_3{^\bullet}COH + O_2 \rightarrow C_2COHCQ^{\bullet}$	3.6×10^{12}		0.0
k_{-1}	$C_2COHCQ^{\bullet} \rightarrow C_3{^\bullet}COH + O_2$	8.25×10^{14}		32.23
k_2	$C_2COHCQ^{\bullet} \rightarrow C_2CO{^\bullet}CQ$	7.56×10^{7}	1.06165	17.83
k-$_2$	$C_2CO{^\bullet}CQ \rightarrow C_2COHCQ^{\bullet}$	9.16×10^{6}	1.33667	0.99
k_3	$C_2CO{^\bullet}CQ \rightarrow C_2C*O + C^{\bullet}H_2OOH$	7.80×10^{14}		12.41
k_4	$C_2COHCQ^{\bullet} \rightarrow C_2{^\bullet}COHCQ$	2.53×10^{8}	1.084	8.06
k_{-4}	$C_2{^\bullet}COHCQ \rightarrow C_2COHCQ^{\bullet}$	8.47×10^{7}	0.85274	21.68
k_5	$C_2{^\bullet}COHCQ \rightarrow C*C(C)CQ + OH$	8.89×10^{13}		32.10
k_6	$C_2{^\bullet}COHCQ \rightarrow C*C(C)OH + C^{\bullet}H_2OOH$	1.90×10^{14}		28.83

geometric mean frequency (from CPFIT ref 34)
$C_2COHCQ^{\bullet}$ 270.0 cm^{-1} (12.085), 1109.5 cm^{-1} (16.601), 2859.8 cm^{-1} (10.814)
$C_2CO{^\bullet}CQ$ 277.7 cm^{-1} (12.704), 1121.3 cm^{-1} (17.851), 2824.5 cm^{-1} (8.945)
$C_2{^\bullet}COHCQ$ 298.6 cm^{-1} (13.666), 1139.6 cm^{-1} (15.948), 2851.4 cm^{-1} (9.386)
Lennard-Jones parameters: $\sigma = 5.8569$ Å, $\epsilon/k = 632.06$ K (ref 37)

k_1 $A_1 = 3.6E12$, from Atkinson et al. for $CCC^{\bullet} + O_2$; $E_{a1} = 0$ (ref 61)
k_{-1} via k_1 and $\langle MR \rangle$, $E_{a-1} = \Delta U_{rxn}$
k_2 A_2 estimated using TST, PM3-determined entropies and fitting with three-parameter modified Arrhenius equation, Ea_2 evaluated from ring strain (0.1) + ΔH_{rxn} (16.84) + E_a abstraction (6.89) − 6 (H-bond)
k_{-2} A_{-2} estimated using TST, PM3-determined entropies and fitting with three-parameter modified Arrhenius equation, $E_{a-2} = E_{a2} - \Delta U_{rxn}$
k_3 via k_{-3} and $\langle MR \rangle$, $A_{-3} = 3.3E11$, estimated from ($C_2H_4 + CH_3$), $E_{a-3} = 7.7$ (ref 62)
k_4 A_4 estimated using TST, PM3-determined entropies and fitting with three parameter modified Arrhenius equation, E_{a4} evaluated from ring strain (0.1) + E_a abstraction (7.96)
k_{-4} A_{-4} estimated using TST, PM3-determined entropies and fitting with three-parameter modified Arrhenius equation, $E_{a-4} = E_{a4} + \Delta U_{rxn}$
k_5 k_5 via k_{-5} and $\langle MR \rangle$, $A_{-5} = 2.7E12$, estimated from 1/2($C_2H_4 + OH$), $E_{a-5} = 1.0$ (ref 66)
k_6 k_6 via k_{-6} and $\langle MR \rangle$, $A_{-6} = 3.3E11$, estimated from 1/2($C_2H_4 + CH_3$), $E_{a-6} = 7.7$ (ref 62)

$C^{\bullet}H_2OOH \rightarrow CH_2O + OH$

	reaction	A (s^{-1} or cc/mol s)	E_a (kcal/mol)
k_1	$C^{\bullet}H_2OOH \rightarrow CH_2O + OH$	2.90E12	1.0

geometric mean frequency (from CPFIT ref 34)
$C^{\bullet}H_2OOH$ 100.3 cm^{-1} (3.429), 986.7 cm^{-1} (4.763), 2506.4 cm^{-1} (2.808)
Lennard-Jones parameters: $\sigma = 4.3451$ Å, $\epsilon/k = 422.61$ K (ref 37)

k_1 A_1 via A_{-1} and $\langle MR \rangle$, $A_{-1} = 2.70E12$, estimated from 1/2($C_2H_4 + OH$), $E_{a-1} = 1.0$ (ref 66)

geometries and vibration frequencies, relative to MP2 at reduced computation expense. Petersson et al.[53−55] currently recommends use of B3LYP or BLYP for geometries and frequencies in CBS calculations.

Jungkamp and Seinfeld[56] report rms errors for CBS-q//B3LYP/6-31g(d,p) calculated enthalpies of 1.7 kcal/mol for a test set of 10 transition state barriers. They also show DFT optimized geometries result in significantly improved structures, enthalpies, and bond energies over the recommended HF/3-21g(d) level where a rms error of 4.1 kcal/mol was noted.

Mebel at al.[57] report use of B3LYP/6-31g(d,p) for geometries in their modified G2M(RCC,MP2) method as leading to improved accuracy for intermediates and transition states in application to vinyl radical reaction with O_2. They show several comparisons to experimental data where G2M(RCC,MP2) energy is underestimated by 2.5 kcal/mol for vinyl radical.

Jungkamp and Seinfeld[10] analyze the reaction system of primary and secondary butyl radicals with O_2 using CBS-q//B3LYP/6-31g(d,p) level calculations and show good agreement with group additivity calculated reaction enthalpies. Yamada et al.[32,58,59] show very good agreement between G2 and CBS-q//MP2(full)/6-31g(d,p) calculations, within 2 kcal/mol for stable and radical species in ethylene + OH and dimethyl ether radical + O_2 reaction systems. Yamada reports that transition state energies show a maximum difference of 4.2 kcal/mol between the two composite methods for his two chemical activated systems with an average absolute difference of 1.6 kcal/mol for eight transition state structures.

Wang and Brezinsky[60] implemented a B3LYP/6-31g(d) optimized structure into the G2(MP2) calculation method and demonstrated accuracy of B3LYP/6-31g(d) structures. They compare calculated energies on the 55 molecules used in the original G2 study.[50] Their calculations resulted in improved energies over G2(MP2) with G2(B3LYP/MP2) average and maximum deviation of 1.32 and 3.7 kcal/mol, respectively.

It is difficult to accurately estimate error for TST species in these peroxy radical reaction systems. Our adjustment to match experimental data in this work is 2.4 kcal/mol decrease in the

TABLE 13: Input Parameters and High-Pressure Limit Rate Constants (k_∞) for QRRK Calculations

$\mathrm{C_2C{*}C + OH \rightarrow C_2C^{\bullet}COH}$

	reaction	A (s^{-1} or cc/mol s)	E_a (kcal/mol)
k_1	$\mathrm{C_2C{*}C + OH \rightarrow C_2C^{\bullet}COH}$	8.5×10^{12}	−0.3
k_{-1}	$\mathrm{C_2C^{\bullet}COOH \rightarrow C_2C{*}C + OH}$	5.54×10^{13}	29.39

geometric mean frequency (from CPFIT ref 34)
C2C$^{\bullet}$COH 389.3 cm^{-1} (10.799), 1475.6 cm^{-1} (15.383), 3185.2 cm^{-1} (7.818)
Lennard-Jones parameters: $\sigma = 5.1983$ Å, $\epsilon/k = 553.08$ K (ref 37)

k_1	ref 63; k_{-1} via k_1 and $\langle MR \rangle$

$\mathrm{C_2C^{\bullet}COH + O_2 \rightarrow Products}$

	reaction	A s^{-1} or cc/mol s)	n	E_a (kcal/mol)
k_1	$\mathrm{C_2C^{\bullet}COH + O_2 \rightarrow C_2CQ^{\bullet}COH}$	3.6×10^{12}		0.0
k_{-1}	$\mathrm{C_2CQ^{\bullet}COH \rightarrow C_2C^{\bullet}COH + O_2}$	3.3×10^{15}		32.28
k_2	$\mathrm{C_2CQ^{\bullet}COH \rightarrow C_2CQCO^{\bullet}}$	5.06×10^{7}	1.15410	17.83
k_{-2}	$\mathrm{C_2CQCO^{\bullet} \rightarrow C_2CQ{\cdot}COH}$	6.93×10^{10}	−0.01901	0.99
k_3	$\mathrm{C_2CQCO^{\bullet} \rightarrow C_2C{\cdot}OOH + CH_2O}$	1.23×10^{15}		13.87
k_4	$\mathrm{C_2CQ^{\bullet}COH \rightarrow C_2{}^{\bullet}CQCOH}$	4.61×10^{9}	1.04074	27.94
k_{-4}	$\mathrm{C_2{}^{\bullet}CQCOH \rightarrow C_2CQ^{\bullet}COH}$	2.30×10^{9}	0.43903	14.23
k_5	$\mathrm{C_2{}^{\bullet}CQCOH \rightarrow C{*}C(C)Q + C^{\bullet}H_2OH}$	3.68×10^{14}		33.22
k_6	$\mathrm{C_2{}^{\bullet}CQCOH \rightarrow C{*}C(C)COH + HO_2}$	1.30×10^{13}		16.37
k_7	$\mathrm{C_2CQ^{\bullet}COH \rightarrow C_2CQC^{\bullet}OH}$	2.80×10^{8}	1.32767	23.47
k_{-7}	$\mathrm{C_2CQC^{\bullet}OH \rightarrow C_2CQ^{\bullet}COH}$	8.34×10^{8}	0.75095	16.47
k_8	$\mathrm{C_2CQC^{\bullet}OH \rightarrow C_2C{*}COH + HO_2}$	2.67×10^{13}		15.93

geometric mean frequency (from CPFIT ref 34)
C2CQ$^{\bullet}$COH 291.4 cm^{-1} (12.538), 1135.9 cm^{-1} (16.437), 2997.8 cm^{-1} (10.525)
C2CQCO$^{\bullet}$ 295.9 cm^{-1} (13.107), 1144.8 cm^{-1} (17.750), 2992.0 cm^{-1} (8.643)
C2$^{\bullet}$CQCOH 311.9 cm^{-1} (13.953), 1174.6 cm^{-1} (16.498), 3055.0 cm^{-1} (8.348)
C2CQC$^{\bullet}$OH 309.2 cm^{-1} (14.390), 1147.0 cm^{-1} (15.883), 3022.3 cm^{-1} (8.727)
Lennard-Jones parameters: $\sigma = 5.8569$ Å, $\epsilon/k = 632.06$ K (ref 37)

k_1	$A_1 = 3.6E12$,, from Atkinson et al. for $\mathrm{CCC^{\bullet} + O_2}$; $E_{a1} = 0$ (ref 61)
k_{-1}	via k_1 and $\langle MR \rangle$, $E_{a-1} = \Delta U_{rxn}$
k_2	A_2 estimated using TST, PM3-determined entropies and fitting with three-parameter modified Arrhenius equation, Ea_2 evaluated from ring train (0.1) + ΔH_{rxn} (16.84) + E_a abstraction (6.89) − 6 (H-bond)
k_{-2}	A_{-2} estimated using TST, PM3-determined entropies and fitting with three-parameter modified Arrhenius equation, $E_{a-2} = E_{a2} - \Delta U_{rxn}$
k_3	via k_{-3} and $\langle MR \rangle$, $A_{-3} = 1.67E11$, estimated from $1/2(\mathrm{C_2H_4 + CH_3})$, $E_{a-3} = 7.7$ (ref 62)
k_4	A_4 estimated using TST, PM3-determined entropies and fitting with three-parameter modified Arrhenius equation, E_{a4} evaluated from ring strain (6.3) + ΔH_{rxn} (13.71) + E_a abstraction (7.93)
k_{-4}	A_{-4} estimated using TST, PM3-determined entropies and fitting with three-parameter modified Arrhenius equation, $E_{a-4} = E_{a4} - \Delta U_{rxn}$
k_5	k_5 via k_{-5} and $\langle MR \rangle$, $A_{-5} = 9.64E10$, estimated from $(\mathrm{C{=}C{-}C + CH_3})$, $E_{a-5} = 8.006$ (ref 65)
k_6	via k_{-6} and $\langle MR \rangle$, $A_{-6} = 2.8E11$, estimated from $1/2(\mathrm{C_2H_4 + HO_2})$, $E_{a-6} = 8.46$ (ref 66)
k_7	A_7 estimated using TST, PM3-determined entropies and fitting with three-parameter modified Arrhenius equation, E_{a4} evaluated from ring strain (6.3) + ΔH_{rxn} (10.17) + E_a abstraction (7.0)
k_{-7}	A_{-7} estimated using TST, PM3-determined entropies and fitting with three-parameter modified Arrhenius equation, $E_{a7} = E_{a-7} - \Delta U_{rxn}$
k_8	via k_{-8} and $\langle MR \rangle$, $A_{-8} = 2.8E11$ estimated from $1/2(\mathrm{C_2H_4 + HO_2})$, $E_{a-8} = 8.46$ (ref 66)

$\mathrm{C_2C^{\bullet}OOH \rightarrow C_2C{*}O + OH}$

	reaction	A (s^{-1} or cc/mol s)	E_a (kcal/mol)
k_1	$\mathrm{C_2C^{\bullet}OOH \rightarrow C_2C{*}O + OH}$	1.54E12	1.0

geometric mean frequency (from CPFIT ref 34)
C2C$^{\bullet}$OOH 100.3 cm^{-1} (7.507), 1069.9 cm^{-1} (12.133), 2730.8 cm^{-1} (8.360)
Lennard-Jones parameters: $\sigma = 5.1983$ Å, $\epsilon/k = 533.08$ K (ref 37)

k_1	A_1 via A_{-1} and $\langle MR \rangle$, $A_{-1} = 2.70E12$, estimated from $1/2(\mathrm{C_2H_4 + OH})$, $E_{a1} = 1.0$ (ref 66)

calculated value for one transition state. A similar decrease in one calculated barrier was noted by Yamada et al.,[32] 3 kcal/mol, to match calculated falloff data with experiment in the dimethyl ether radical + O_2 system.

Summary

A thermodynamic and chemical activation reaction analysis is done on the important reaction systems *tert*-butyl radical + O_2, isobutene + HO_2, isobutene + OH, and isobutene−OH + O_2. Thermodynamic proprieties, reaction paths, and elementary reactions for these systems are presented versus temperature and pressure. An elementary reaction mechanism has been developed to model the experimental system—decomposition of 2,2,3,3 tetramethylbutane in the presence of oxygen—where reactions of *tert*-butyl radical and isobutene are of primary importance. Our modeling indicates the isobutene + HO_2 formation via the HO_2 molecular elimination channel is faster than the hydrogen shift channel at 773 K and 60 Torr for $\mathrm{C_3C^{\bullet}}$ + O_2 reaction. The reaction barrier for the $\mathrm{C_3{}^{\bullet}COOH}$ reaction to 2,2-dimethyloxirane + OH is evaluated as 15.58 (18.1) kcal/mol by fitting experimental data. Data in parentheses are thermodynamic properties based on CBS-q//B3LYP/6-31g(d) calculation. Barriers for reactions of HO_2 + isobutene →

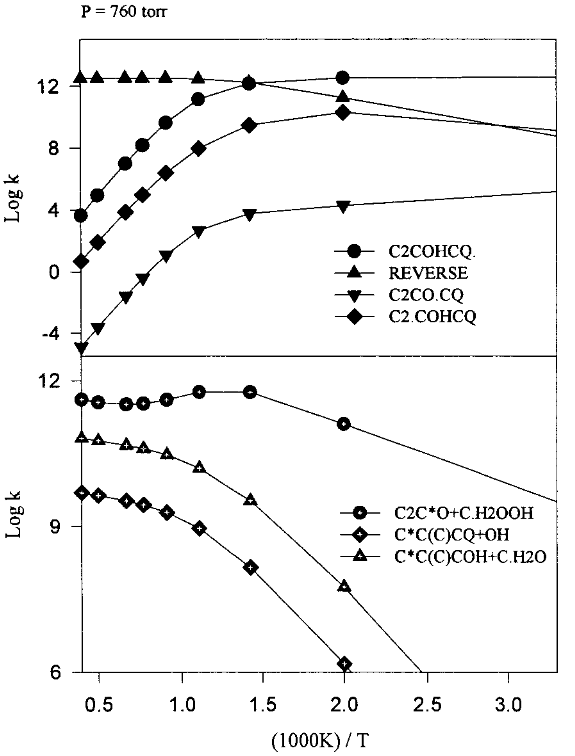


Figure 12. Calculated rate constants at different temperatures and 760 Torr for chemically activated reactions $C_3{}^{\bullet}COH + O_2 \Rightarrow [C_2OHCQ^{\bullet}]^* \Rightarrow$ products.

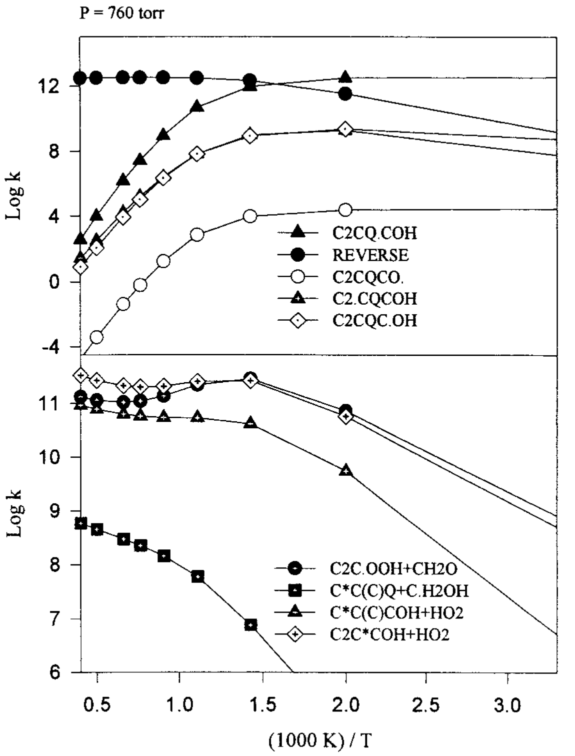


Figure 13. Calculated rate constants at different temperatures and 760 Torr for chemically activated reactions $C_2C^{\bullet}COH + O_2 \Rightarrow [C_2\text{-}CQ^{\bullet}COH]^* \Rightarrow$ products.

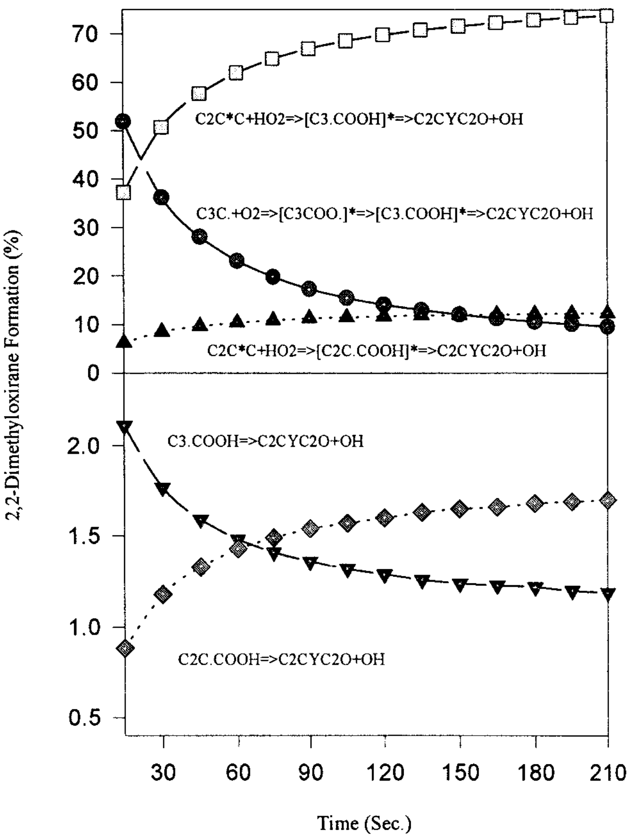


Figure 14. Relative contribution of specific reaction paths to 2,2-dimethyloxirane formation at 773 K and 60 Torr.

$C_3{}^{\bullet}COOH$ (HO_2 addition at CD/C2 carbon atom of isobutene) and HO_2 + isobutene → $C_2C^{\bullet}COOH$ (HO_2 addition at CD/H2 carbon atom of isobutene) are determined to be 7.74 (7.38) and 10.69 (10.82) kcal/mol, respectively. Detailed pathway explanations of the Waddington mechanism and rate constants for elementary steps are presented. Results from the mechanism are in good agreement with experimental data reported by Atri et al.[11]

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Supporting Information Available: Structures and frequencies for intermediates and transition states of *tert*-butyl radical + O_2 and isobutene−OH + O_2 reaction systems are available. This material is available free of charge via the Internet at http://pubs.acs.org. Disk copies of the mechanism can be obtained by writing to the authors.

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