

Kinetics of Polyatomic Free Radicals Produced by Laser Photolysis. 4. Study of the Equilibrium $i\text{-C}_3\text{H}_7 + \text{O}_2 \rightleftharpoons i\text{-C}_3\text{H}_7\text{O}_2$ between 592 and 692 K

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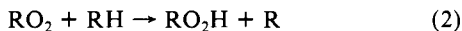
Abstract: The equilibrium involving the gaseous reaction between isopropyl radicals and molecular oxygen to form isopropylperoxy radicals has been studied at seven temperatures between 592 and 692 K. The $i\text{-C}_3\text{H}_7$ radicals were generated homogeneously in a tubular reactor by the pulsed 193-nm photolysis of $i\text{-C}_3\text{H}_7\text{Br}$. The relaxation of the $i\text{-C}_3\text{H}_7$ radicals to equilibrium in the presence of O_2 was monitored in real-time experiments with photoionization mass spectrometry. The experiments yielded at least one value of the equilibrium constant at each temperature. The enthalpy change for the equilibrium $i\text{-C}_3\text{H}_7 + \text{O}_2 \rightleftharpoons i\text{-C}_3\text{H}_7\text{O}_2$ was obtained from the measured equilibrium constants and a Third Law calculation of the entropy change. From structural information on reactions and products, thermodynamic variables including $S^\circ(T)$, $C_p^\circ(T)$, and $H^\circ(T) - H^\circ(0)$ were calculated as a function of temperature for $i\text{-C}_3\text{H}_7$ and $i\text{-C}_3\text{H}_7\text{O}_2$. The calculated value of $\Delta S^\circ(298) = -39.9 \pm 1.5$ cal/(mol K), when combined with the other calculated thermodynamic variables and the measured equilibrium constants, yields $\Delta H^\circ(298) = -37.7 \pm 1.8$ kcal/mol for the title reaction and an intrinsic $i\text{-C}_3\text{H}_7\text{-O}_2$ bond strength $\Delta H^\circ(0) = 36.4 \pm 1.8$ kcal/mol. These results indicate a significantly stronger R-O₂ bond in $i\text{-C}_3\text{H}_7\text{O}_2$ than is predicted by group additivity methods. The possible sources of this difference are discussed. Analogous experiments were conducted on the $\text{C}_3\text{H}_5 + \text{O}_2 \rightleftharpoons \text{C}_3\text{H}_5\text{O}_2$ equilibrium between 352 and 413 K to establish the accuracy of the experimental method. The measured equilibrium constants for this second reaction are in close agreement with prior determinations.

The reactions of alkyl and other hydrocarbon free radicals (R) with molecular oxygen are important elementary steps in most oxidation processes, including the combustion of fossil fuels,¹⁻⁶ the formation of tropospheric smog,⁷⁻⁹ and the chemistry of the stratosphere.^{10,11} Changes that occur in the mechanisms of these elementary reactions as temperature increases (particularly between 300 and 500 °C) are largely responsible for important changes that occur in combustion processes such as the ultimate stable products that are produced and the rate of the oxidation process itself.^{5,12,13}

Near ambient temperature hydrocarbon free radicals react primarily with molecular oxygen by a reversible addition process¹⁴⁻¹⁹



The peroxy radicals formed in these reactions abstract hydrogen atoms from fuel molecules with relatively weak C-H bonds forming alkyl hydroperoxides and completing a free-radical chain¹⁻⁶



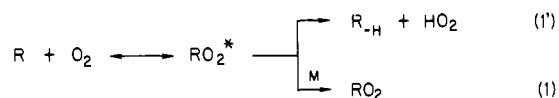
The principal products of the early stages of low-temperature combustion ($T < 250$ °C) are these hydroperoxides and products that result from their decomposition and further reaction (e.g., aldehydes and ketones).

Between 250 and 450 °C there is a major change in the mechanism of hydrocarbon combustion caused by the reversible nature of reaction 1. The peroxy radical is no longer stable relative to its dissociation back to R and O_2 .^{12,13} The increasing importance of this dissociation process as temperature increases lowers the concentration of RO_2 at elevated temperatures. Reduced RO_2 concentrations are in part responsible for the decreasing maximum rate of oxidation of some hydrocarbons with increasing temperature that occurs near 350 °C. In this same temperature range the stable carbon-containing products produced during the early stages of oxidation change from oxygen-containing species to olefins.^{1,2,12} There is still uncertainty whether these new products

are produced by an uncoupled parallel H atom metathesis reaction involving R and O_2



or by an alternate but coupled decomposition pathway of the energy-rich RO_2 adduct formed during reaction 1, a second pathway that becomes increasingly important as temperature increases³⁻⁶



In 1965 Knox and Benson independently consolidated prior knowledge of combustion kinetics and thermochemistry into

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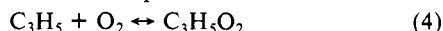
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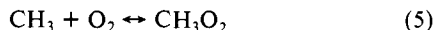
quantitative models of low-temperature combustion that are still the basis of most of our understanding of these processes today.^{12,13} Because of the importance of reaction 1, careful attention was paid to estimating the thermochemistry of this reaction. The methods developed for this purpose, particularly the concept of group additivity developed by Benson to estimate thermodynamic variables of molecules and free radicals, are still the major source of much of this information.²⁰ This is particularly true of the thermochemistry of the peroxy radicals for which there is very little information available that is based on direct experiments.^{21,22}

There is enough uncertainty in the values of the enthalpies of formation of both R and RO₂ to create doubt as to whether the values of the equilibrium constant for reaction 1 calculated by using such enthalpies are sufficiently accurate for the modeling of gaseous oxidation processes. Measured heats of formation of alkyl radicals depend on the type of experiment performed to obtain them (creating a 2–3 kcal/mol uncertainty in their values).^{23,24} The heats of formation of alkyl peroxy radicals are still based almost solely on group additivity concepts (which depend on an assumed “no next nearest neighbor” contribution to any bond energy in a molecule or radical).^{21,22} Because of the importance of this information in quantitative combustion modeling and because of the renewed interest in accurate computer-assisted modeling of a variety of combustion processes,^{25–27} there is a need to directly establish ΔH° for reaction 1 by experiment, at least for representative free radicals.

In complementary studies Bayes and co-workers and Pilling et al. have directly studied the equilibrium^{14,28}



Their measured values of the equilibrium constant of reaction 4 and its temperature dependence between 75 and 180 °C yielded values of ΔH° and ΔS° for this reaction that are in very good agreement with those derived from group additivity estimates. This close agreement has increased confidence in the accuracy of group additivity concepts to estimate the thermochemical parameters of reaction 1. A more indirect set of determinations of the equilibrium constant of the reaction

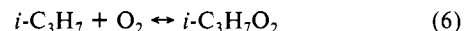


by Khachatryan et al. has yielded a value for the enthalpy change of this reaction that is also in agreement with estimates obtained from the same group additivity concepts.²⁹

The entropies of R and RO₂ (and hence ΔS° for reaction 1) can be estimated with adequate accuracy to calculate meaningful equilibrium constants for this reaction by using the measured entropies of closely allied stable species (with suitable corrections) or by group additivity concepts,²⁰ and they can also be accurately calculated if the structure and internal motions of the species are known.³⁰

As part of our continuing interest in the kinetics of polyatomic free radicals, we are currently studying a series of R + O₂ reactions that are capable of undergoing mechanism changes of the type described above. We are also studying the equilibrium shown as reaction 1 in the temperature range where it can be directly

observed. We have now completed the first direct study of reaction 1 involving an alkyl radical, that involving the isopropyl radical



Equilibrium constants were measured between 319 and 419 °C. The *i*-C₃H₇ radicals were generated homogeneously in a heated tubular reactor by the pulsed photolysis of *i*-C₃H₇Br, and the relaxation of the *i*-C₃H₇ radical to equilibrium was observed directly in time-resolved experiments using photoionization mass spectrometry. Values of ΔS° for reaction 6 were calculated from information on the structural properties and internal motions of the species involved,³⁰ and ΔH° was subsequently determined by a Third law method.¹⁴ The experiments, the thermochemical calculations, and a discussion of these results are presented here.

Experimental Apparatus

The experimental apparatus and most procedures used were essentially the same as those described in parts 1–3.^{31–33} Unfocused, pulsed, 193-nm radiation from a Lumonics TE-860-4 excimer laser is directed along the axis of a 35-cm-long, 0.95-cm-i.d. tubular Pyrex reactor. Gas flowing through the tube contains the free-radical source at low concentration ($\approx 0.05\%$ *i*-C₃H₇Br), O₂ (in varying amounts but normally less than 5%), and an excess of He (typically 98%). A simple aperture was used to collimate the laser beam to the size of the tubular reactor just before the radiation entered it through a quartz window. The laser was operated at 10 Hz and at a fluence of ≈ 70 mJ/cm². Typically 0.5% of the *i*-C₃H₇Br decomposed during each laser pulse.

The gas mixture flowed through the reactor at 5–10 m/s in order to replace the photolyzed gas with a fresh gas mixture between laser pulses. The high percentage of He in the gas mixture assured its rapid thermal equilibration as it entered the heated zone and also acted as a buffer against additional heating caused by the photolysis process.

Gas was continuously sampled through a 0.044-cm-diameter hole in the side of the reactor. The emerging gas was formed into a beam by a conical skimmer before it entered the vacuum chamber containing the photoionization mass spectrometer. As the gas beam traversed the ion source, a portion was photolized (using an atomic resonance lamp) and mass selected. The distance from the sampling orifice in the reactor wall to the center of the ionizing region of the mass spectrometer is 2.4 cm.

Temporal ion signal profiles of reactants, possible products, and the free radical precursor were recorded with a multichannel scalar from a period just before each laser pulse to 10–30 ms following the pulse. Typically data from 20000–50000 repetitions of the experiment were accumulated before the data were analyzed. The resonance-radiation energies used to photoionize the molecular and radical species in the mass spectrometer were 10.2 eV (*i*-C₃H₇Br, C₃H₆, C₆H₁₀), 9.5 eV (*i*-C₃H₇), and 8.9–9.1 eV (C₃H₅).

The tubular reactor is heated by a 1-cm-wide nichrome ribbon tightly wrapped around it in a spiral that extends from 20-cm upstream to 5-cm downstream from the sampling orifice. The temperature during an actual experiment is monitored by a thin (¹/₁₆-in.-diameter) in situ thermocouple placed along the axis of the reactor from the downstream end. The end of the thermocouple is in the heated zone 3-cm downstream from the sampling orifice. The temperature readings there agree with those recorded with a movable thermocouple when the latter is placed farther upstream (in the middle of the 15-cm-long uniformly heated zone from which gas is sampled during an experiment). The uniformity of the temperature in this zone is ± 4 °C. Axial temperature uniformity is presumed based on the low gas densities used in these studies (see Table I), the small diameter of the tubular reactor, and the carrier gas used.

The inside of the tubular reactor was periodically cleaned with a 5% NH₄F-HF solution and coated with a 1% boric acid solution to minimize heterogeneous free radical wall-loss processes.

i-C₃H₇Br (>97%, Eastman), C₃H₆ (Matheson, C. P. Grade), and 1,5-hexadiene (>98%, Aldrich) were purified by fractional distillation. Helium (High Purity) and O₂ (Extra Dry) were obtained from Linde and were used without extra purification.

Experimental Results

I. 193-nm Photolysis of *i*-C₃H₇Br. A survey was conducted to determine the products produced by the 193-nm photolysis of *i*-C₃H₇Br. These experiments were conducted at 500 K. A gas mixture was flowed through the reactor at a pressure of 3.1 torr that contained *i*-C₃H₇Br

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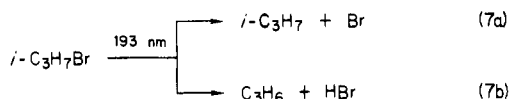
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Table I. Conditions and Results of Experiments To Measure Equilibrium Constants

<i>T</i> , K	$M \times 10^{-16}$, molecules cm^{-3}	O_2 pressure \times 10^5 , atm	k_w , s^{-1}	m_1 , s^{-1}	m_2 , s^{-1}	R_{AB}	K_6 and K_4 , atm^{-1}
Experiments on the $i\text{-C}_3\text{H}_7 + \text{O}_2 \leftrightarrow i\text{-C}_3\text{H}_7\text{O}_2$ Equilibrium ($K_6 \times 10^{-3}$)							
692	5.83	23.0	8.2	1110	189	1.12	2.36
672	5.84	9.06	13.2	1150	173	0.696	4.54
672	5.84	7.55	13.2	848	147	0.393	3.12
652	5.83	9.20	24.8	889	128	1.81	9.07
652	5.83	4.67	24.8	735	106	0.541	7.30
632	5.83	6.09	24.2	559	50.7	3.46	27.2
632	5.83	4.09	24.2	774	84.5	2.66	31.0
612	5.82	2.83	23.6	350	15.4	4.17	96.1
602	5.81	3.50	28.1	460	31.0	4.04	62.0
592 ^a	5.82	1.32	29.5	392	60.8	1.91	61.5
Experiments on the $\text{C}_3\text{H}_5 + \text{O}_2 \leftrightarrow \text{C}_3\text{H}_5\text{O}_2$ Equilibrium ($K_4 \times 10^{-3}$)							
413	6.80	77.2	11.2	1320	18.2	1.20	1.46
411	6.12	68.7	11.2	921	11.1	1.05	1.45
401	7.05	33.7	10.8	706	13.9	1.27	3.45
391	7.02	12.1	11.7	390	10.3	0.805	6.05
382	7.12	11.0	10.5	327	8.34	1.27	10.3
373	7.37	5.27	11.0	195	9.04	1.12	17.5
372	7.37	10.2	11.1	283	7.80	2.12	17.5
363	7.55	8.37	12.0	247	8.11	3.50	31.5
362	7.55	5.45	12.0	185	8.29	2.31	31.8
354 ^b	7.75	5.17	14.1	174	6.46	4.39	58.2
353	7.75	2.56	14.1	110	6.31	2.40	64.4
352	6.97	3.18	11.9	114	7.73	2.85	54.7

^aData from this experiment shown in the insert in Figure 1. ^bData from this experiment shown in the insert in Figure 2.

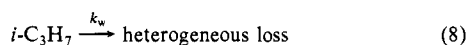
(0.04%) and He (balance). Possible products were monitored by using photoionizing energies of 10.2 and 11.8 eV. The only significant products that were detected were $i\text{-C}_3\text{H}_7$, C_3H_6 , Br, and HBr. This indicated two important photolysis routes



Products searched for but not detected include CH_3 , C_2H_4 , C_3H_8 , C_6H_{14} , CH_2Br , $\text{C}_2\text{H}_3\text{Br}$, and $\text{C}_2\text{H}_4\text{Br}$.

The extent of photolysis by reaction 7b was also determined at 500 K. C_3H_6 formation was compared to $i\text{-C}_3\text{H}_7\text{Br}$ depletion on photolysis by monitoring the respective ion-signal profiles during photolysis experiments. Ion-signal changes on photolysis were translated into concentration changes by using the results of separate calibration experiments in which known flows of these same two gases were combined with the carrier gas and flowed through the reactor, and ion signals were recorded. The yield of C_3H_6 ($-\Delta[\text{C}_3\text{H}_6]/\Delta[i\text{-C}_3\text{H}_7\text{Br}]$) was 0.65 ± 0.10 . The larger than usual error limits are caused by the difficulty in measuring the very low $i\text{-C}_3\text{H}_7\text{Br}$ loss ($-\Delta[i\text{-C}_3\text{H}_7\text{Br}]/[i\text{-C}_3\text{H}_7\text{Br}]_0 \approx 0.007$) at the laser fluence used in these experiments. The branching fraction for reaction 7a was presumed to be 0.35 ± 0.10 by difference since no other photolysis products were detected.

The $i\text{-C}_3\text{H}_7$ ion signal decays exponentially after photolysis in the absence of O_2 . The decay constant is essentially independent of the radical precursor concentration provided that the initial $i\text{-C}_3\text{H}_7$ concentrations are kept low enough ($<10^{11} \text{ cm}^{-3}$) to suppress radical-radical reactions during the observation period (typically 15 ms). This decay is presumed to be caused by an undefined heterogeneous reaction



The measured value of k_w becomes lower as temperature increases. At 298 K it is $\approx 150 \text{ s}^{-1}$ and at 600 K it is near 30 s^{-1} . The exact value depends on the condition of the reactor walls at the time of the experiment. The rate of this heterogeneous reaction could be reduced somewhat by pretreating the reactor with a gas flow containing oxygen atoms for 30 min prior to a series of experiments.

II. Products of the $i\text{-C}_3\text{H}_7 + \text{O}_2$ Reaction. In order to analyze our experimental results it was necessary to determine the extent to which the $i\text{-C}_3\text{H}_7 + \text{O}_2$ reaction yields C_3H_6 via either a direct or an indirect mechanism (reactions 1' or 3). These experiments were difficult to analyze accurately because C_3H_6 is already produced by the original photolysis process (reaction 7b) and also to some extent by the heterogeneous wall process (reaction 8). The measurements involved determining the additional C_3H_6 produced after each laser pulse when sufficiently high O_2 concentrations were used to scavenge over 90% of the $i\text{-C}_3\text{H}_7$ radicals before they could react on the wall of the tubular reactor.

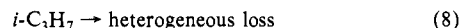
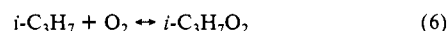
These experiments were performed at 500 K. The total C_3H_6 yield when the reaction was completed ($-\Delta[\text{C}_3\text{H}_6]/[i\text{-C}_3\text{H}_7]_0$) was below the detectable limits imposed by the above constraints, less than 0.07.

There is confirmation that there is not a significant homogeneous reaction path leading to C_3H_6 formation from the experiments discussed below.

III. Measurement of the Equilibrium Constant of Reaction 6. Between 592 and 692 K the equilibrium in reaction 6 is clearly observable. In this temperature range the $i\text{-C}_3\text{H}_7$ ion signal decay profiles no longer decay exponentially to the base line when high O_2 concentrations are used, as is the case at lower temperatures, but rather they decay rapidly to an intermediate level and then more slowly. An example of such an ion-signal profile is shown as an insert in Figure 1.

When extraordinarily high O_2 concentrations are used (10 times that used to observe this equilibrium), then the $i\text{-C}_3\text{H}_7$ ion signals do decay rapidly to the base line. Thus, the late, slowly decaying signal is not due wholly or in part to any fragmentation processes of primary or secondary products of $i\text{-C}_3\text{H}_7$ reactions of higher mass than the $i\text{-C}_3\text{H}_7$ radical.

Because of the extremely low initial $i\text{-C}_3\text{H}_7$ radical concentrations used ($<10^{11} \text{ cm}^{-3}$), and because C_3H_6 is not produced to any measurable extent during these experiments, the only reactions that need to be considered in the analysis of these temporal $i\text{-C}_3\text{H}_7$ ion signal profiles are



Under these conditions, the $i\text{-C}_3\text{H}_7$ concentration profile (and hence that of the $i\text{-C}_3\text{H}_7$ ion signal, $I(i\text{-C}_3\text{H}_7^+)$) is given simply by the sum of two exponential terms^{34,35}

$$I(i\text{-C}_3\text{H}_7^+) = A \exp(-m_1 t) + B \exp(-m_2 t) \quad (I)$$

Three parameters— R_{AB} (which is A/B), m_1 , and m_2 —are functions of the three rate constants k_6 , k_{-6} , and k_8 and the oxygen pressure, $P(\text{O}_2)$. The equations for these dependences can be readily inverted to yield the equilibrium constant (in units of atm^{-1}) for reaction 6 ($K_6 = k_6/k_{-6}$)

$$K_6 = R_{AB}(m_1 - m_2)^2 / \{(m_2 R_{AB} + m_1)^2 P(\text{O}_2)\} \quad (II)$$

(If the rate constant for reaction 8 is zero, then $K_6 = R_{AB}/P(\text{O}_2)$.)

Temporal $i\text{-C}_3\text{H}_7$ ion-signal profiles were fit to eq I to obtain A , B , m_1 , and m_2 by using standard nonlinear least-squares procedures,³⁶ and then eq II was used to determine K_6 . To maximize the accuracy of R_{AB} , which is the most important term in the equation for K_6 , experiments were

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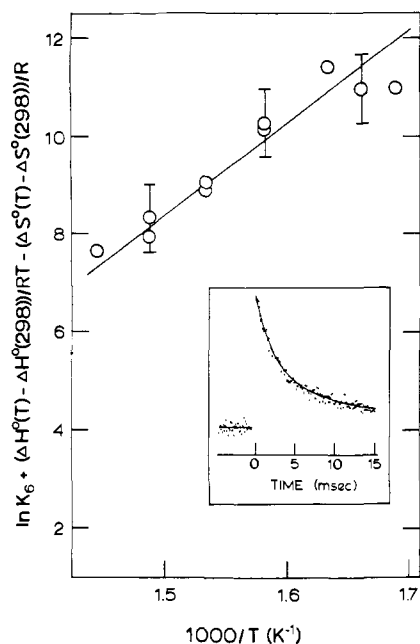


Figure 1. Modified van't Hoff plot of the measured equilibrium constants (K_6) for the equilibrium $i\text{-C}_3\text{H}_7 + \text{O}_2 \leftrightarrow i\text{-C}_3\text{H}_7\text{O}_2$. See text for the significance of the ordinate variable. The straight line through the data was obtained by a least-squares fit through the plotted points and a Third law determined value of $\Delta S^\circ(298)/R$ which is the ordinate variable at $1/T = 0$. The slope of this line is $-\Delta H^\circ(298)/R$ for the title reaction. The representative error bars indicate the factor of 2 estimated uncertainty in each determination of K_6 . The insert is a plot of the data from one of the plotted experiments ($I(i\text{-C}_3\text{H}_7^+) \text{ vs. } t$). For the conditions of this experiment, see Table I.

performed by using temperatures and O_2 concentrations that permitted the clear observation of both the fast and slow relaxation processes. The criteria used to determine the acceptability of an experiment were $0.2 < A/B < 5$, $m_1 > 5m_2$, and the standard relative errors in both A and B less than 20%. The fitted lines through the data obtained in two experiments are shown in the inserts of Figures 1 and 2.

Experiments were performed at seven temperatures between 592 and 692 K. Below 592 K, low O_2 pressures had to be employed to observe the equilibrium. This slowed the first relaxation process to an extent that m_1 was no longer at least five times greater than m_2 . Above 700 K the slow relaxation was reached before significant reaction had occurred ($A/B < 0.3$) even when very large O_2 partial pressures were used. At three temperatures two different experiments were performed by using different O_2 concentrations, both of which met the above criteria. The results of this study and the conditions of the experiments are given in Table I.

The accuracy of K_6 is determined by the accuracy of certain experimental parameters, the nonlinear least-squares fitting procedure, and the correctness of the presumed mechanism used to reduce the data. The experimental observations that are incorporated into the calculation of K_6 are the ambient O_2 pressure and the ratio of two ion signals (A/B). The O_2 pressure is measured with an accuracy of $\pm 10\%$, and the ratio of two ion signals has no significant inherent error associated with it. The fitting procedure together with the statistical errors in the ion signals introduces an estimated uncertainty of $\pm 60\%$ in the determination of K_6 . Separate experiments performed at the same temperature but at different O_2 concentrations yielded values of K_6 that are 15, 23, and 45% apart. The direction of these differences is not correlated with the O_2 pressures of the individual experiments at the same temperature. We conclude that 60% is a reasonable representative composite uncertainty in each determination of K_6 introduced by the statistical error in the ion signal and by the fitting procedure employed. The total uncertainty in each K_6 determination is less than a factor of 2.

We consider the presumed mechanism to be accurate for our experimental conditions and for the purpose that it is used. It is, of course, difficult to test any presumed mechanism for completeness. Initial conditions were chosen to eliminate interference from any radical-radical reactions. Production of C_3H_6 was not included because it was not observed to be produced to a significant extent at temperatures below the 100 K range of this study. The fitting procedure does not presume that the kinetically first-order irreversible loss of $i\text{-C}_3\text{H}_7$ (reaction 8) is simply the wall reaction. Thus, if the wall rate changed when O_2 was introduced

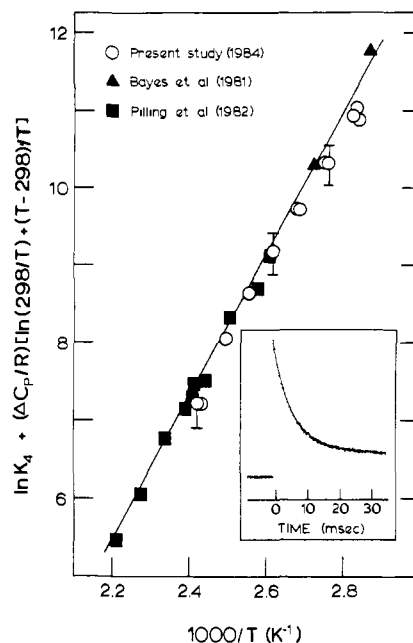


Figure 2. Modified van't Hoff plot of the measured equilibrium constants (K_4) for the equilibrium $\text{C}_3\text{H}_5 + \text{O}_2 \leftrightarrow \text{C}_3\text{H}_5\text{O}_2$. See ref 14 for the significance of the ordinate variable. Also shown are the results obtained in two prior studies of the same equilibrium (indicated in the plot as Bayes et al.²⁸ and Pilling et al.¹⁴). The straight line through the data was obtained in ref 14 by a least-squares fit of the combined results of the two prior investigations. The insert is a plot of the data from one of the plotted experiments ($I(\text{C}_3\text{H}_5^+) \text{ vs. } t$). For the conditions of this experiment, see Table I.

into the system, or if there were a contribution to the overall loss of $i\text{-C}_3\text{H}_7$ by a parallel olefin-producing route like reaction 3, the fitting procedure automatically takes this into account by attributing it to reaction 8. The data reduction procedure is insensitive to the identity of these irreversible parallel first-order radical loss processes.

If reaction 1' (the coupled olefin-producing route) were important in the temperature range of this study, it would introduce a systematic error in the calculated values of K_6 . To obtain an estimate of the maximum magnitude of this possible error, values of K_6 were recalculated from the ion-signal parameters (m_1 , m_2 , and R_{AB}) by using a new expression for K_6 in place of eq II that was derived from an extended mechanism that includes reactions 6 and 8 and the reaction



k_8 was fixed at the value of the measured wall reaction rate constant. Any mechanism that includes formation of C_3H_6 via the decomposition of $i\text{-C}_3\text{H}_7\text{O}_2$ lowers the final calculated value of $\Delta H^\circ(298)$. In the "worst case", i.e., if all irreversible loss of $i\text{-C}_3\text{H}_7$ not attributable to the wall reaction is assigned to reaction 9, the final calculated value of $\Delta H^\circ(298)$ for reaction 6 is 1.5 kcal/mol lower (more negative) than that reported below.

An indication that the mechanism is accurate is given by the fact that when $m_1 \gg m_2$, m_2 should be nearly equal to the wall rate constant, k_w , which is measured before O_2 is introduced into the system. Near 600 K, $m_1 \approx 10m_2$ and the values of m_2 are near those of k_w .

IV. Measurement of the Equilibrium Constant of Reaction 4. As a final check of the precision and accuracy of our experimental procedure, we also measured the equilibrium constant of reaction 4 to obtain thermochemical variables for which there are already accurate experimental determinations for comparison. These experiments were conducted in a manner identical with that described above for the $i\text{-C}_3\text{H}_7 + \text{O}_2 \leftrightarrow i\text{-C}_3\text{H}_7\text{O}_2$ equilibrium. The only differences were the free radical precursor used to produce C_3H_5 with 193-nm radiation (1,5-hexadiene) and the temperature range 75–136 °C. About 5% of the C_6H_{10} decomposed during each laser pulse. We did not repeat the study of the photolysis branching in this reaction reported by Pilling et al.,³⁷ but we used their results to choose initial C_6H_{10} concentrations that would yield initial C_3H_5 concentrations below 10^{11} cm^{-3} . Our detection sensitivity for the allyl radical is significantly greater than that for the $i\text{-C}_3\text{H}_7$ radical. For this

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Table II. Molecular Properties of $i\text{-C}_3\text{H}_7$, $i\text{-C}_3\text{H}_7\text{O}_2$, and O_2 Used in Calculations of Thermodynamic Variables of Reaction 6

	O_2	$i\text{-C}_3\text{H}_7$	$i\text{-C}_3\text{H}_7\text{O}_2$
external rotations			
moments of inertia, amu \AA^2			
I_1	0.0	13.55	61.76
I_2	11.65	60.94	124.69
I_3	11.65	68.31	170.35
symmetry no.	2	2	1
internal rotations			
C-CH ₃			
reduced moments of inertia, amu \AA^2		2.63	3.04 ^a
symmetry no.		9	3
barrier, kcal/mol		0.5	3.6
C-O ₂			
reduced moments of inertia, amu \AA^2			10.56
symmetry no.			3
barrier, kcal/mol			2.36
no. of rotomeric forms			2
electronic symmetry	3	2	2
vibration frequencies, cm ⁻¹			
C-H stretches and bends		3064, 2920 2920, 2920 2920, 2840 2840, 1468 1468, 1440 1440, 1388 1378, 1338 1167, 1017 963, 938 248,	2979, 2979 2943, 2943 2941, 2941 2883, 1459 1459, 1445 1445, 1381 1381, 1379 1359, 1127 1127, 1119 1119,
skeletal stretches and bends	1580.25	1138, 870 354	1092, 1023 1020, 813 568, 461 367, 356
skeletal torsions and free rotations (FR)		FR FR	215 209 93

^aThe reduced moment of inertia for the C-CH₃ in the trans C-C-O-O part of the skeleton. The other C-CH₃ would have internal rotor characteristics similar to the one listed.

reason fewer repetitions (typically 10 000) of the experiment were required to obtain C₃H₃ ion-signal decay profiles of even better quality than those recorded for the $i\text{-C}_3\text{H}_7$ radical (see Figure 2). The results of these experiments are also given in Table I. The estimated uncertainty in the values of K_4 determined in this study is $\pm 25\%$.

Determination of Thermochemical Parameters of the $i\text{-C}_3\text{H}_7 + \text{O}_2 \leftrightarrow i\text{-C}_3\text{H}_7\text{O}_2$ Equilibrium

I. Calculation of ΔS° for Reaction 6. Since ΔS° for reaction 6 can be determined from first principles more accurately than it could be obtained from the results of this study (using Second law methods), it was calculated from models of the structure and frequencies of $i\text{-C}_3\text{H}_7$ and $i\text{-C}_3\text{H}_7\text{O}_2$ derived from available experimental and theoretical information. These models also permit calculation of $C_p^\circ(T)$ and $H^\circ(T) - H^\circ(0)$, variables needed to calculate ΔH for reaction 6 by using a procedure based on the Third law.¹⁴ In this section, the most important parts of the models for $i\text{-C}_3\text{H}_7$ and $i\text{-C}_3\text{H}_7\text{O}_2$ are described, and the calculated thermodynamic variables are presented. (This analysis is part of a more detailed study of the thermodynamic properties of R + O₂ reactions (R = CH₃, C₂H₅, and $i\text{-C}_3\text{H}_7$).)³⁸

The structure of $i\text{-C}_3\text{H}_7$ has been studied with an ab initio unrestricted Hartree-Fock (UHF) calculation by Pacansky and Dupuis, who examined the seven lowest energy conformations in detail.³⁹ The lowest energy conformer has the C-H bond on the radical center out of the C-C-C plane by 5.8°. However, the amplitude of the lowest frequency bend of that C-H bond inverts the molecule through the plane, making the molecule dynamically planar. An external symmetry number of 2 is thus presumed for this planar structure. The conformational structure of the radical

is complex due to the low barriers to internal rotation of the methyl groups about the bond to the radical center (≈ 0.5 kcal/mol). Threefold hindered rotation of two independent methyl groups (resulting in an internal symmetry number of 9) is used in our calculation. The moments of inertia, the reduced moments of inertia for internal rotation, the external, internal, and electronic symmetry numbers, and the barrier to internal rotation are all listed in Table II.

The vibration frequencies of the isopropyl radical are available from a mixture of both experimental⁴⁰ and theoretical^{39,41} studies. The experimental measurements of Pacansky and Coufal determined the CH and CH₃ stretches and the CH₃ deformations.³⁹ The experiment also determined an out-of-plane deformation frequency of the CH bond at ≈ 375 cm⁻¹. However, Pacansky and Dupuis concluded that this frequency was associated with a higher energy conformation and that the lowest energy conformation frequency for this vibration was probably too low to be observed. This deformation frequency and the remaining skeletal frequencies were calculated by Pacansky and Dupuis.^{39,41} These directly calculated frequencies were in turn scaled (as recommended by Blom and Altona⁴²) by using a comparison of identically calculated frequencies for propane and its well-known experimentally determined values. The complete set of vibration frequencies for $i\text{-C}_3\text{H}_7$ used in our calculations is also given in Table II.

There are no direct experimental measurements or calculations of the structure or frequencies of the $i\text{-C}_3\text{H}_7\text{O}_2$ radical. However, there are measurements and calculations on CH₃O₂.^{43,44} These

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(39) Pacansky, J.; Dupuis, M. *J. Chem. Phys.* **1980**, *73*, 1867.

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(42) Blom, C., E.; Altona, C. *Mol. Phys.* **1976**, *31*, 1377.

(43) Snelson, A., IITRI, Chicago, IL 60616, private communication.

studies and others on related stable molecules provide information for making reasonable estimates of the structure and internal motions of the $i\text{-C}_3\text{H}_7\text{O}_2$ radical.

The structure of $i\text{-C}_3\text{H}_7\text{O}_2$ was obtained from the structure of CH_3O_2 calculated by Bair and Goddard⁴⁴ and from the measured structure of $\text{C}_2\text{H}_5\text{-O-CH}_3$.⁴⁵ The Bair and Goddard calculation sets the two angles and two bond lengths involving oxygen atoms in the C-C-O-O trans part of the heavy-atom skeleton. The structure of the $i\text{-C}_3\text{H}_7$ group was formed from that of the C_2H_5 group of ethyl methyl ether by replacing a hydrogen atom on the CH_2 part of C_2H_5 by a CH_3 group that is identical in structure with that on the end of the C_2H_5 moiety on the ether. The resulting structure is not symmetric and therefore has an external symmetry number of 1.

The movement of the radical center from the central carbon atom of $i\text{-C}_3\text{H}_7$ to the end oxygen atom of $i\text{-C}_3\text{H}_7\text{O}_2$ substantially increases the barrier to internal rotation of the CH_3 groups. This motion is described by a torsional frequency.

The barrier to rotation of the O_2 group about the CO bond is also fairly high and will similarly be characterized by a torsional frequency.⁴⁶ The height of this barrier is taken from an estimated barrier to a similar rotation in CH_3O_2 and from a scaling to $i\text{-C}_3\text{H}_7\text{O}_2$. The scaling is based on the measured barriers to OH rotation in CH_3OH ⁴⁷ and $i\text{-C}_3\text{H}_7\text{OH}$.⁴⁸ The rotational barrier about the CO bond in CH_3O_2 has not been measured. However, the orbital structure of the radical suggests that it should have a barrier similar to or slightly smaller than that of CH_3OF , which has been calculated to be 1.84 kcal/mol.⁴⁹ The UHF calculations used to determine this barrier were performed on a number of other rotational barriers that are known experimentally, and on the average the calculated barriers were 0.3 kcal/mol too high. Thus, a reasonable estimate for the barrier to this internal rotation in CH_3O_2 is 1.5 kcal/mol. The measured rotational barrier in CH_3OH is 1.07 kcal/mol,⁴⁷ and in $i\text{-C}_3\text{H}_7\text{OH}$ it is 1.68 kcal/mol.⁴⁸ Since the barriers to rotation of an O_2 and an OH group about the CO bond appear similar, we conclude that the O_2 rotational barrier in $i\text{-C}_3\text{H}_7\text{O}_2$ is 2.36 kcal/mol. The O_2 rotation causes the potential to pass through three minima, of which two are equivalent and of the lowest energy. However, the two lowest minima are physically distinct and thus $i\text{-C}_3\text{H}_7\text{O}_2$ has two rotomeric forms.

The vibration frequencies of the $i\text{-C}_3\text{H}_7\text{O}_2$ radical must be estimated. Again, scaling procedures were used.⁴⁶ All frequencies in $i\text{-C}_3\text{H}_7\text{O}_2$ are scaled from the known frequencies of isopentane.⁵⁰ The scaling factor for all vibrations except the torsional motion of the O_2 group is derived from a comparison of the partially determined frequencies of CH_3O_2 ⁴³ and the known frequencies of $\text{CH}_3\text{CH}_2\text{CH}_3$.⁵⁰ The torsion frequency of O_2 was obtained from scaling that of the C_2H_5 rotation in isopentane by the ratio of the square roots of the barriers to rotation in isopentane (measured) and that of $i\text{-C}_3\text{H}_7\text{O}_2$ (estimated, see above). The structural parameters of $i\text{-C}_3\text{H}_7\text{O}_2$, symmetry numbers, and the frequencies of this radical derived in this study are also presented in Table II.

The calculated entropies, heat capacities, and enthalpy functions of $i\text{-C}_3\text{H}_7$, O_2 , and $i\text{-C}_3\text{H}_7\text{O}_2$ and the changes in these variables in reaction 6 were calculated by using partition functions, including those for harmonic oscillators and free rotors and including the entropy of mixing for the rotomeric structures. The input data are in Table II, which includes information on O_2 taken from the JANAF tables.⁵¹ The computed value of $\Delta S^\circ(298)$ is -38.89

cal/(mol K). The correction factor for $\ln K_6$ in $F(T)$ can be seen to be small, less than 0.12 over the temperature range of this study.

The most important uncertainties in the models proposed for $i\text{-C}_3\text{H}_7$ and $i\text{-C}_3\text{H}_7\text{O}_2$ that affect the calculated entropy change of reaction 6 are the lowest frequencies of the internal motions. For the $i\text{-C}_3\text{H}_7$ radical these include the two internal rotations treated as free rotors and the very low frequency CH out-of-plane bend. For the potential energy and reduced moment of inertia listed in Table II for this motion, a hindered-rotor treatment of this internal rotation lowers $S^\circ(298)$ of $i\text{-C}_3\text{H}_7$ by less than 0.2 cal/(mol K). The CH bend frequency is derived from an empirically scaled calculation based on the propane frequencies. The experimental spectrum of $i\text{-C}_3\text{H}_7$ indirectly suggests that the frequency of this bend is more than 50 cm^{-1} lower than that scaled from the calculation by Pacansky and Dupuis.⁴⁰ Such a reduction in this frequency would increase the entropy by 0.4 cal/(mol K). We conclude that the calculated entropy of $i\text{-C}_3\text{H}_7$ is accurate to ± 0.5 cal/(mol K).

For $i\text{-C}_3\text{H}_7\text{O}_2$, the three lowest torsional frequencies used are all indirectly determined. Comparison of the calculated entropy of this radical with those of analogous stable molecules (suitably corrected²⁰) and with group-additivity estimates²⁰ suggests the $i\text{-C}_3\text{H}_7\text{O}_2$ entropy has an uncertainty of about 1.0 cal/(mol K).³⁸ The combined uncertainty in the estimated entropies of $i\text{-C}_3\text{H}_7$ and $i\text{-C}_3\text{H}_7\text{O}_2$ produce an estimated possible error in $\Delta S^\circ(298)$ for reaction 6 of ± 1.5 cal/(mol K).

II. Determination of $\Delta H^\circ(298)$ and $\Delta H^\circ(0)$ for Reaction 6.

Values of ΔH° for reaction 6 were determined from the measured equilibrium constants for this reaction and the calculated thermodynamic variables presented above.

Values of the variable $F(T)$ were calculated for each K_6 measured in this study by using the equation

$$F(T) = \ln K_6 + (\Delta H^\circ(T) - \Delta H^\circ(298))/RT - (\Delta S^\circ(T) - \Delta S^\circ(298))/R = \Delta S^\circ(298)/R - \Delta H^\circ(298)/RT \quad (\text{III})$$

(They are shown in the modified van't Hoff plot (Figure 1)). $\Delta H^\circ(298)$ for reaction 6 was obtained from the slope of the least-squares-fitted straight line that passes through these plotted values of $F(T)$ and which has an intercept $\Delta S^\circ(298)/R$ at $1/T = 0$ (not shown in Figure 1).¹⁴ $F(T)$ nearly equals $\ln K_6$. The "correction" to $\ln K_6$ in eq III is small at all temperatures (less than 2%).

The value of $\Delta H^\circ(298)$ for reaction 6 determined from this Third law procedure is

$$\Delta H^\circ(298) = -37.7 \pm 1.8 \text{ kcal/mol}$$

The intrinsic $i\text{-C}_3\text{H}_7\text{-O}_2$ bond strength, $\Delta H^\circ(0)$, was obtained from $\Delta H^\circ(298)$ and the calculated values of the enthalpy functions given in Table II. Its value is

$$\Delta H^\circ(0) = -36.4 \pm 1.8 \text{ kcal/mol}$$

The error estimates shown above take into account a possible cumulative 1.5 cal/(mol K) error in $\Delta S^\circ(298)$, the factor of 2 uncertainty in each of the 10 measurements of K_6 (each of which separately yields a value of ΔH°), and the estimated 4 °C uncertainty in the temperature of each experiment.

Discussion

I. Accuracy and Precision of the Experimental Method. This study is the first of a series of investigations that will be performed to characterize $\text{R} + \text{O}_2 \leftrightarrow \text{RO}_2$ equilibria. The free radical generation and detection procedures used here are sufficiently versatile to permit many studies of this type to be performed in the future. Therefore, additional special attention has been directed at establishing the precision and accuracy of our experimental method and the data reduction procedures through a reinvestigation of the $\text{C}_3\text{H}_5 + \text{O}_2 \leftrightarrow \text{C}_3\text{H}_5\text{O}_2$ equilibrium. The two recent studies of this equilibrium that were mentioned above were conducted in adjacent temperature ranges by using different experimental techniques.^{14,28} Both involved direct determinations

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Table III. Calculated Thermodynamic Functions Associated with the Equilibrium $i\text{-C}_3\text{H}_7 + \text{O}_2 \leftrightarrow i\text{-C}_3\text{H}_7\text{O}_2$ as a Function of Temperature^a

	temp in K =							
	298	400	500	600	700	1000	1500	
			O_2					
S°	48.98	51.07	52.69	54.06	55.25	58.13	61.56	
$H^\circ(T) - H^\circ(0)$	2.07	2.80	3.53	4.28	5.05	7.47	11.70	
C_p°	7.01	7.17	7.40	7.63	7.84	8.27	8.60	
			$i\text{-C}_3\text{H}_7$					
S°	70.05	75.38	80.32	85.02	89.50	101.68	118.36	
$H^\circ(T) - H^\circ(0)$	3.66	5.52	7.74	10.32	13.23	23.54	44.22	
C_p°	16.22	20.22	24.09	27.56	30.60	37.60	44.37	
			$i\text{-C}_3\text{H}_7\text{O}_2$					
S°	79.15	86.59	93.46	99.95	106.07	122.40	144.22	
$H^\circ(T) - H^\circ(0)$	4.42	7.02	10.10	13.67	17.65	31.45	58.50	
C_p°	22.57	28.24	33.40	37.83	41.58	49.82	57.44	
			$i\text{-C}_3\text{H}_7 + \text{O}_2 \leftrightarrow i\text{-C}_3\text{H}_7\text{O}_2$					
ΔS°	-39.87	-39.86	-39.55	-39.14	-38.69	-37.41	-35.69	
$\Delta(H^\circ(T) - H^\circ(0))$	-1.31	-1.30	-1.16	-0.93	-0.64	0.44	2.57	
ΔC_p°	-0.67	0.85	1.90	2.63	3.14	3.95	4.46	
$F(T) - \ln K_6$	0.00	0.00	-0.02	-0.06	-0.12	-0.36	-0.80	

^aThe units are cal/(mol K) (S° , C_p°) and kcal/mol (H°).

of the equilibrium constant from the results of time-resolved experiments. We have chosen to use the findings of these two investigations as a benchmark for assessing the accuracy and precision of our own procedures. Our study of this same equilibrium overlaps the temperature ranges of both of the earlier ones.

The results of this reinvestigation of reaction 4 which are given in Table I are also plotted on a van't Hoff plot in Figure 2 together with the earlier results of Bayes and Pilling.^{14,21} The correction to $\ln K_4$ on the ordinate variable of this plot is a simpler correction to yield $F(T)$ that presumes ΔC_p° for reaction 4 is independent of temperature. The correction again is a minor one, so this assumption results in no significant error in determining the thermodynamic variables. The value of ΔC_p° used (3.9 cal/(mol K)) was determined by group additivity procedures by Benson.¹³ (This same correction to $\ln K_4$ was used by Pilling et al. in the analysis of their data.¹⁴) The results of the three studies displayed in Figure 2 show the very close agreement between our measurements of K_4 and those obtained earlier. The differences between our determinations and those represented by the line in Figure 2 (which is the least-squares-fitted line through the combined measurements of K_4 of the two earlier studies) are all less than that calculated from the estimated $\pm 25\%$ maximum uncertainty in each of our measurements of K_4 .

Because of the greater accuracy of the K_4 determinations (compared to those for K_6), it was possible to obtain accurate values for both of the thermodynamic variables of reaction 4 ($\Delta H^\circ(298)$ and $\Delta S^\circ(298)$) from the results of this study. They were calculated from the slope and intercept of the straight line fitted through our data in Figure 2.¹⁴ The values obtained for these variables for reaction 4 from this Second law procedure are

$$\Delta H^\circ(298) = -18.0 \pm 0.9 \text{ kcal/mol}$$

and

$$\Delta S^\circ(298) = -29.1 \pm 2.5 \text{ cal/(mol K)}$$

The error limits are two standard deviations for these parameters of the straight line fit through the data. The lower error limits, compared to those obtained for the thermodynamic parameters of the $i\text{-C}_3\text{H}_7 + \text{O}_2 \leftrightarrow i\text{-C}_3\text{H}_7\text{O}_2$ in this study, reflect the greater precision of these experiments caused by significantly greater detection sensitivity for the allyl radical.

The same thermodynamic variables obtained in a similar fashion from the combined results of the two earlier investigations of Bayes and Pilling are¹⁴

$$\Delta H^\circ(298) = -18.2 \pm 0.5 \text{ kcal/mol}$$

and

$$\Delta S^\circ(298) = -29.2 \pm 1.2 \text{ cal/(mol K)}$$

Analyses conducted using Third law entropies of C_3H_5 and $\text{C}_3\text{H}_5\text{O}_2$ yielded very similar results.¹⁴

The close agreement of the magnitudes of our measured equilibrium constants for reaction 4 with those obtained in the two earlier studies indicates the high precision of these kinds of direct determinations. It was possible in our investigation to also obtain accurate values for the important thermodynamic variables of this reaction directly from the temperature dependence of the equilibrium constant in spite of its rather limited temperature range. These results taken together indicate that the accuracy and precision of our experimental procedure is primarily limited by the statistical uncertainties associated with the detection sensitivity to the hydrocarbon free radical under study. This was the conclusion reached in the prior section.

In summary, it appears that the criteria we have chosen to select our experimental conditions yield determinations of equilibrium constants that are free of systematic error, and our assessments of the accuracies of our procedures and results are correct.

II. Comparison of $\Delta H^\circ(298)$ for $i\text{-C}_3\text{H}_7 + \text{O}_2 \leftrightarrow i\text{-C}_3\text{H}_7\text{O}_2$ with Thermochemical Estimates. Our measured enthalpy change at 298 K for reaction 6 (-37.7 kcal/mol) is significantly lower than that derivable from group additivities (-30.7 kcal/mol).^{20,22,52} The difference is outside the limits of accuracy claimed for the additivity procedure. A high estimate from group additivity calculations could result from either an underestimate of the heat of formation of the isopropyl radical (calculated to be 18.6 kcal/mol^{20,52}) or an overestimate of the heat of formation of the $i\text{-C}_3\text{H}_7\text{O}_2$ radical. There are indications that both may be the case. Several studies have obtained higher heats of formation for alkyl radicals (typically 2-3 kcal/mol) than those from which group contributions to heats of formation of these intermediates are derived. This disparity, which is tied to the type of experiment performed to obtain the heats of formations, has been discussed in detail recently by Tsang as well as by McMillan and Golden.^{23,24} Its cause is still undetermined.

The "no next nearest neighbor contribution" to bond energies assumed by the principle of group additivities leads to the conclusion that all R-O₂ bond strengths are essentially the same ($\Delta H^\circ(298) \approx -30.7$ kcal/mol for reaction 1, independent of the identity of R). This principle may be in error when applied to RO₂ compounds to determine R-O₂ bond strengths. Melius and Binkley have developed a new quantum chemical method (BAC-MP4) to calculate accurate heats of formation for H, C, N, and O containing species.^{53,54} The method involves the use

(52) Benson, S. W., private communication.

(53) Melius, C. F., Sandia National Laboratory, Livermore, CA 94550, private communication.

(54) Melius, C. F.; Binkley, J. S. *Symp. (Int.) Combust. [Proc.]*, in press.

of Hartree-Fock theory with a split-valence plus polarization basis set to determine the equilibrium geometry and zero-point vibrational energy of a given molecule or radical. With use of the geometry determined at the Hartree-Fock level, the total energy is determined with fourth-order Møller-Plesset perturbation theory (MP4). Bond additivity corrections (BAC) are added to the theoretically calculated energies. The resulting heats of formation have been demonstrated to be accurate to within 3 kcal/mol.⁵⁴ Relative energies in a homologous series would have greater accuracy.

These calculations have confirmed some of the important assumptions used in applying group additivity concepts, but they have also revealed differences that are not in agreement with the additivity principle.⁵³ For example, Melius has found that ROO-H bond energies are the same for different R groups, a result predicted by the no-next-nearest-neighbor assumption of group additivity. For R = H, CH₃, and OH, the ROO-H calculated bond strengths differ by about 1 kcal/mol.⁵³ However, R-O₂ bond strengths in alkyl peroxy radicals were found to increase significantly with increasing complexity of the R group. The C₂H₅-O₂ bond energy was determined to be 3.3 kcal/mol greater than that of the CH₃-O₂ bond, and the *i*-C₃H₇-O₂ bond was estimated to be an additional 1.7 kcal/mol stronger than the C₂H₅-O₂ bond based on analogous trends found for R-OH bonds for the same R groups. This trend is not predicted by group additivity concepts. The intrinsic R-O₂ bond strengths calculated by Melius ($\Delta H^\circ(0)$) are about 4 kcal/mol lower than measured values: 26.3 kcal/mol for CH₃-O₂ vs. 30.7 from experiment,²⁹ and 31.3 kcal/mol (extrapolated) for *i*-C₃H₇-O₂ vs. 36.4 measured in the current study. Because of this disagreement, it is uncertain whether the heat of formation of *i*-C₃H₇O₂ predicted by group

additivities is actually an overestimate, but it is likely that group methods lead to significant inaccuracies when applied to RO₂ radicals.

This study has yielded the first direct determination of the enthalpy change associated with an alkyl radical-oxygen equilibrium, and hence it provides the most exacting test to date of group additivity methods for predicting the energy changes associated with reactions in this class. Future studies on additional equilibria involving other alkyl radicals and oxygen should help to establish more clearly the source or sources of the small but notable disagreement between experiment and estimation.

III. The Stability of *i*-C₃H₇O₂ and Combustion Modeling. The stability of RO₂ radicals in combustion systems is often characterized by a "ceiling temperature".¹³ It is that temperature at which the equilibrium constant for reaction 1 predicts that the ratio of pressures $P(R)/P(RO_2) = 1$ for the oxygen pressure in the reacting system. It is a useful parameter for estimating the dividing temperature between low- and high-temperature combustion mechanisms. The results of this study indicate that the *i*-C₃H₇O₂ is more stable towards dissociation than was predicted previously. The ceiling temperature for the *i*-C₃H₇ + O₂ \leftrightarrow *i*-C₃H₇O₂ equilibrium calculated by using the results of this study is 40 °C higher than earlier estimates.

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Electrocatalysis of Proton-Coupled Electron-Transfer Reactions at Glassy Carbon Electrodes

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Abstract: The activation of glassy carbon electrodes toward electron-transfer pathways involving proton-coupled electron transfer has been investigated. Oxidative activation of glassy carbon electrodes leads to the catalysis of heterogeneous charge transfer for couples involving catechol (1,2-dihydroxybenzene), (bpy)₂(H₂O)Ru(OH)²⁺ (bpy is 2,2'-bipyridine), and (NH₃)₅Ru(OH)²⁺ where there are changes in proton content upon oxidation. X-ray photoelectron spectroscopy has been used to determine the changes induced at the electrode surface by the activation procedure. Comparison of the spectral and electrochemical results with earlier studies on related homogeneous proton-coupled electron-transfer reactions suggests that, although a number of effects may be operative, an important basis for electrode activation may be the appearance of phenolic-like groups on the glassy carbon surface and their subsequent involvement in proton-coupled electron transfer.

Electrochemical investigations using solid electrodes are frequently complicated by effects arising from the nature of the electrode surface. This is particularly true of carbon electrodes, where a variety of different materials are available¹ which are quite sensitive to chemical and electrochemical pretreatment procedures.² In fact, the possibility of the deliberate modification of *vitreous* (glassy) carbon or carbon paste electrodes via chemical^{3,4} or electrochemical⁵⁻⁷ activation has been investigated.

Our interest in possible surface activation effects at carbon electrodes arose from the fact that the interconversion of redox

couples like (bpy)₂(H₂O)Ru^{IV}(O)²⁺/(bpy)₂(H₂O)Ru^{III}(OH)²⁺ or H₂O₂/HO₂ is slow at electrode surfaces, and the heterogeneous charge-transfer characteristics depend upon the electrode material,

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