

Rates of Reaction of Propyl Radicals with Molecular Oxygen

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The rates of reaction of 1-propyl and 2-propyl radicals with O₂ have been measured in the gas phase at room temperature. The rate constants are $k_1(1\text{-C}_3\text{H}_7 + \text{O}_2) = (5.5 \pm 0.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_2(2\text{-C}_3\text{H}_7 + \text{O}_2) = (14.1 \pm 2.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Limited pressure studies suggest that both of these reactions are at or near their high-pressure limits at pressures of a few torr. The logarithms of these and previously measured rate constants show an excellent correlation with the ionization potential of the alkyl radical (Figure 2). Adiabatic channel model calculations have been carried out for these reactions with various long-range potential functions. It is concluded that some mixing of the charge-transfer surface ($\text{R}^+ + \text{O}_2^-$) into the neutral surface ($\text{R} + \text{O}_2$) is responsible for the correlation of $\log(k)$ with ionization potential.

Introduction

The reactions of hydrocarbon free radicals with molecular oxygen are widespread in the combustion of fossil fuels and air pollution chemistry. While it is generally accepted that these reactions are fast, very few absolute rate constants have been measured by direct means. Until recently, only rate constants for the reaction of methyl radicals with O₂ were reported in the literature and these showed only fair agreement for different studies.¹⁻⁵ A previous report from this laboratory gives high-pressure limiting rate constants for the reaction of three isomeric butyl radicals with O₂.⁶ Very recently the rate constants for ethyl + O₂ were reported as a function of pressure by Plumb and Ryan.⁷

This present report continues the determination of absolute rate constants for hydrocarbon radicals reacting with O₂ by using direct monitoring of the radicals with photoionization mass spectrometry. The rates of reaction of the two isomeric propyl radicals with O₂ have been measured for a variety of conditions. These results confirm the trend of rate constants with radical structure which was noted previously.⁶ Possible reasons for this correlation are discussed. Finally, adiabatic channel model calculations have been done in an attempt to model these association reactions.

Experimental Section

A uniform concentration of propyl radicals was formed in a cylindrical reaction cell (33.5-mm diameter by 46 mm) by flash photolysis of an appropriate precursor molecule. The radical concentration was sampled through a 0.2 mm diameter pinhole located on the cylindrical axis of the cell. A small fraction of the radicals exiting the pinhole was photoionized and mass analyzed with a quadrupole mass filter. Ion counts were stored as a function of time after the photolyzing flash on a multichannel analyzer.

Initially propyl radicals were formed by photolyzing the propyl iodides or the butyl nitrites with a 10-J xenon flash lamp (ILC Model 403 with a Xenon Corp. Model 457 power supply). Later experiments generated propyl radicals by photolyzing the nitropropanes with the 193-nm radiation from an ArF laser (Lumonics, Model 161). The 1-nitropropane (Matheson Coleman and Bell) and 2-nitropropane (Eastman Kodak) were used at partial pressures of approximately 5 mtorr. Larger partial pressures of the propyl iodides and butyl nitrites (~50 mtorr) were needed when the xenon flash lamp was used.

The initial experiments were done on an apparatus described by Lenhardt et al.⁶ This apparatus had a partially enclosed ionization chamber (chamber I) that consequently required a double-exponential function to fit the radical signal as a function of time (a fast exponential rise corresponding to the time constant for filling the ionization chamber with radicals and an exponential decay due to the slower radical loss within the reaction cell). Subsequent measurements were carried out with a more open ionization chamber (chamber II), designed to improve the time response of the radical signals;⁸ a single-exponential decay was

TABLE I: Summary of the Experimental Rate Constants for the Reaction of 1-Propyl and 2-Propyl Radicals with O₂ at 25 ± 3 °C

precursor	chamber	M	P/torr	k_1 or $k_2 / (10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$
1-C ₃ H ₇ I	I	He	1	4.6 ± 1.3
1-C ₃ H ₇ I	I	He	4	3.4 ± 1.1
1-C ₄ H ₉ ONO	II	He	4	3.6 ± 0.5
1-C ₃ H ₇ NO ₂	II	N ₂	4	5.5 ± 0.9
2-C ₃ H ₇ I	I	He	1	10.4 ± 3.8
2-C ₃ H ₇ I	I	He	4	16.1 ± 3.4
2-CH ₃ -1-C ₃ H ₆ ONO	I	He	4	13.7 ± 6.4
2-CH ₃ -1-C ₃ H ₆ ONO	II	He	4	15.1 ± 2.2
2-C ₃ H ₇ NO ₂	II	N ₂	4	14.1 ± 2.4

sufficient to describe the time dependence of the observed radical signal in the improved system.

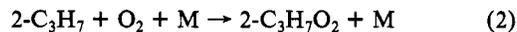
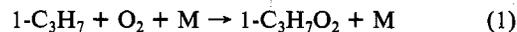
Radical concentrations were kept small, on the order of 10¹¹ cm⁻³, in order to reduce the importance of radical-radical reactions. Radical concentrations could be increased by a factor of 10 before an increase in the radical decay rate was noticed. Additional experimental details and all of the individual measurements may be found elsewhere.⁹

Results

When the propyl radical signal, S , was fitted to an exponential decay of the form

$$S = S_0 \exp(-t/\tau) + S_1$$

where S_1 represents the background count rate (10-100 counts/s), it was observed that the decay rate, τ^{-1} , was linearly dependent on the partial pressure of O₂, as can be seen in Figure 1. This behavior is expected for a reaction scheme in which the propyl radicals either react with O₂ (reactions 1 and 2) or are lost by



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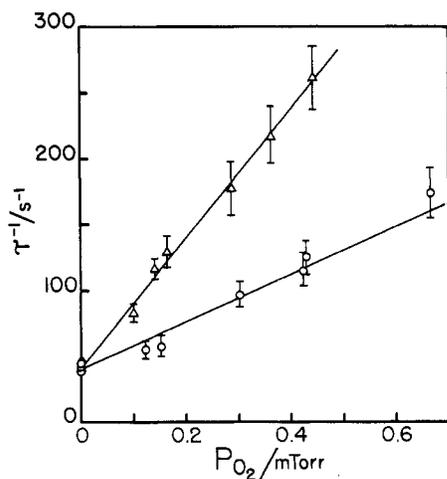
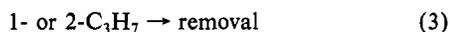


Figure 1. Dependences of the radical decay rate on the partial pressure of oxygen. The circles (O) represent 1-propyl radicals generated from 1-nitropropane in 4 torr of N_2 . The triangles (Δ) show data for 2-propyl radicals generated from 2-butyl nitrite in 4 torr of He. The error bars represent one standard deviation as derived from the CURFIT program.¹⁰ Both experiments were done with chamber II at a temperature of 25 \pm 3 $^{\circ}C$.

other first-order processes, such as reaction on the walls or being pumped out of the cell (reaction 3). No radical-radical reaction



is included in this scheme because none was required by the experimental data.

Application of the above reaction scheme to the present experiments results in the expectation that the decay constant should be linear in reactant concentration, e.g.

$$\tau^{-1} = k_3 + k_1[O_2]$$

Thus, the slopes of the lines shown in Figure 1 are taken to be the absolute rate constants for reactions 1 and 2. A summary of such rate constant determinations for a variety of conditions is given in Table I.

Examination of the various rate constants in Table I shows that the experiments done with chambers I and II give essentially identical results; e.g., the rate constants for the 2-propyl radical derived from isobutyl nitrite and by using 4 torr of He bath gas are $(14 \pm 6) \times 10^{-12}$ with chamber I and $(15 \pm 2) \times 10^{-12}$ with chamber II. This agreement is comforting since the analogous rate constants for the reactions of the three isomeric butyl radicals with O_2 were done by using only chamber I.⁶

The results reported in Table I also suggest that the nature of the precursor molecule does not influence the rate of reaction of the propyl radicals. The three different photolysis reactions used to generate the radicals have different overall exothermicities: 1-propyl formed from 1-butyl nitrite is 15 kcal/mol exothermic, from 1-propyl iodide 48 kcal/mol, and from 1-nitropropane 89 kcal/mol exothermic. During a typical radical lifetime in these experiments (~ 0.01 s), the radicals would experience approximately 10^6 collisions with the 4 torr of bath gas and 10 collisions with the walls of the cell. Thermalization of the radicals is thus expected for these conditions.

The consistency of rate constants shown in Table I also suggests that isomerization of hot 1-propyl radicals to the more stable 2-propyl radicals does not occur; significant isomerization of hot 1-propyl radicals would result in a rate constant characteristic of 2-propyl radicals. Clearly the behaviors of the two different propyl radicals are distinct, and the observed rate constant for 1-propyl + O_2 does not depend on the excess energy available in its generation step. However, a small amount of isomerization cannot be ruled out by the present experiments.

Assessing the pressure dependence of these rate constants is only marginally possible with the present data. As can be seen in Table I, the rate constants show little or no pressure dependence

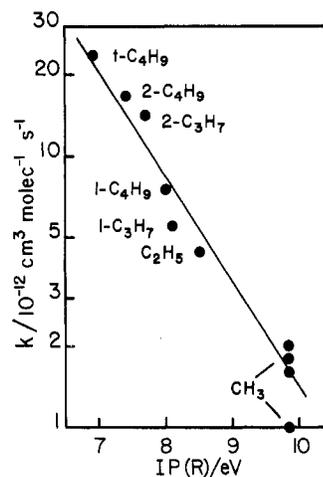


Figure 2. Plot of the rate constant for the $R + O_2$ reaction in the limit of high pressures vs. the ionization potential of the radical R. The straight line is a linear least-squares fit of $\log(k)$ to IP.

in going from 1 torr of He to 4 torr of He to 4 torr of N_2 . For 1-propyl, the experiments in N_2 give a slightly higher rate constant; however, the spread of values is comparable to the calculated errors. Since the reaction $CH_3 + O_2$ does not reach its high-pressure limit until approximately 1000 torr and the reaction $C_2H_5 + O_2$ requires 100 torr, it is likely that the values reported in Table I are only close to the high-pressure limiting rate constant. Therefore, the values measured in 4 torr of N_2 (a more effective third body than He) will be accepted as the best estimates of the high-pressure limiting values:

$$k_1 = (5.5 \pm 0.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_2 = (14.1 \pm 2.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where the error limits represent both the scatter in the data (standard deviation 5–10%) and the estimated uncertainty in the absolute O_2 concentrations. If an average of all the values in Table I had been used instead, k_1 would be about 25% lower and k_2 would be essentially unchanged.

Discussion

The rate constants determined above are consistent with those reported earlier for similar alkyl radicals reacting with O_2 . The value for k_1 falls between the reported values for ethyl + O_2 ⁷ and 1-butyl + O_2 .⁶ Similarly, k_2 is slightly smaller than the reported rate constant for 2-butyl + O_2 .

As was suggested previously,⁶ the high-pressure limiting rate constants correlate with the ionization potential of the alkyl radical. This can be seen in Figure 2 where the rate constants $k(R + O_2)$ are plotted on a logarithmic scale against the ionization potential of radical R.^{11,12} The present results, the previous values for the three butyl radicals, Plumb and Ryan's recent rate constant for ethyl + O_2 , and the several estimates for methyl + O_2 all fall close to a single straight line. The root mean square deviation of $\ln(k)$ from the least-squares line shown in Figure 2 is only 0.24 (using the recommended high value for $k(CH_3 + O_2)$ ¹³). The average deviation is comparable to the experimental uncertainties in both rate constants and ionization potentials. This correlation does not appear to apply to hydrocarbon radicals other than alkyl radicals; the rate constants for benzyl + O_2 and allyl + O_2 do not fall close to the straight line shown in Figure 2, as has been noted.^{14,16}

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TABLE II: Parameters Used in the Adiabatic Channel Model Calculations for R + O₂ → RO₂

	CH ₃	C ₂ H ₅	1-C ₃ H ₇	2-C ₃ H ₇	1-C ₄ H ₉	2-C ₄ H ₉	<i>t</i> -C ₄ H ₉
ΔH^\ominus /(kcal/mol)	-30	-30	-30	-31	-30	-31	-33
ΔS^\ominus /(cal/(mol K))	-31	-32	-32	-31	-32	-31	-31
$\Delta(H_T^\ominus - H_0^\ominus)$ /(kcal/mol)	-1.46	-0.94	-0.47	-0.87	-0.62	-1.03	-0.94
ω /cm ⁻¹	1033	1052	1052	1074	1052	1074	1099
$A/\text{\AA}^2$	0.364	1.198	2.372	0.364	3.76	0.617	0.364
$B/\text{\AA}$	0.312	0.312	0.312	0.312	0.312	0.312	0.312
W	-3.87	-5.30	-6.27	-4.56	-6.21	-4.32	-4.38
$\beta/\text{\AA}^{-1}$	3.42	3.42	3.42	3.37	3.42	3.37	3.27
C_6 /(eV \text{\AA}^6)	96	206	348	348	422	422	470
IP of R/eV	9.84	8.51	8.1	7.69	8.01	7.41	6.92

The trend of rate constants shown in Figure 2 is not what one would expect from steric effects alone. The radical center in the *tert*-butyl radical is shielded by the three methyl groups, and yet the rate of reaction of *tert*-butyl with O₂ is 10 times faster than methyl + O₂. It is also unlikely that the trend of reactivity is caused by the lowering of an energy barrier to reaction; the limited experimental evidence suggests that there are no energy barriers for these reactions. The rate of reaction of benzyl + O₂ appears to be independent of temperature.¹⁵ While the R + O₃ rate constants show a very similar trend with ionization potential,¹⁷ the slowest rate constant for that series is for CH₃ + O₃ and this shows no evidence for an energy barrier.⁸

In an attempt to understand the observed trend in rate constants, we have modeled these reactions by using Quack and Troe's simplified adiabatic channel model (ACM).¹⁸ The form of the ACM and the nomenclature used in these calculations are given in the following paper.¹⁷ The ACM uses as input parameters the thermodynamic properties of the reactants and products. The transition state is located by smoothly scaling the molecular properties with the reaction coordinate and using an exponential switching function of the form $\exp[-\gamma(r - r_c)]$; for the calculations reported below, the empirical parameter γ is taken to be 0.75 \text{\AA}^{-1} as recommended by Quack and Troe and the equilibrium C-O bond distance, r_c , is taken as 1.43 \text{\AA} for all of the reactions. Not all of the needed thermodynamic parameters were available in the literature; missing values were estimated by extrapolation with particular attention paid to group additivity methods.¹⁹ Table II gives the values of parameters used in the calculations.

The adiabatic channel model calculations were done initially with a Morse potential for the C-O bond:

$$V_I = D_c[-2 \exp(-\beta(r - r_c)) + \exp(-2\beta(r - r_c))] \quad (\text{I})$$

where D_c is the total well depth, taken to be $-\Delta E_0^\ominus + \omega/2$, the vibrational frequency of the C-O bond, ω , was estimated,⁶ and β is the usual Morse parameter.²⁰ The resulting rate constants, shown in the first column of Table III, are in the range $(19-44) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This calculation is moderately successful in giving an absolute magnitude of the rate constants, at least for the larger radicals, with no adjustable parameters beyond the empirical value of γ recommended by Quack and Troe. However, the standard ACM calculation fails completely to reproduce the trend of the rate constants with radical ionization potential shown in Figure 2.

The standard calculation resulted in transition states at carbon-oxygen bond distances near 3 \text{\AA}. At this large distance the Morse function is not expected to be a good representation of the actual potential. The ACM calculations were repeated by using a potential of the form

$$V_{II} = -C_6/r_c^6 \quad (\text{II})$$

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TABLE III: Comparison of Calculated and Experimental Rate Constants for the R + O₂ Reaction in the Limit of High Pressures^a

radical	k (calcd) with potential			k (exptl)	ref
	V_I	V_{II}	V_{III}		
CH ₃	42	160	4.2	2.0	13
C ₂ H ₅	24	180	4.5	4.4	7
1-C ₃ H ₇	18	200	4.2	5.5	this work
2-C ₃ H ₇	27	240	11.7	14.1	this work
1-C ₄ H ₉	19	210	5.3	7.5	6
2-C ₄ H ₉	28	250	16.5	16.6	6
<i>t</i> -C ₄ H ₉	29	260	24.6	23.4	6

^a All rate constants are reported as $k/(10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$.

with the C_6 constants taken to be the same as those for the corresponding alkanes colliding with O₂²¹ and r_c , the distance between the center of masses of the recombining R and O₂, was calculated from the approximate formula

$$r_c^2 = A + Br + r^2$$

by using the constants A and B shown in Table II. The rate constants calculated by using V_{II} , shown in the second column of Table III, are much too large. This result demonstrates that the ACM calculations are very sensitive to the form of the long-range potential used.

In an attempt to mimic the observed trend of rate constants with radical ionization potential, a long-range potential of the following form was assumed:

$$V_{III} = -H^2/((IP - EA) - e^2/r) + H^2/(IP - EA) \quad (\text{III})$$

This potential was developed by using the following simple model: at large C-O distances, r , it is assumed that the doublet surface corresponding to R + O₂ is perturbed by the doublet surface of R⁺ + O₂⁻; as a result of this perturbation, the R + O₂ surface is made attractive by an amount $H^2/\Delta E$, where ΔE is the unperturbed energy separation between the two surfaces and H is a interaction matrix element, which is assumed to be independent of r ; the ΔE is just IP - EA, the difference between the ionization potential of radical R and the electron affinity of O₂, minus the Coulomb attraction between two singly charged ions, e^2/r ; the same value of H will be used for all of the alkyl radicals. While several of these assumptions are very crude, the use of V_{III} in the ACM calculation gives good agreement with experiment. The matrix element is treated as an adjustable parameter to give the results shown in the third column of Table III. The average deviation of calculated and experimental rate constants is only a factor of 1.4, and the maximum deviation is a factor of 2.1. The potential V_{III} with $H = 0.189 \text{ eV}$ is capable of reproducing the trend shown in Figure 2.

Two conclusions can be drawn from the above calculations. First, the form of the long-range potential is very important in an adiabatic channel model calculation. For recombination re-

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actions of the type considered here, more realistic potentials should probably be used, which means that the empirical value of γ will probably have to be reevaluated. Second, the success of potential V_{III} suggests that some mixing in of the charge-transfer surface is occurring in these reactions and that the resulting polarity in the transition state is the reason for the correlation of radical ionization potentials with rate constants. Additional evidence to

support this conclusion is presented in the following paper.¹⁷

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Registry No. 1-Propyl, 2143-61-5; 2-propyl, 2025-55-0; oxygen, 7782-44-7.

Rates of Reaction of Alkyl Radicals with Ozone

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The rate constants for a series of alkyl radicals reacting with ozone have been measured at 298 K and 2 torr by using a photoionization mass spectrometer. The radical (R) + ozone rate constants (in units of 10^{-12} cm³ molecule⁻¹ s⁻¹) are 2.53 ± 0.54 for CH₃, 25.3 ± 5.8 for C₂H₅, 24.4 ± 5.9 for 1-C₃H₇, 46.5 ± 10.6 for 2-C₃H₇, and 54.5 ± 11.4 for *t*-C₄H₉. As was observed for the R + O₂ reactions, the R + O₃ reactions show a trend of increasing rate constant k_1 with decreasing ionization potential (IP) of the radical. When $\log(k_1)$ vs. IP(R) - EA(O₂ or O₃) is plotted, where EA represents electron affinity, the two families of rate constants are brought into close proximity (Figure 1). In addition, rate constants for fluorescence quenching of substituted benzenes by O₂ are cited which extend the $\log(k)$ vs. IP - EA plot to lower ionization potential. Adiabatic channel model calculations have been done by using a long-range potential resulting from the perturbation between the R⁺ + O₃⁻ and R + O₃ surfaces. These calculations give good agreement with the experimental cross sections (Figure 2) and they predict rate constants faster than those derived from the classical harpoon model at low IP - EA.

Introduction

Rate constants have been measured for the reaction of several alkyl radicals with ozone in the gas phase. Except for previous studies of the CH₃ + O₃ reaction,¹ there have been no other measurements of alkyl radical-ozone rate constants. In the present work, the radicals were formed by laser flash photolysis and their concentration was followed as a function of time by using a photoionization mass spectrometer. The variation of the rate constants with radical structure is closely analogous to that observed for these same alkyl radicals reacting with O₂.^{2,3} Some possible reasons for this unexpected trend are discussed below.

Radicals are thought to be formed as intermediates during the reaction of ozone with olefins.^{4,5} The fate of these radicals depends on the ratio of O₃/O₂ in the ambient gas and the respective rate constants. The measurements reported below suggest that any alkyl radicals formed in ozone-olefin mixtures will react primarily with O₂, unless the O₃/O₂ ratio is greater than 0.1 or the total pressure is very low.

Description of Experiment

The experimental system has been described previously^{1a,6} and will be discussed only briefly here. Radical precursor molecules were transported in a flow system with 2 torr of He carrier gas into a cylindrical reaction cell of about 50-cm³ volume. Inside the cell, the precursors were subjected to dissociating radiation at 193 nm from an ArF excimer laser (Lumonics TE 261-2). Typically, an alkyl radical was generated from photolysis of the corresponding nitroalkane except for *tert*-butyl, which was made by dissociating 2,4,4-trimethyl-1-pentene. A 0.2 mm diameter pinhole in the rear window of the cell allowed a small fraction of the cell contents to escape into a high-vacuum region where the radicals were photoionized by vacuum-ultraviolet radiation from rare gas resonance lamps.^{7,8} Methyl radicals were ionized with a Kr lamp (MgF₂ window) and the other radicals were ionized with a Xe lamp (sapphire window). The ions were mass selected with a quadrupole mass filter (Extranuclear 270-9) and

detected with a Daly electrode,⁹ scintillator, and photomultiplier. The ion counts were accumulated and stored on a multichannel analyzer (Canberra 8100) for later analysis by computer.

The ozone was prepared by using a commercial ozonizer (Welsbach Style T-23) and trapped on silica gel at 196 K.¹⁰ After the O₂ was pumped off from the silica gel, the O₃ was allowed to expand into a 10-L bulb, diluted with He, and stirred by convection to give a homogeneous mixture. Before the ozone entered the reaction cell, its concentration was measured by absorption at 253.7 nm with a low-pressure Hg lamp (Pen Ray), 254-nm interference filter, and photomultiplier. The O₃ cross section at 253.7 nm was taken to be 1.157×10^{-17} cm²/molecule.¹¹ The pressure of the reactant ozone mixture was measured with a capacitance manometer (MKS type 77) and converted to absolute concentration by using the absorption data and separate flow calibrations.

Typically 100-1000 laser flashes were necessary to accumulate enough radical signal for analysis. The laser intensity was kept sufficiently low so that radical-radical reactions were negligible. The radical decay was then a composite of reaction with O₃,

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