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THE REACTION OF HYDROPEROXY-PROPYL RADICALS WITH MOLECULAR OXYGEN

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ABSTRACT

The addition of hydroperoxy-alkyl radicals to molecular oxygen is an important process leading to chain branching at conditions related to autoignition and engine knock, and in the low temperature oxidation of paraffins. Rate constants and product channels for the reaction of hydroperoxy-propyl radicals with O_2 are estimated using thermodynamic properties, bimolecular quantum Kassel analysis and transition state theory. Thermochemistry of the relevant molecules and radicals is estimated using group additivity and bond dissociation groups for radicals. Results show that the rates of the hydroperoxy-propyl radical addition to O_2 are near their high pressure limits for pressures of 1 atm and above. The main products at 1-15 atm are stabilization, reverse reaction to hydroperoxy-propyl + O_2 , and alkyl carbonyl + OH. Reactions of the stabilized adducts, dissociation rates and product channels are estimated using unimolecular quantum Kassel analysis, because stabilization is the most important hydroperoxy-propyl radical + O_2 product channel. At low temperatures, below about 700 K, the stabilized peroxy adducts react primarily to hydroperoxy-carbonyl + OH, products which lead to chain branching. At higher temperatures, above about 700 K, the stabilized peroxy adducts react primarily to hydroperoxy-propyl radical + O_2 ,

initial reactants, which inhibits the overall oxidation. This switchover in product channels, from low to high temperature, correlates well with the experimentally observed negative temperature coefficient behavior for propane oxidation. Rate expressions for reaction of each of the three hydroperoxy-alkyl isomers with O_2 and for dissociation of the associated stabilized adducts are calculated for a series of pressures over a temperature range of 300 - 2100 K. Accurate rate expressions for these reactions are essential to predict the negative temperature coefficient behavior for paraffins.

INTRODUCTION

The reaction of hydroperoxy-alkyl radicals with molecular oxygen is an important process in the low (typically below 900 K) temperature chemistry of hydrocarbon oxidation. In reduced mechanisms [1-3] that retain only the essential features of the low temperature chemistry related to autoignition and engine knock, this is the principal reaction leading to the formation of OH radicals and chain branching. The reaction of molecular oxygen with hydroperoxy-alkyl radicals is also an essential part of fully-detailed chemical kinetic mechanisms used to simulate the chemistry leading to autoignition and knock [4-6]. The addition of molecular oxygen to hydroperoxy-alkyl radicals is illustrated in the following reactive sequence:

(In the above notation, each carbon atom is fully saturated with H-atoms except where a radical site is noted.) The key feature of this reaction sequence is that two OH radicals plus an alkoxy radical are generated (reaction 4 and 5) for each OH radical consumed, thus the sequence is chain branching. The rates and products of addition of hydroperoxy-alkyl radicals to molecular oxygen (e.g., Reaction 3) have not been experimentally measured or theoretically calculated. We have estimated thermodynamic parameters, rate constants and product channels for O₂ addition to the three isomers of hydroperoxy-propyl radicals using transition state theory [7] for estimation of the isomerizations, bimolecular QRRK theory[8] and accurate thermochemical estimations [9]. QRRK calculations estimate the kinetic rates to products of the chemically activated adduct that forms when hydroperoxy-alkyl

radicals add to molecular oxygen. QRRK gives the pressure and temperature dependencies of the rate constants for the various reaction channels. If the chemically activated adduct becomes stabilized, DISSOC[10] is used to calculate the pressure and temperature dependencies of the rates of its decomposition channels. These computational tools allow a thermochemical kinetics based estimation of the rates and product paths that evolve from the addition of hydroperoxy-alkyl radicals to molecular oxygen.

In the following sections, we first describe the estimation of high pressure rate constants using transition state theory and literature data. These high pressure rate constants are used as input for QRRK code (CHEMACT) [8] which calculates the rate constants for chemically activated paths and for stabilized adducts. All the computed rate constants are given as a functions of pressure and temperature. The rate constants can then be input to an detailed chemical kinetic mechanism to elucidate the dominant reaction paths at conditions relevant to automotive engine knock.

HIGH PRESSURE RATE CONSTANTS

The reaction of O₂ with the three isomers of hydroperoxy-propyl radicals was examined:

Reaction paths considered for all three cases are given in Tables I-III. Accurate estimates of the thermodynamic properties for the relevant radicals and stable parents were obtained by group additivity using THERM [9] (Table IV). The H/C/O groups and bond dissociation groups for oxygen containing hydrocarbons have been recently updated [15]. The thermochemical data obtained allowed the calculation of reverse reaction rate constants by the principle of microscopic reversibility.

There are several types of reactions that need to be considered for each of the hydroperoxy-alkyl radicals. High pressure limit reaction rates were estimated for each of these reaction types and used as input to the QRRK calculations.

Addition to O₂ (e.g., CC.COOH + O₂ → CC(OO.)COOH)

The forward rate constant was based on CH₂OH + O₂ times a factor of 1/2 for steric effects [16]. The reverse rate constant was obtained by microscopic reversibility.

Hydrogen Transfer (e.g., CC(OO.)COOH → C.C(OOH)COOH)

This reaction represents the intramolecular transfer of an H atom . The activation energy (E_a) for the forward rate of this reaction was estimated by,

$$E_a = \text{ring strain} + E_{\text{abstraction}} \begin{matrix} \text{primary} \\ \langle \text{sec ondary} \rangle \\ \text{tertiary} \end{matrix} + \Delta H_{\text{reaction}}$$

where $\Delta H_{\text{reaction}}$ is the enthalpy of reaction (only included if reaction is endothermic).

The ring strain is given as follows [17] and was validated with comparisons of modeling and experimental results on the ethyl + O₂ reaction system [13,18]:

Number of Ring Members	Ring Stain [kcal/mole]
5	6.0
6	0.1
7	6.0

The activation energy for abstraction ($E_{\text{abstraction}}$) was estimated from the reverse reaction (exothermic direction). The reverse reaction is assumed to be a similar process to an alkyl radical abstracting an H-atom from an propylhydroperoxide,

where R is an alkyl radical. The activation energy of this reaction was estimated from an Evans-Polanyi plot ($E_{\text{abstraction}}$ versus $\Delta H_{\text{reaction}}$) [19]) of the similar H-atom abstraction reaction

A reduction of 0.3 kcal/mole in $E_{abstraction}$ for each kcal/mole reduction in $\Delta H_{reaction}$ was obtained.

The pre-exponential factors for the RO₂ isomerization were obtained using RADICALC [7], a computer code which implements transition state theory. RADICALC calculates the change in entropy of the radical to the transition state, due to loss of internal rotors, loss or gain of specific vibrations and, in this case, the gain of an optical isomer. Table V gives the output from the RADICALC code which describes these changes in entropy from the CC(OOH)COO. radical to the transition state for the isomerization:

The results of the RADICALC calculations show that the loss of internal rotors is the major contribution to the loss of entropy and thus reduction in Arrhenius pre-exponential factor. The pre-exponential factors show a decrease with increasing size of the molecule in this mass range due to the increase in moments of inertia of the rotors which are tied up in the transition state. Further analyses will be discussed in future work.

The reverse rate constants for HO₂ addition to the C=CCOOH species (there are three isomers) were estimated and the forward rate was calculated by microscopic reversibility. The rate of HO₂ addition was assumed to be similar to the rate of addition of methyl radicals to alkenes. The pre-exponential factor of alkene + CH₃ was multiplied by a factor of two ($\exp(R\ln 2/R)$) because of the gain of an optical isomer in dihydroperoxyl-propyl species. The addition of methyl radicals to alkenes was chosen as an analogous reaction because a large data set of rate constants is available in the literature [20,21].

OH Elimination (e.g., $\text{HOOC.CCOOH} \rightarrow \text{O=CCCOOH} + \text{OH}$)

The reverse rate constant for OH addition was estimated and the forward rate was then calculated by microscopic reversibility. The reverse reaction is considered analogous to the addition of an OH radical to one carbon of the double bond in ethylene.

Alkyl group Elimination (e.g., $\text{C.C(OOH)COOH} \rightarrow \text{C=COOH} + \text{.COOH}$)

The reverse rate constant was estimated and the forward rate was calculated by microscopic reversibility. The reverse reaction is the addition of the alkyl radical .COOH to a double bond. This is considered to be analogous to the addition of a propyl radical to one carbon of the double bond in ethylene.

CALCULATIONS

Energized-complex/QRRK theory as described by Dean [10] was used to model the addition of hydroperoxy-alkyl radicals to O_2 . Details of the CHEMACT code used for the calculations are given in Reference 8. The geometric mean frequencies required for the calculations were obtained from the heat capacity data in Table IV using the method described in Reference 22. Lennard-Jones parameters were obtained from tabulations [23] and a calculation method based on group additivity where groups representing transport properties were developed [24]. Data was also take from estimations based on molar volumes and compressibility [25]. Collision efficiencies (β) were evaluated using Troe's method [26], with energies transferred per collision taken from Gardiner and Troe [27]. The bath gas was assumed to be nitrogen. Important modifications to the code include use of the Ω integral [23], for calculation of the collision frequency and the calculation of the collision efficiency, β , as a function of temperature using an exact calculation of $f(E)$ [26]. Detailed comparison of the modified QRRK calculations with RRKM is reported to be in excellent agreement [18].

RESULTS AND DISCUSSION

Chemical Activation Reactions

The energy level diagram and input parameters are shown in Fig. 1 and Table I, respectively. The reaction channels for $CC(OOH)COO^{\ddagger}$ include:

- 1) Dissociation back to reactants
- 2) Stabilization to $CC(OOH)COO.$
- 3) Isomerization via hydrogen shifts with subsequent β -scission/stabilization

The barriers to isomerization are about 12 kcal/mole lower than dissociation back to reactants (Fig. 1) so that there is opportunity for the $CC(OOH)COO^{\ddagger}$ adduct to isomerize rather than stabilize. The dominant reaction (non-stabilization) channel for the excited adduct is dissociation back to reactants. The dominant product channel is stabilization. The next important product channel is $CC(=O)COOH + OH$ (carbonyl formation) which is the only channel considered in the literature [28]. The channel to $CC(OOH)COOH$ also has some significance (Fig. 1). We considered a total of six product channels (Table I and Fig. 1).

Figure 2 shows the apparent rate constants for the various product channels of $CC(OOH)C. + O_2$ with pressure. Results are shown at 800 K because hydroperoxy-alkyl + O_2 reactions are most important in the temperature range of 600 - 900 K where low and intermediate temperature chemistry controls the oxidation of hydrocarbons [4]. At temperatures above 900 K, alkyl radicals decompose by β -scission more rapidly than they add with molecular oxygen to form alkylperoxy and, subsequently, hydroperoxy-alkyl radicals. Figure 2 (filled circles) shows the dominant channel for $CC(OOH)C. + O_2$ is the stabilization ($CC(OOH)COO.$), except at very low pressure. This is the case for oxygen addition to all three isomers of hydroperoxy-propyl. A

fraction (ca. 1 % at 1 atm) of the chemically activated $CC(OOH)COO^{\cdot}$ reacts over the barrier to other products. The dominant path to other products involves an intramolecular abstraction of the H-atom that is attached to the same carbon as the hydroperoxide group (filled squares in Fig. 2):

This C-H bond is somewhat weakened (ca. 4 kcal/mole) from the usual secondary H because of the presence of the C-OO bond. The above path identified by Benson [28] is the only path to products that we have found discussed in the literature. Additionally, we considered five other product paths as illustrated in Fig. 1. The next most important is an intramolecular abstraction of the H-atom that is attached to the *terminal* carbon atom:

This path is about a factor of 6 slower than carbonyl formation at all pressures above 1 atm and 800 K (triangles in Fig. 2). The rates for reaction to other products shown in Fig. 2 are considerably less important, except at very low pressures (0.01 atm) where the product channel $C=CCOOH + HO_2$ becomes significant. This product channel is the result of decomposition of $\dot{C}C(OOH)COOH^{\#}$ to $C=CCOOH + HO_2$ before stabilization.

In Fig. 3, the rates to product channels are plotted versus temperature. Rates are given at 15 atm because hydroperoxy-alkyl + O₂ reactions are most relevant under conditions of high pressures related to engine knock. The dominant channels are the same as in Fig. 2 with product paths competing more effectively with stabilization as the temperature increases.

The important product channels are similar to those of $CC(OOH)C^{\cdot} + O_2$ at 15 atm. Stabilization of the peroxy adduct is the most important product channel. The

product channel with the next highest rate at 15 atm is carbonyl formation ($\text{CC}(\text{OOH})\text{C}=\text{O} + \text{OH}$). The next significant path involves an intramolecular abstraction of the H-atom that is attached to the *terminal* carbon atom to give the $\text{C.C}(\text{OOH})\text{COOH}$. This adduct will decompose to $\text{C}=\text{CCOOH} + \text{HO}_2$. Its rate at 15 atm is about a factor of four below the rate to $\text{CC}(\text{OOH})\text{C}=\text{O} + \text{OH}$. The rates of the remaining three product channels considered are more than two orders of magnitude lower in comparison over the temperature range of interest (600 - 900 K) at 15 atm.

$\text{C.CCOOH} + \text{O}_2$

The potential energy diagram showing the six product channels considered is shown in Fig. 4. The apparent rate constants at 15 atm are given in Fig. 5. Again, stabilization of the peroxy adduct is the most important product channel. After stabilization and reverse reaction, two product channels are competitive. For temperatures below about 730 K, carbonyl formation ($\text{HOOCCC}=\text{O} + \text{OH}$) exceeds HOOCC.COOH formation. For temperatures above about 730 K, HOOCC.COOH formation exceeds carbonyl formation. HOOCC.COOH formation involves an intramolecular abstraction of the secondary H-atom and has not been considered previously in the literature. The HOOCC.COOH adduct will decompose to $\text{C}=\text{CCOOH} + \text{HO}_2$. Production of an HO_2 radical from HOOCC.COOH above 730 K is less reactive than production of an OH radical from carbonyl formation ($\text{HOOCCC}=\text{O} + \text{OH}$) below 730 K. We considered three other paths to products. The rate of the product channel to $\text{C}=\text{CCOOH} + \text{HO}_2$ becomes significant above 1000 K. The rates of the remaining product channels are much too low to be important.

Dissociation Reactions - Fate of Stabilized Adducts

The computed results for the rate of O_2 addition to hydroperoxy-propyl radicals show that the main product path is to form a stabilized adduct for pressures of 1 atm and higher (Fig. 2). It is therefore most important to determine the fate of these

stabilized peroxy adducts as a function of temperature at pressures relevant to combustion applications.

CC(OOH)COO. → Products

The computed rate versus inverse temperature for important product channels is shown in Fig. 6 at 15 atm. The results for this case have important implications with respect to negative temperature coefficient behavior for propane oxidation. At 600 K, the dominant products are CC(=O)COOH + OH which lead to chain branching because a second OH radical is produced via

As the temperature is raised to 900 K, the dominant path is dissociation back to molecular oxygen and the CC(OOH)C., a radical which mainly dissociates to propene + HO₂. An HO₂ radical is relatively unreactive compared to an OH radical. Therefore, as the temperature is raised from 600 to 900 K, the dominate path changes from chain branching and the production of highly reactive OH radicals to one of chain propagation with production of relatively unreactive HO₂ radicals. This behavior contributes to the negative temperature coefficient behavior observed over this temperature range at 15 atm [29].

CC(OO.)COOH → Products

.OOCCCOOH → Products

The trends at 15 atm are similar to CC(OOH)COO. decomposition, (Fig. 6) with OH radical production and chain branching dominating below 650 K and reverse reaction back to O₂ dominating above 650 K. Again, this behavior contributes to the negative temperature coefficient behavior experimentally observed over this temperature regime and 15 atm.

Reaction Rate Parameters

The reaction rates of the three isomers of hydroperoxy-propyl with molecular oxygen and of the stabilized adducts were fitted to modified Arrhenius expressions at

pressures of 1, 15 and 50 atm. The rates for all significant product channels considered are given in Table VI. Minor product channels that contributed less than 1 % to total reaction over 300-2100 K and the indicated pressure were omitted. The fits approximate the computed QRRK results to within the maximum error listed in the table. These rate constants are useful for inclusion in a chemical kinetic mechanism to treat propane oxidation over the low to intermediate temperature regime (600 - 900 K). For temperatures above about 900 K, the decomposition of alkyl and alkylperoxy radicals are rapid, so that hydroperoxy-propyl + O₂ no longer plays a significant role. Thermodynamic property and kinetic data may be obtained by Internet electronic mail (pitz@llnl.gov or bozzelli_p%admin1@njit.edu) or on disk by writing to the authors.

SUMMARY

The addition of the three isomers of hydroperoxyl-propyl radicals to molecular oxygen was analyzed using QRRK theory and transition state theory. Bond additivity and H-bond dissociation groups were used to obtain accurate thermochemical parameters of the stable parents and radicals. The dominant channels ranked by order of importance are stabilization, followed by reverse reaction to hydroperoxyl-propyl + O₂, and reaction to carbonyl + OH. The radical addition to O₂ rates are near the high pressure limits for pressures of 1 atm and above. Several reaction channels were found to be important which had not been identified previously in the literature. These paths involved the intramolecular abstraction of an H-atom that was bonded to a carbon without an attached O atom. The resulting products are olefinic hydroperoxide + HO₂. The calculated reaction rates from the QRRK analysis were fit to modified Arrhenius expressions for use in chemical kinetic mechanisms. Rate constants for dissociation of the stabilized adducts are also presented. Product channels for dissociation of the stabilized adducts switch from chain propagation to dissociation back to alkyl-hydroperoxide radical + O₂ which is a near effective termination, in the observed

negative temperature coefficient regime. The associated rate constants are expected to be essential in predicting properly negative temperature regime behavior.

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REFERENCES

1. Hu, H., and Keck, J. SAE paper No. 872110, 1987.
2. Morley, C., *Combust. Sci. Tech.* 55:115 (1987).
3. Griffiths, J. F. *Combust. Flame* 93:202-206 (1993).
4. Westbrook, C. K., Pitz, W. J., and Leppard, W. M. *SAE Transactions* (1991), SAE-912314.
5. Chevalier, C., Pitz, W. J., Warnatz, J. and Westbrook, C. K. *Twenty-Fourth (International) Symposium on Combustion*, The Combustion Institute, The Combustion Institute, Pittsburgh, PA, 1992, pp. 93-101.
6. Chevalier, C., Louessard, P., Muller, U.-C., and Warnatz, J. *Second International Symposium on Diagnostics and Modeling of Combustion in Internal Combustion Engines*, p. 93 Kyoto, 1990.
7. Bozzelli, J. W., Ritter, E. R. RADICALC: A Computer Code To Estimate Entropies And Heat Capacities For Radical Species And Transition State Structures, In preparation, 1993.
8. Dean, A. M., Bozzelli, J. W., Ritter, J. W. *Combust. Sci. Tech.* 80:63-85 (1991).
9. Ritter, E. R. and Bozzelli, J. W. *Int. J. Chem. Kinet.* 23:767(1991).
10. Dean, A. M., *J. Phys. Chem.* 89:4600 (1985).
11. Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., Troe, J. *J. Phys. Chem. Ref. Data* 18:881 (1989).
12. Bozzelli, J.W., and Dean, A.M. Hydrocarbon Radical Reactions with O₂: Comparison of Allyl, Formyl and Vinyl to Ethyl, in preparation (1993).
13. Bozzelli, J.W., and Dean, A.M. *J. Phys. Chem.* 94:3313 (1990).
14. Tsang, W., and Hampson, R.F. *J. Phys. Chem. Ref. Data* 15:1087-1279 (1986).
15. Lay, T., and Bozzelli, J. W. Chemical and Physical Processes in Combustion, The Eastern States Section Meeting of the Combustion Institute, Paper #100 (1-4), 1993.

16. Benson S. W., *Can. J. Chem.* 61:881(1983).
17. Dorofeeva, O. V., Gurvich, L. V., and Jorish, V. S. *J. Phys. Chem. Ref. Data* 15:437-464 (1986).
18. A. Y. Chang and A. M. Dean, Exxon Research and Engineering, Annandale, N.J., personal communication, 1993.
19. Evans, M. G. and Polanyi, M. *Trans. Faraday Soc.* 34:11 (1938).
20. Allara, D. L., and Shaw, R. J. *J. Phys. Chem. Ref. Data* 9:523-559 (1980).
21. Mallard, W. G., Westley, F., Herron, J. T., Hampson, R. F. , and Frizzell, D. H. *NIST Chemical Kinetics Database: Version 5.0*, National Institute of Standards and Technology, Gaithersburg, MD (1993).
22. Ritter, E. R. Ph.D Thesis, New Jersey Institute of Technology, May, 1989.
23. Reid, R. C., Prausnitz, J. M., and Poling, B. E. *Properties of Gases and Liquids*. 4th edition, McGraw Hill, New York, 1987.
24. Bozzelli, J. W. Transcal Code, personal communication (1993).
25. Ben-Amotz, D. and Herschback, D. *J. Phys. Chem.* 94:3393 (1990).
26. Troe, J. *J. Phys. Chem.* 83:114-126 (1979).
27. Gardner, W. C., Jr., and Troe, J. in *Combustion Chemistry* (W. C. Gardner Jr., Ed.), Springer-Verlag, New York, 1984, p. 114-126.
28. Benson, S. W. *Prog. Energy Combust. Sci.* 7:125-134 (1981).
29. Koert, D.N., Miller, D.L. and Cernansky, N.P., "Experimental Studies of Propane Oxidation through the Negative Temperature Coefficient Region at 10 and 15 Atmospheres," *Combust. Flame*, (in press), 1993.

Table I
CC(OOH)C. + O₂ → products

Reaction	A (s ⁻¹ or cm ³ /mole-s)	E _a (kcal/mole)
1 CC(OOH)C. + O ₂ → CC(OOH)COO.	3.0E12	0.0
-1 CC(OOH)COO. → CC(OOH)C. + O ₂	2.95E14	30.62
2 CC(OOH)COO. → CC.(OOH)COOH	2.02E11	20.10
-2 CC.(OOH)COOH → CC(OOH)COO.	4.14E10	15.45
3 CC.(OOH)COOH → CC(=O)COOH + OH	4.53E13	3.00
4 CC.(OOH)COOH → C=C(OOH)C + HO ₂	1.42E13	24.53
5 CC(OOH)COO. → C.C(OOH)COOH	4.86E10	20.84
-5 C.C(OOH)COOH → CC(OOH)COO.	8.89E8	7.66
6 C.C(OOH)COOH → C=CCOOH + HO ₂	1.41E12	17.22
7. C.C(OOH)COOH → C=COOH + CH ₂ O + OH	1.64E13	37.04

k₁ 1/2 of CH₂OH + O₂, the 1/2 is for steric effects.
k-1 from microscopic reversibility (MR).
k₂ A₄ = 10^{13.66}10^{ΔS/4.6} degeneracy (1), ΔS = -10.83 cal/mole-K (loss of 2 rotors). E₄ = ring strain + ΔH + E_{abstraction} = 6 + 4.21 + 9.9 = 20.1 kcal/mole.
k-2 from MR.
k₃ A₃ from A-3 = 1/2 of C₂H₄ + OH (addition) = 0.5*5.4E12 [11] and MR. E₃ = 3.0 kcal [12].
k₄ A₄ from MR and A-4 = C₂H₄ + HO₂ (addition) = 10^{11.5}. E₄ = ΔU + 10.0 kcal/mole [13].
k₅ A₅ = 10^{13.66}10^{ΔS/4.6} degeneracy (3), ΔS = -15.87 (loss of 3 rotors). E₅ = ring strain + ΔH + E_{abstraction} = 0.1 + 13.18 + 7.5 = 20.84 kcal/mole.
k-5 from MR.
k₆ A₆ from MR and A-6 = C₂H₄ + HO₂ (addition) = 10^{11.5}. E₆ = ΔU + 10.0 kcal/mole [13].
k₇ A₇ and E₇ from MR. k-7 is 1/2 of C₂H₄ + CH₃ (addition) where A-7 = 0.5*1.26E11 and E-7 = 7.7 kcal/mole [14].

Table II
CC.COOH + O₂ → products

Reaction	A (s ⁻¹ or cm ³ /mole-s)	E _a (kcal/mole)
1 CC.COOH + O ₂ → CC(OO.)COOH	3.0E12	0.0
-1 CC(OO.)COOH → CC.COOH + O ₂	8.2E14	31.40
2 CC(OO.)COOH → CC(OOH)C.OOH	1.45E12	22.80
-2 CC(OOH)C.OOH → CC(OO.)COOH	2.97E11	14.71
3 CC(OOH)C.OOH → CC(OOH)C=O + OH	5.07E13	3.00
4 CC(OOH)C.OOH → CC=COOH + HO ₂	1.41E13	22.05
5 CC(OO.)COOH → C.C(OOH)COOH	2.17E12	26.70
-5 C.C(OOH)COOH → CC(OO.)COOH	3.96E10	13.55
6 C.C(OOH)COOH → C=CCOOH + HO ₂	1.42E12	17.23
7 C.C(OOH)COOH → C=COOH + CH ₂ O + OH	1.64E13	37.00

k₁ 1/2 of CH₂OH + O₂, the 1/2 is for steric effects.

k₋₁ from microscopic reversibility (MR).

k₂ A₄ = 10^{13.66}10^{ΔS/4.6} degeneracy (2), ΔS = -8.27 cal/mole-K (loss of 2 rotors). E₄ = ring strain + ΔH + E_{abstraction} = 6 + 7.64 + 9.2 = 22.8 kcal/mole.

k₋₂ from MR.

k₃ A₃ from A₋₃ = 1/2 of C₂H₄ + OH (addition) = 0.5*5.4E12 [11] and MR. E₃ = 3.0 kcal [12].

k₄ A₄ from MR and A₋₄ = C₂H₄ + HO₂ (addition) = 10^{11.5}. E₄ = ΔU + 10.0 kcal/mole [13].

k₅ A₅ = 10^{13.66}10^{ΔS/4.6} degeneracy (3), ΔS = -8.29 cal/mole-K (loss of 2 rotors). E₅ = ring strain + ΔH + E_{abstraction} = 6.0 + 13.18 + 7.5 = 26.7 kcal/mole.

k₋₅ from MR.

k₆ A₆ from MR and A₋₆ = C₂H₄ + HO₂ (addition) = 10^{11.5}. E₆ = ΔU + 10.0 kcal/mole [13].

k₇ A₇ and E₇ from MR. k₋₇ is based on 1/2 of C₂H₄ + CH₃ (addition) where A₋₇ = 0.5*1.26E11 and E₋₇ = 7.7 kcal/mole [14].

Table III
C.CCOOH + O₂ → products

Reaction	A (s ⁻¹ or cm ³ /mole-s)	E _a (kcal/mole)
1 C.CCOOH + O ₂ → .OOCCCCOOH	3.0E12	0.0
-1 .OOCCCCOOH → C.CCOOH + O ₂	2.91E14	30.60
2 .OOCCCCOOH → HOOCCC.OOH	1.14E10	16.80
-2 HOOCCC.OOH → .OOCCCCOOH	2.38E9	8.72
3 HOOCCC.OOH → HOOCCC=O + OH	8.06E13	3.00
4 HOOCCC.OOH → C=COOH + CH ₂ O + OH	9.75E13	38.14
5 .OOCCCCOOH → HOOCC.COOH	4.57E11	24.37
-5 HOOCC.COOH → .OOCCCCOOH	1.29E10	14.55
6 HOOCC.COOH → C=CCOOH + HO ₂	1.14E12	16.58

k₁ 1/2 of CH₂OH + O₂, the 1/2 is for steric effects.

k₋₁ from microscopic reversibility (MR).

k₂ A₄ = 10^{13.66}10^{ΔS/4.6} degeneracy (2), ΔS = -17.96 cal/mole-K (loss of 3 rotors). E₄ = ring strain + ΔH + E_{abstraction} = 0.1 + 7.5 + 9.2 = 16.8 kcal/mole.

k₋₂ from MR.

k₃ A₃ from A₋₃ = 1/2 of C₂H₄ + OH (addition) = 0.5*5.4E12 [1] and MR. E₃ = 3.0 kcal [12].

k₄ A₄ and E₄ from MR. k₋₄ based on 1/2 of C₂H₄ + CH₃ (addition) where A₋₄ = 0.5*1.26E11 and E₋₄ = 7.7 kcal/mole [14].

k₅ A₅ = 10^{13.66}10^{ΔS/4.6} degeneracy (2), ΔS = -10.58 cal/mole-K (loss of 2 rotors). E₅ = ring strain + ΔH + E_{abstraction} = 6.0 + 9.82 + 8.55 = 24.37 kcal/mole.

k₋₅ from MR.

k₆ A₆ from MR and A₋₆ = C₂H₄ + HO₂ (addition) = 10^{11.5}. E₆ = ΔU + 10.0 kcal/mole [13].

Table IV: Thermodynamic Data

SPECIES	Hf (298)	S (298)	Cp (300)	Cp (400)	Cp (500)	Cp (600)	Cp (800)	Cp (1000)
OH	9.32	43.89	7.16	7.09	7.06	7.06	7.15	7.32
HO2	3.80	54.73	8.33	8.95	9.49	9.97	10.77	11.39
CH3	35.12	46.38	9.29	10.09	10.87	11.61	12.97	14.15
CH2O	-26.02	52.26	8.56	9.60	10.61	11.56	13.28	14.71
C=COOH	-6.37	75.63	18.40	21.50	24.22	26.54	30.24	33.02
C.CCOOH	3.44	88.60	25.00	30.56	35.23	39.02	44.71	48.94
CC.COOH	0.79	90.51	24.28	29.42	33.75	37.72	43.97	48.29
CCC.OOH	-1.66	85.19	25.14	30.70	35.41	39.27	45.25	49.78
C.C(OOH)C	-.93	86.61	25.50	31.24	36.18	39.76	45.36	49.44
CC.(OOH)C	-8.43	85.14	25.77	30.81	35.41	38.97	44.93	49.50
C=CCOOH	-14.24	84.00	23.48	28.36	32.54	36.03	41.46	45.50
C=C(OOH)C	-15.57	83.54	23.98	28.87	32.85	36.13	41.45	45.41
HOCCCC=O	-67.63	92.83	26.79	32.64	37.57	41.18	46.98	51.07
CC(=O)COOH	-70.31	91.46	27.08	31.97	36.09	39.59	45.53	49.88
CC(OOH)C=O	-67.63	90.65	26.79	32.64	37.57	41.18	46.98	51.07
CC(OO.)COOH	-34.06	100.88	32.59	39.72	45.52	49.73	56.29	61.07
CC(OOH)COO.	-34.06	100.88	32.59	39.72	45.52	49.73	56.29	61.07
C.C(OOH)COOH	-21.16	108.18	33.40	40.36	45.98	49.94	55.97	60.30
CC.(OOH)COO	-28.66	105.34	33.67	39.93	45.21	49.15	55.54	60.36
CC(OOH)C.O	-26.26	103.39	33.54	40.50	46.16	50.19	56.51	61.14
HOCCC.COOH	-19.44	110.70	32.18	38.54	43.55	47.90	54.58	59.15
.OCCCCOOH	-29.69	102.87	32.09	39.04	44.57	48.99	55.64	60.57
HOCCCCOO.	-29.69	102.87	32.09	39.04	44.57	48.99	55.64	60.57
HOCCCC.OOH	-21.89	105.38	33.04	39.82	45.21	49.45	55.86	60.64

Units: Hf in kcal/mole; S in cal/(mole-K); Cp in cal/(mole-K);
Temperatures in K.

Table V
RADICAL Transition State Theory Calculation

CCQCOO. => CC.QCQ (Transition State)
= - IR/CCQC-OO/ - IR/CCQ-COO/ - V/C-H/ - 2V/H-C-C/
- V/H-C-O/+ V/C.H/ + 2V/H.C-C/ + V/H.C-O/ + V/cs ring/

ENTROPY INCREMENTS (cal/mol K)		
Temperature (K)	298	1500
-1 * IR/CCQC-OO/	-6.200	-8.462
-1 * IR/CCQ-COO/	-5.949	-8.675
-1 * V/C-H/	.000	-.455
-2 * V/H-C-C/	-.101	-3.777
-1 * V/H-C-O/	-.076	-2.053
V/C.H/	.001	.834
2 * V/H.C-C/	.414	5.120
V/H.C-O/	.207	2.560
V/cs ring/	.252	2.682

net entropy increments applied:

Temperature (K)	entropy (cal/mol K)
298.1500	-11.4530
500.0000	-11.8756
600.0000	-12.0056
800.0000	-12.1664
1500.0000	-12.2271

Reaction Path Degeneracy assumed to be 1

AFACTOR = 7.5823E+08 /sec
TEXP = 7.3741E-01

Notation: IR denotes internal rotor, V denotes bending or stretching vibration.
TEXP is the temperature exponent of the modified Arrhenius form of the rate constant. Q denotes "OOH". The A-factor above needs to be multiplied by a factor of two for the gain of an optical isomer.

Table VI

Rate Expressions for Hydroperoxy-Propyl + O₂ and for Decomposition of Adducts

	A	n	Ea	Pressure	Maximum
				[atm]	Fit Error
CC.COOH + O ₂					
<=> CCQ.CQ	9.60E+40	-9.21	7830.	1.	11%
<=> CCQ.CQ	7.30E+31	-6.17	5700.	15.	24%
<=> CCQ.CQ	1.70E+27	-4.67	4439.	50.	24%
<=> CCQC*O + OH	1.44E+33	-6.42	12096.	1.	14%
<=> CCQC*O + OH	1.51E+26	-4.31	11377.	15.	35%
<=> CCQC*O + OH	4.87E+21	-2.98	10482.	50.	43%
<=> CC*CCQ + HO ₂	6.14E+17	-2.46	14054.	1.	7%
<=> CC*CCQ + HO ₂	3.76E+14	-1.44	14792.	15.	25%
<=> CC*CCQ + HO ₂	1.79E+11	-0.44	14389.	50.	38%
<=> C.CQCQ	1.47E+43	-9.79	16245.	1.	17%
<=> C.CQCQ	1.68E+29	-5.35	13864.	15.	44%
<=> C.CQCQ	2.27E+22	-3.26	12300.	50.	49%
<=> C*CCQ + HO ₂	6.15E+40	-8.53	21768.	1.	16%
<=> C*CCQ + HO ₂	1.90E+30	-5.39	21308.	15.	19%
<=> C*CCQ + HO ₂	4.95E+23	-3.50	20155.	50.	27%
C.CCOOH + O ₂					
<=> CQ.CCQ	3.89E+37	-8.04	7176.	1.	22%
<=> CQ.CCQ	2.61E+27	-4.72	4519.	15.	26%
<=> CQ.CCQ	6.95E+22	-3.26	3196.	50.	22%
<=> CQCC*O + OH	7.13E+33	-6.98	11349.	1.	14%
<=> CQCC*O + OH	9.12E+23	-4.04	9398.	15.	25%
<=> CQCC*O + OH	6.81E+18	-2.55	8152.	50.	24%
<=> CQC.CQ	1.25E+41	-9.22	15208.	1.	16%
<=> CQC.CQ	6.01E+25	-4.39	12242.	15.	35%
<=> CQC.CQ	2.66E+18	-2.17	10422.	50.	33%
<=> C*CCQ + HO ₂	8.74E+39	-8.31	20550.	1.	14%
<=> C*CCQ + HO ₂	1.82E+27	-4.55	19222.	15.	18%
<=> C*CCQ + HO ₂	6.24E+19	-2.41	17668.	50.	21%
CC(OOH)C. + O ₂					
<=> CCQCQ.	5.33E+37	-8.11	7115.	1.	18%
<=> CCQCQ.	7.98E+27	-4.88	4624.	15.	24%
<=> CCQCQ.	2.22E+23	-3.42	3325.	50.	20%
<=> CC*OCQ + OH	4.80E+32	-6.34	11728.	1.	16%
<=> CC*OCQ + OH	6.52E+23	-3.70	10220.	15.	33%
<=> CC*OCQ + OH	7.45E+18	-2.25	9082.	50.	35%
<=> C.CQCQ	3.68E+43	-10.05	15308.	1.	34%
<=> C.CQCQ	5.05E+26	-4.83	11550.	15.	44%
<=> C.CQCQ	4.15E+19	-2.71	9756.	50.	41%
<=> C*CCQ + HO ₂	6.88E+39	-8.46	20533.	1.	8%
<=> C*CCQ + HO ₂	1.26E+25	-4.13	18285.	15.	18%
<=> C*CCQ + HO ₂	5.76E+17	-2.06	16713.	50.	20%
CC(OO.)COOH					
<=> CCQC*O + OH	4.18E+39	-8.81	30182.	1.	31%
<=> CCQC*O + OH	1.04E+29	-5.37	27320.	15.	30%
<=> CCQC*O + OH	2.29E+24	-3.89	25989.	50.	26%
<=> C.CQCQ	2.00E+49	-11.88	36747.	1.	41%
<=> C.CQCQ	1.31E+33	-6.63	32365.	15.	36%
<=> C.CQCQ	7.65E+26	-4.64	30566.	50.	29%

C.C (OOH) COOH

<=> CCQC*O + OH	7.38E+44	-10.73	30413.	1.	34%
<=> CCQC*O + OH	2.90E+28	-5.61	26931.	15.	53%
<=> CCQC*O + OH	2.02E+21	-3.45	25194.	50.	53%
<=> C*CCQ + HO2	4.01E+26	-4.70	20775.	1.	9%
<=> C*CCQ + HO2	4.80E+17	-1.79	18424.	15.	10%
<=> C*CCQ + HO2	5.02E+14	-0.84	17537.	50.	6%
<=> C*CQ + CH2O + OH	3.97E+23	-3.62	38659.	1.	5%
<=> C*CQ + CH2O + OH	3.07E+19	-2.07	38301.	15.	8%
<=> C*CQ + CH2O + OH	3.82E+16	-1.12	37539.	50.	6%
<=> CC*OCQ + OH	1.04E+41	-9.97	25268.	1.	56%
<=> CC*OCQ + OH	6.70E+22	-4.43	20743.	15.	52%
<=> CC*OCQ + OH	7.69E+15	-2.38	18918.	50.	44%

.OCCCCOOH

<=> CQCC*O + OH	4.86E+31	-6.88	22765.	1.	41%
<=> CQCC*O + OH	1.27E+21	-3.51	19670.	15.	28%
<=> CQCC*O + OH	1.37E+17	-2.26	18487.	50.	20%
<=> CQC.CQ	1.05E+45	-10.66	33716.	1.	47%
<=> CQC.CQ	2.37E+28	-5.30	29074.	15.	34%
<=> CQC.CQ	2.10E+22	-3.38	27271.	50.	24%
<=> C*CCQ + HO2	2.64E+46	-10.60	41893.	1.	23%
<=> C*CCQ + HO2	1.11E+29	-5.24	37901.	15.	29%
<=> C*CCQ + HO2	5.65E+21	-3.06	35996.	50.	23%

HOCC.COOH

<=> C*CCQ + HO2	5.27E+25	-4.47	19752.	1.	9%
<=> C*CCQ + HO2	7.22E+16	-1.57	17421.	15.	9%
<=> C*CCQ + HO2	9.27E+13	-0.65	16564.	50.	5%

CC (OOH) COO.

<=> CC*OCQ + OH	2.50E+34	-7.38	26371.	1.	35%
<=> CC*OCQ + OH	5.27E+23	-3.96	23347.	15.	27%
<=> CC*OCQ + OH	3.09E+19	-2.61	22104.	50.	20%
<=> C.CQCQ	1.75E+41	-9.73	29463.	1.	54%
<=> C.CQCQ	4.52E+25	-4.75	24952.	15.	33%
<=> C.CQCQ	1.69E+20	-3.03	23312.	50.	23%

Reaction rate parameters are in cm**3-mole-sec-cal units. Reaction rate constants are described by the three-parameter expression, $k = A T^{*n} \exp(-E_a/RT)$. Expressions are valid over the temperature range of 300-2100K. Reverse rates can be obtained using thermodynamic data in Table IV and microscopic reversibility. Notation: q denotes OOH, q. denotes OO., m denotes a methyl group, and * denotes a double bond.

FIGURE CAPTIONS:

- Figure 1. Potential energy level diagram for $CC(OOH)C\cdot + O_2$. The line thickness gives an indication of the relative importance for a particular reaction channel.
- Figure 2. Rate constants of the various channels of $CC(OOH)C\cdot + O_2$ at 800 K as a function of pressure.
- Figure 3. Rate constants of the various channels of $CC(OOH)C\cdot + O_2$ at 15 atm as a function of temperature.
- Figure 4. Potential energy level diagram for $\cdot CCCOOH + O_2$.
- Figure 5. Rate constants of the various channels of $\cdot CCCOOH + O_2$ at 15 atm as a function of temperature.
- Figure 6. Rate constants for the decomposition of $CC(OOH)C\cdot$ at 15 atm as a function of temperature.

Fig. 1

CC(OOH)C. + O2 => products
(800 K)

ccqc.+o2 press plot 11/30/93

Fig. 2.

Fig. 3

ccqc+02 plot 15 atm 11/30/93

Fig. 4

c.ccq+o2 plot 11/30/93

Fig. 5.

**CC(OOH)COO. => products
(15 atm)**

cc(ooh)coo prod plot 3, 11/30/93

Fig. 6.

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