

Kinetics of Polyatomic Free Radicals Produced by Laser Photolysis. 5. Study of the Equilibrium $\text{CH}_3 + \text{O}_2 \rightleftharpoons \text{CH}_3\text{O}_2$ between 421 and 538 °C

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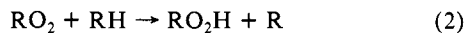
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Abstract: The gas-phase equilibrium involving the reaction of methyl radicals with molecular oxygen to form methylperoxy radicals has been studied at seven temperatures between 421 and 538 °C. The CH_3 radicals were generated homogeneously in a tubular reactor by the pulsed 248-nm photolysis of CH_3I . The relaxation of the CH_3 radicals to equilibrium in the presence of O_2 was monitored in real-time experiments using photoionization mass spectrometry. The experiments yielded at least one value of the equilibrium constant at each temperature. The enthalpy change for the reaction $\text{CH}_3 + \text{O}_2 \rightleftharpoons \text{CH}_3\text{O}_2$ was obtained from the measured equilibrium constants using both Second and Third Law methods. Both procedures yielded essentially the same result, the latter being more accurate; $\Delta H^\circ_{298} = -30.9 \pm 2.5$ kcal mol⁻¹ was obtained from the Second Law analysis and $\Delta H^\circ_{298} = -32.4 \pm 0.7$ kcal mol⁻¹ using the Third Law procedure. The intrinsic $\text{CH}_3\text{-O}_2$ bond strength of 30.9 ± 0.8 kcal mol⁻¹ ($-\Delta H^\circ_0$ for the title reaction) was determined using the measured enthalpy changes at 298 K and calculated relative enthalpy functions. This study provides the most direct determination of the enthalpy change associated with the simplest $\text{R} + \text{O}_2 \rightleftharpoons \text{RO}_2$ equilibrium that involves an alkyl free radical. The results are in substantial agreement with prior less direct determinations and with thermochemical estimates.

The reactions of hydrocarbon free radicals (R) with molecular oxygen are important elementary steps in most gaseous oxidation processes including the burning of fossil fuels,¹⁻⁶ the formation of tropospheric smog,⁷⁻⁹ and the chemistry of the stratosphere.¹⁰⁻¹² Up to 300 °C (at modest oxygen pressures) these reactions proceed primarily by a reversible addition process:^{1-6,13,14}



The peroxy radicals thus formed abstract hydrogen atoms from fuel molecules with relatively weak C-H bonds, forming alkyl hydroperoxides and regenerating a chain carrier:



The principal products of the early stages of low-temperature combustion ($T < 300$ °C) are these hydroperoxides and other oxygen-containing products (such as aldehydes and ketones) that result from their further reactions.¹⁻⁵

Between 300 and 450 °C the reversible nature of reaction 1 causes a major change in the oxidation mechanism of hydro-

carbons. The increasing importance of the dissociation of RO_2 (back to R and O_2) as temperature increases lowers the concentration of RO_2 . The resulting decrease in the importance of RO_2 as a chain carrier at higher temperatures is responsible for important changes that appear in the properties of gaseous hydrocarbon oxidations in this temperature range including a decrease in the maximum rate of oxidation with increasing temperature near 350 °C and a change in the nature of the stable products that are produced from oxygen-containing compounds to olefins.^{2,3,13,14} These new products result from the increasing importance of additional reaction pathways of $\text{R} + \text{O}_2$ reactions as temperature increases, routes that can be expressed as the overall process



Because of the importance of reaction 1 in the oxidation of all hydrocarbons at lower temperatures, we are studying a series of these reactions under the conditions where their equilibria can be directly observed and measurements made to obtain equilibrium constants as a function of temperature. These results yield the thermodynamic variables for these reactions (ΔH° and, in favorable cases, ΔS°) that are needed to accurately portray the role of reaction 1 in quantitative kinetic models of gaseous oxidation processes.^{13,14} The first of these investigations was reported in part 4.¹⁵

Today essentially all our knowledge of the thermochemistry of reaction 1 is obtained by estimation, principally using the concept of group additivity, introduced by Benson and Buss in 1958¹⁶ and subsequently refined by Benson and others.¹⁷⁻²⁰ The group additivity concept and the group contribution tables for thermodynamic variables are widely used in many branches of chemistry to obtain values of the thermodynamic functions of

(1) Minkoff, G. J.; Tipper, C. F. H. "Chemistry of Combustion Reactions"; Butterworths: London, 1962.

(2) Pollard, R. T. In "Comprehensive Chemical Kinetics"; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: New York, 1977; Vol. 17, Chapter 2.

(3) Baldwin, R. R.; Bennett, J. P.; Walker, R. W. *Symp. (Int.) Combust. [Proc.]* 1977, 16, 1041-1051.

(4) Fish, A. *Angew. Chem., Int. Ed. Engl.* 1968, 7, 45-60.

(5) McKay, G. *Prog. Energy Combust. Sci.* 1977, 3, 105-126.

(6) Benson, S. W.; Nangia, P. S. *Acc. Chem. Res.* 1979, 12, 223-228.

(7) Seinfeld, J. H.; Reynolds, L. D.; Roth, P. M. *Adv. Chem. Ser.* 1972, No. 113, 58.

(8) Carter, W. P. L.; Lloyd, A. C.; Sprung, J. L.; Pitts, J. N. *Int. J. Chem. Kinet.* 1979, 11, 45-101.

(9) Graedel, T. E.; Farrow, L. A.; Weber, T. A. *Atm. Environ.* 1976, 10, 1095.

(10) Heicklen, J. "Atmospheric Chemistry"; Academic Press: New York, 1976.

(11) McEwan, M. J. "Chemistry of the Atmosphere"; Arnold: London, 1975.

(12) DeMore, W. B.; Molina, M. J.; Watson, R. T.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R. "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation Number 6"; Jet Propulsion Laboratory Publication 83-62; Pasadena, CA, 1982.

(13) Knox, J. H. *Combust. Flame* 1965, 9, 297-310.

(14) Benson, S. W. *J. Am. Chem. Soc.* 1965, 87, 972-979.

(15) Slagle, I. R.; Ratajczak, E.; Heaven, M. C.; Gutman, D.; Wagner, A. F. *J. Am. Chem. Soc.* 1985, 107, 1838-45.

(16) Benson, S. W.; Buss, J. H. *J. Chem. Phys.* 1958, 29, 546.

(17) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* 1969, 69, 279.

(18) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(19) Benson, S. W.; Shaw, R. In "Organic Peroxides"; Swern, D., Ed.; Wiley-Interscience: New York, 1970; Vol. 1, Chapter 2.

(20) Baldwin, A. C. In "The Chemistry of Functional Groups, Peroxides"; Patai, S., Ed.; Wiley: New York, 1983; Chapter 3.

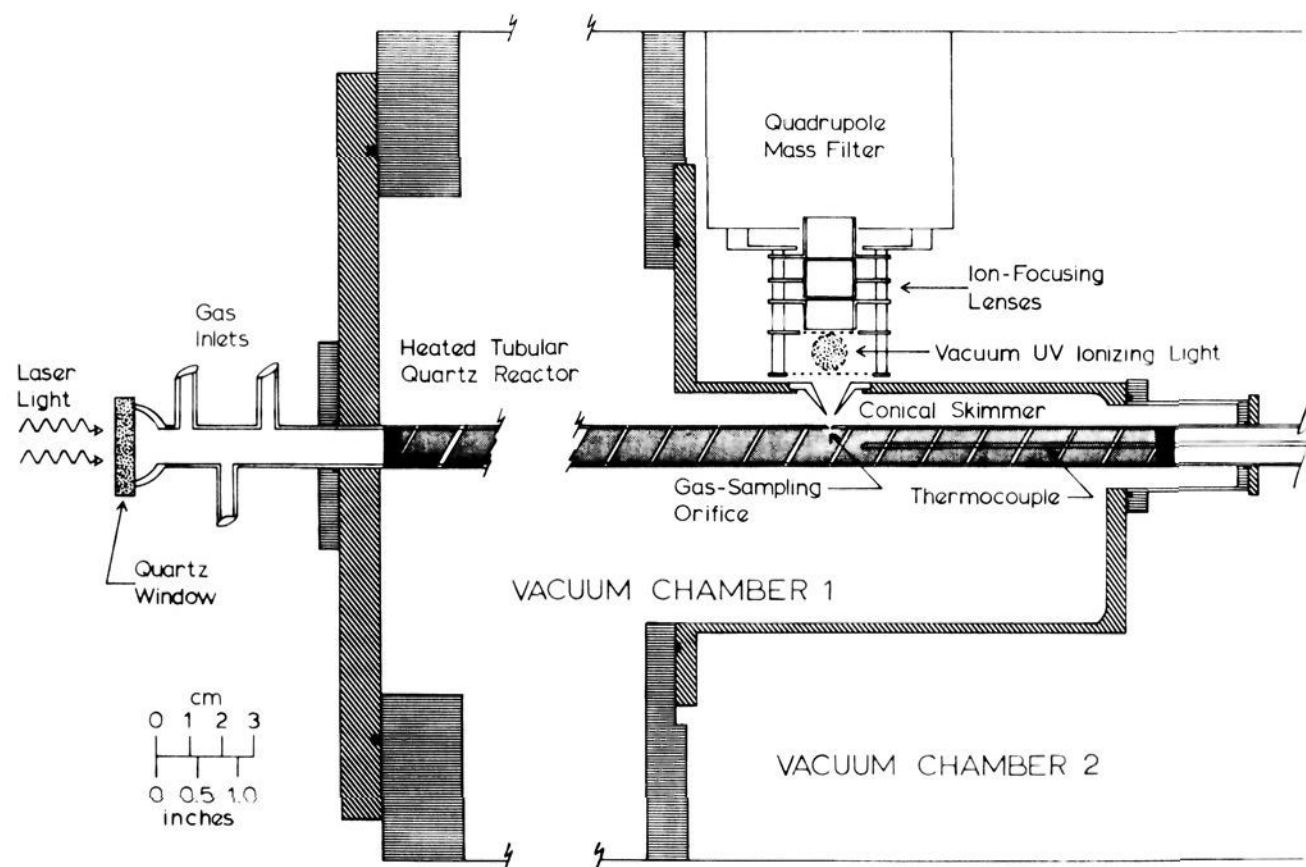


Figure 1. Drawing of experimental apparatus.

molecules, of free radicals, and of the reactions in which they participate whenever this information is not available from actual experiments.¹⁸

In part 4 we reported the direct measurement of the equilibrium constant for the reaction

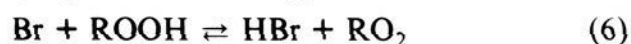


between 319 and 419 °C. The value of ΔH°_{298} obtained in this study (-37.7 ± 1.8 kcal mol⁻¹) is 7 kcal mol⁻¹ lower than that obtained by a group additivity calculation. This disparity is markedly greater than that expected from the suggested accuracy of the group additivity method.²¹ In this same study, we also measured the temperature dependence of the equilibrium constant for the reaction



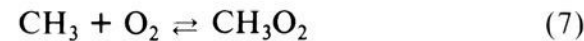
In this case the values of ΔH°_{298} and ΔS°_{298} obtained from the results of the experiments are in accord with those derived from group additivity estimates. Reaction 5 is the only gaseous equilibrium involving R and O₂ that has been isolated for direct quantitative investigation by other groups. In complementary studies, Bayes and co-workers and Pilling et al. have both measured the equilibrium constant of reaction 5.^{22,23} Our measured values of K_5 and the values for ΔH°_{298} and ΔS°_{298} that were derived from these measurements agree very closely with those obtained in these two earlier investigations.¹⁵

Other less direct studies have been performed that have yielded information on the thermochemistry of reaction 1. They have generally produced results that are very close to those predicted using group additivity calculations. Benson and co-workers are currently studying equilibria of the type



using the very-low-pressure reactor technique.^{24,25} The equilibrium constants measured in their studies to date have resulted in a determination of the heat of formation of *t*-C₄H₉O₂²⁴ and an upper limit for that of the CH₃O₂ radical,²⁵ both of which are in accord

with thermochemical estimates based on group contributions. These studies require estimates of the thermochemistry of ROOH to obtain the thermochemistry of RO₂. Khachatryan et al. have studied the equilibrium



by an indirect method that involved CH₃O₂ trapping on cold matrices and their quantitative analysis by ESR as well as measurements of C₂H₆ production rates to infer CH₃ concentrations.²⁶ They obtained a heat of formation of the CH₃O₂ radical at 298 K (-32.2 ± 1.5) that is within 1 kcal of the estimated value.

We have now completed a study of reaction 7 between 421 and 538 °C. Equilibrium constants were measured at seven temperatures in this range. The experiments have yielded the most direct determination of the enthalpy change for this reaction to date. This particular equilibrium is one of the most important in its class. Reaction 7 is a significant elementary reaction in the oxidation of many hydrocarbons.¹⁻⁶ Its thermochemistry is one of the benchmarks for assessing the accuracy of group additivity concepts and is also used in the determination of the group contribution O-[(O)(C)] for calculating the heats of formation of other alkylperoxy radicals.²⁰ The thermochemistry of CH₃O₂ is also of current interest to theoretical chemists who are now studying the structure and bonding of alkylperoxy radicals using ab initio methods.²⁷⁻²⁹ The results of our study of reaction 7 are reported here. The disparity between the measured enthalpy change for reaction 4 reported in part 4 and that estimated for this reaction using group additivity concepts is discussed in the context of the current results.

Experimental Section

The experimental apparatus and most of the procedures used were essentially the same as those described in parts 1-4.^{15,30-32} Unfocused pulsed 248-nm radiation from a Lambda Physik EMG 101E excimer laser was directed along the axis of a 51-cm-long, 1.05-cm i.d. tubular quartz reactor. Gas flowing through the tube contained the free-radical source at low concentration ($\approx 0.03\%$ CH₃I), O₂ (in varying amounts

(21) The claimed uncertainty of the group additivity calculation is near ± 3 kcal mol⁻¹ (concluded from comments made in ref 19 and 20).

(22) Morgan, C. A.; Pilling, M. J.; Tulloch, J. M.; Ruiz, R. P.; Bayes, K. D. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 1323-1330.

(23) Ruiz, R. P.; Bayes, K. D.; Macpherson, M. T.; Pilling, M. J. *J. Phys. Chem.* **1981**, *85*, 1622-1624.

(24) Heneghan, S. P.; Benson, S. W. *Int. J. Chem. Kinet.* **1983**, *15*, 815-822.

(25) Kondo, O.; Benson, S. W. *J. Phys. Chem.* **1984**, *88*, 6675-6680.

(26) Khachatryan, L. A.; Niazyan, O. M.; Mantashyan, A. A.; Vedenev, V. I.; Teitel'boim, M. A. *Int. J. Chem. Kinet.* **1982**, *14*, 1231-1241.

(27) Bair, R. A.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 2719.

(28) Wagner, A.; Melius, C. F., manuscript in preparation.

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

(30) Slagle, I. R.; Yamada, F.; Gutman, D. *J. Am. Chem. Soc.* **1981**, *103*, 149-153.

(31) Slagle, I. R.; Gutman, D. *J. Am. Chem. Soc.* **1982**, *104*, 4741-4748.

(32) Slagle, I. R.; Park, J.-Y.; Heaven, M. C.; Gutman, D. *J. Am. Chem. Soc.* **1984**, *106*, 4356-4361.

from 20 to 90% of the total flow), and N₂ (which provided the required balance). 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 4 Hz and at a fluence of ≈ 70 mJ/cm². The gas mixture flowed through the reactor at 3 m/s in order to replace the photolyzed gas with a fresh reactant gas mixture between laser pulses.

Gas was continuously sampled through a 0.044-cm-diameter hole in the side of the reactor. The emerging flow 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 photoionized (using an atomic resonance lamp) and then mass selected.

The detection sensitivity was improved by moving the tubular reactor and skimmer to new positions that results in the gas beam being coaxial with the quadrupole mass spectrometer instead of perpendicular to it. In the new arrangement (which is shown in Figure 1) the distance between the sampling orifice in the reactor wall and the center of the ionizing region in the ion source of the mass spectrometer is maintained at 2.4 cm. The detector sensitivity improved between a factor of 5 and 10 over that of the prior sampling and detection configuration. No changes in any of the other performance features of the apparatus have been observed. This increase in the sensitivity has improved the quality, and hence the accuracy of the data, significantly and has also made it possible to quantitatively study complex processes involving free radicals that have lower photoionization cross sections (like reaction 7).

Temporal ion signal profiles of reactants, possible products, and the free-radical precursor were recorded with a Tracor Northern 570A multichannel scalar from a period just before each laser pulse to 10–40 ms following the pulse. Typically data from 20 000 to 50 000 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 (CH₃, CH₃I, CH₃O₂) and 11.6 eV (CH₂ and CH₃O₂).

The tubular reactor is heated by a 1-cm-wide nichrome ribbon tightly wrapped around it in a spiral that extends from 22 cm upstream to 15 cm downstream from the sampling orifice. The temperature during an actual experiment is monitored by a thin, sheathed (¹/₁₆-in. o.d.), in situ thermocouple. The uniformity of the temperature in the heated zone of the reactor which is sampled during an experiment is ± 3 °C. The tubular reactor is periodically cleaned with a 5% NH₄F·HF solution and was used uncoated.

CH₃I (99%, Aldrich Chemical Co.) was purified by fractional distillation. O₂ (Extra Dry) and N₂ (Prepurified) were obtained from Linde and used without extra purification.

Results

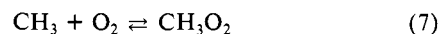
I. 248-nm Photolysis of CH₃I. It was not possible in these experiments to use the available 193-nm laser radiation for the production of CH₃ radicals because radiation at this wavelength is absorbed to a significant extent by the temperature-shifted Schumann–Runge band of O₂ in the higher temperature range and at the higher O₂ densities that were required for these experiments (compared with those used in part 4). CH₃I was chosen as the CH₃-radical precursor because its photolysis with the unfocused laser radiation at 248 nm provided an adequate yield of CH₃ radicals for these experiments ($\approx 1\%$ of the CH₃I decomposed during each laser pulse), and the photolysis did not produce any measurable additional products other than CH₃ and I (CH₂ was not produced in detectable amounts). The CH₃I concentrations used in these experiments were chosen to provide initial CH₃ concentrations near 2.5×10^{11} radicals cm⁻³. At this low initial concentration, possible recombination processes (particularly CH₃ + CH₃) have negligible rates compared with that of the CH₃ + O₂ reaction at the gas densities and temperatures used in these experiments.

II. Measurement of the Equilibrium Constant of Reaction 7.

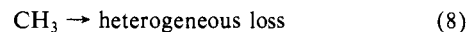
The equilibrium in reaction 7 was clearly observable between 421 and 538 °C at the O₂ densities that had to be used in these studies ($< 8 \times 10^{16}$ molecules cm⁻³). This reaction is essentially at the low-pressure limit under our experimental conditions. Since the total gas density in the flow reactor must be kept below $\approx 10^{17}$ molecules cm⁻³ to limit the flow rate through the sampling orifice, high O₂ mole fractions were required to observe equilibrium during the available testing time (10–40 ms). The upper temperature limit was imposed by the inability to increase the O₂ density any further to establish an observable equilibrium. The lower limit

was caused by an inability to continue to observe the reaction reaching equilibrium during the available testing time. As the temperature of an experiment is reduced, the O₂ concentration must also be lowered in order to continue to observe the equilibrium.

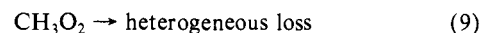
The equilibrium constant for reaction 7 was obtained from the recorded CH₃⁺ ion-signal profiles. From the results of prior investigations of this reaction,^{26,33–38} and from additional observations made during this study, we conclude that the only reactions that occurred during these experiments are



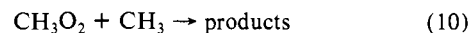
and



The possible additional wall-loss process



did not occur at a significant rate in these experiments. Some experiments were conducted using an excess of O₂ to convert CH₃ to CH₃O₂ in a time that was short compared with the total available testing time. The CH₃O₂ ion signal profile in these tests was essentially flat after the brief period during which this radical was being formed indicating a negligible wall-loss rate during the following 10–40 ms. Also the rates of radical–radical processes, such as the reaction



have negligible rates compared with those involving a single intermediate (CH₃ or CH₃O₂). This was expected as a result of the low initial CH₃ concentrations used in these experiments and was confirmed by the fact that the shape of the ion-signal profiles and the measured equilibrium constants were independent of both the initial O₂ and CH₃ concentrations (see below).

In the presence of an excess of O₂, the CH₃ concentration profile (and hence that of the CH₃⁺ ion signal, $I(\text{CH}_3^+)$), is given by the sum of two exponential terms:^{39,40}

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

Temporal CH₃⁺ ion-signal profiles were fitted to eq I to obtain A , B , m_1 , m_2 using standard nonlinear least-squares procedures, and these parameters (together with the measured O₂ pressure in the tubular reactor during the experiment) were used to calculate K_p for reaction 7.¹⁵ In some of these same experiments CH₃O₂⁺ profiles were also recorded. Although the temporal behavior of this product ion signal was that expected from the above mechanism, it was not possible to analyze these data in detail because of their poorer quality (caused by the very low detection sensitivity for detecting peroxy radicals^{15,33,35}). At three temperatures near the middle of the temperature range studied, measurements of the equilibrium constant were made using different oxygen pressures that were a factor of 2 apart. In all experiments (except one) the total gas density was 8.0×10^{16} molecules cm⁻³. At 479 °C, an additional experiment was performed, at half the usual total density. The equilibrium constants obtained from these experiments are independent of both O₂ pressure and total gas density as expected.

The following criteria were used to assure the accuracy of the equilibrium constants obtained from the data.¹⁵ An experiment was acceptable only if equilibrium was clearly observable ($0.2 < A/B < 5$ and $m_1 > 5m_2$) and the derived value of K_p was re-

(33) Selzer, E. A.; Bayes, K. D. *J. Phys. Chem.* **1983**, *87*, 392–394.

(34) Washida, N. *J. Chem. Phys.* **1980**, *73*, 1665–1672.

(35) Plumb, I. C.; Ryan, K. R. *Int. J. Chem. Kinet.* **1982**, *14*, 861–874.

(36) Pratt, G. L.; Wood, S. W. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 3419–3427.

(37) Baldwin, A. C.; Golden, D. M. *Chem. Phys. Lett.* **1978**, *55*, 350–352.

(38) Klais, O.; Anderson, P. C.; Laufer, A. H.; Kurylo, M. J. *Chem. Phys. Lett.* **1979**, *66*, 598–601.

(39) Capellos, C.; Bielski, B. H. "Kinetic Systems"; Wiley-Interscience: New York, 1972.

(40) Moore, J. W.; Pearson, R. G. "Kinetics and Mechanism", 3rd ed.; Wiley: New York, 1981; Chapter 8.

Table I. Conditions and Results of Experiments To Measure the Equilibrium Constant for the Reaction CH₃ + O₂ ↔ CH₃O₂

<i>T</i> (K)	O ₂ pressure × 10 ³ (atm)	<i>k_w</i> (s ⁻¹)	<i>m</i> ₁ (s ⁻¹)	<i>m</i> ₂ (s ⁻¹)	<i>A/B</i>	<i>K_p</i> (atm ⁻¹)	ln (<i>K_p</i>) + <i>f</i> ^a
694	1.72	9.1	131	6.4	4.28	1540	7.59
713 ^b	1.83	10.0	134	4.5	2.90	1230	7.38
731	4.09	14.2	255	13.3	3.50	550	6.59
732	1.65	14.2	150	17.9	1.65	541	6.57
752 ^c	3.21	11.0	134	12.7	1.44	285	5.94
755	5.98	13.9	368	22.0	2.47	277	5.92
755	2.82	13.9	219	21.6	1.26	288	5.96
772	7.32	12.4	423	16.8	1.70	188	5.55
772	3.53	12.4	291	19.1	0.86	190	5.56
791	7.88	9.3	473	16.3	1.11	122	5.12
811	8.05	9.3	434	17.5	0.51	55.5	4.35

^aln (*K_p*) + *f* is the ordinate variable in Figures 2 and 3. ^bData from this experiment shown in the insert in Figure 2. ^cIn this experiment [M] = 4.0 × 10¹⁶ molecules cm⁻³. In all other experiments, [M] = 8.0 × 10¹⁶ molecules cm⁻³.

producible (and presumed accurate) to ±25% or better. (This required the standard relative errors of both *A* and *B* to be less than 10% each.) The rate constant for the "wall reaction", *k₈*, was also measured at each temperature before O₂ was introduced into the system. It was always low, typically less than 15 s⁻¹. When *m*₁ ≫ *m*₂, *K₇* is nearly equal to *A*/[BP(O₂)] and *m*₂ ≈ *k₈* (*P*(O₂) is the oxygen partial pressure during the experiment). The observed closeness of *m*₂ and *k₈* under the experimental conditions used in this study is further confirmation that CH₃O₂ was lost only by dissociation back to CH₃ and O₂. The results obtained in this investigation are given in Table I.

III. Determination of Thermochemical Parameters of Reaction 7.

ΔH° for reaction 7 was determined from the results of this study using both Second and Third Law methods. The two procedures yielded essentially the same result, the latter being the more accurate. For the Second Law calculation, the measured equilibrium constants were plotted on a modified van't Hoff plot. ΔH°_{298} and ΔS°_{298} for reaction 7 were obtained from the slope and intercept, respectively, of the straight line fitted to the data by a linear least-squares procedure (see Figure 2). They are $\Delta H^\circ_{298} = -30.9 \pm 2.5$ kcal mol⁻¹, and $\Delta S^\circ_{298} = -29.1 \pm 3.5$ cal mol⁻¹ K⁻¹.

The ordinate variable on the modified van't Hoff plot has been discussed by others^{22,41} and also by us.¹⁵ The "correction" to ln *K_p* is an adjustment for the change in ΔH° and ΔS° between 298 K and the temperature of the experiment. It converts the ordinate variable from $-\Delta G^\circ_T/RT$ to $-\Delta G^\circ_{298}/RT$. The relative enthalpy and also the entropy functions for CH₃ and CH₃O₂ needed to calculate this correction were obtained from the study of Wagner and Melius, who have recently calculated these thermodynamic functions from the currently available knowledge of the structure and internal motions of these two radicals.²⁸ The adjustment to ln *K₇* in the ordinate variable of the van't Hoff plot is small (3–8%). The very low uncertainties that exist in the values of these calculated functions contribute no significant additional uncertainties to the values of ΔH°_{298} and ΔS°_{298} derived from the van't Hoff plot. The error limits of ΔH°_{298} and ΔS°_{298} given above take into account the uncertainties of the determinations of *K₇*, which are not uniform (they are lowest at the center of the temperature range covered and largest at its extremes owing to the wider range of conditions that could be studied near the median temperature), the ±5 °C uncertainty in the temperature of each experiment (which could include a systematic contribution), and the small uncertainty in the pressure of O₂ during an experiment (estimated to be <±3%).

This Second Law analysis of the equilibrium data does not provide determinations of ΔH° and ΔS° that are as accurate as those obtained from a Third Law analysis (see below) because ΔS° for reaction 7 can be calculated more accurately than it could be determined in this study from the ordinate intercept on the van't Hoff plot (at 1/*T* = 0), which must be obtained by a long

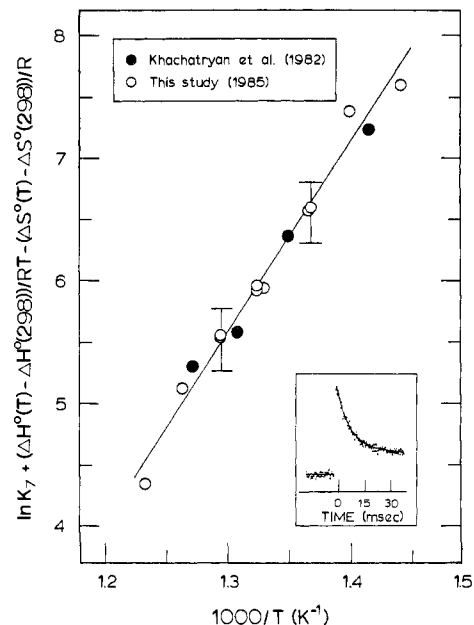


Figure 2. Modified van't Hoff plot of the measured equilibrium constants for the reaction CH₃ + O₂ = CH₃O₂ used to determine ΔH°_{298} for the title reaction by the Second Law procedure (see text for the significance of the ordinate variable). The vertical bars are representative error limits of the ordinate variable. The connected horizontal bars represent the ±5 °C uncertainty in the temperature of each experiment. The straight line through the data was obtained by a least-squares fit through the plotted data. Its slope is $-\Delta H^\circ_{298}/R$ for the title reaction (see text). The insert shows the data from one of the experiments (the conditions of this experiment are given in Table I). The closed circles are from the measured values of *K₇* in ref 26.

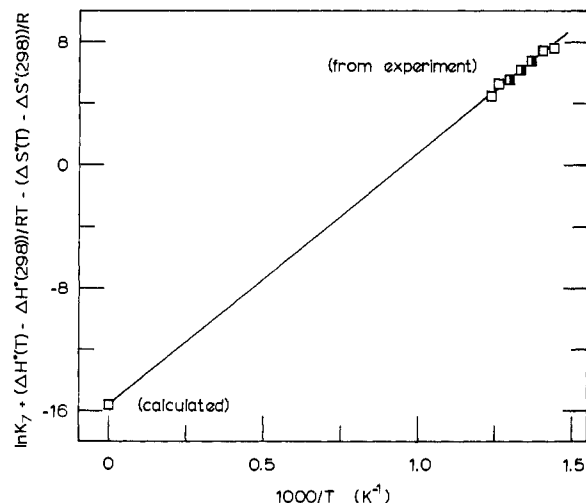


Figure 3. Modified van't Hoff plot of the measured equilibrium constants for the equilibrium CH₃ + O₂ = CH₃O₂ used to determine ΔH°_{298} for the title reaction by the Third Law procedure. The shaded squares represent more than one plotted point. The sizes of the symbols used in the figure are larger than the vertical and horizontal error limits of the plotted points. The straight line through the data, whose slope yields ΔH°_{298} for the title reaction, was obtained by a least-squares fit through the experimentally determined data points and the calculated intercept at 1/*T* = 0 (see text).

extension of the straight line through the data. Nevertheless, the values of ΔH°_{298} and ΔS°_{298} given above are in very good agreement with those determined by the more accurate analysis described below when the wider error limits of the results of the Second Law analysis are taken into account.

The Third Law determination of ΔH°_{298} for reaction 7 was obtained using the measured equilibrium constants and the calculated entropy and relative enthalpy functions of CH₃ and CH₃O₂ calculated by Wagner and Melius.²⁸ ΔH°_{298} was obtained from

the slope of the straight line fitted through the data plotted on a modified van't Hoff plot which has an intercept (at $1/T = 0$) of $\Delta S^\circ_{298} = -31.05^{+0.5}_{-0.2}$ cal mol⁻¹ K⁻¹ (see Figure 3).²⁸ It is $\Delta H^\circ_{298} = -32.4 \pm 0.7$ kcal mol⁻¹.

The uncertainty in this determination of ΔH°_{298} was obtained from those of the experimental quantities discussed above and from those of the calculated thermodynamic variables of Wagner and Melius used to calculate the ordinate variable and the intercept.²⁸ The accuracy of the calculated intercept is due to the large body of existing knowledge of the structure and internal motions of CH₃ and CH₃O₂. Most of the estimated small uncertainty in ΔS°_{298} is due to the lack of direct knowledge of the barrier height for the internal rotation in CH₃O₂, which is presumed to be 1.5 kcal mol⁻¹. The value of ΔS°_{298} for reaction 7 calculated by Wagner and Melius is essentially identical (within <0.6 cal mol⁻¹ K⁻¹) with that obtained using group contributions²⁰ or with a slightly different structural model.²⁶

Discussion

I. Thermochemistry of the CH₃ + O₂ ⇌ CH₃O₂ Reaction. The equilibrium constants for reaction 7 that were measured in this study are in very close agreement with those obtained from the more indirect observation of this equilibrium that were reported by Khachatryan et al. (see Figure 1).²⁶ The enthalpy changes for reaction 7 that were calculated in both studies are therefore also in complete agreement. This enthalpy change is listed again below (as the CH₃-O₂ bond energy) together with additional thermochemical information that was calculated using it:

$$DH^\circ_{298}(\text{CH}_3\text{-O}_2) = 32.4 \pm 0.7 \text{ kcal mol}^{-1}$$

$$DH^\circ_0(\text{CH}_3\text{-O}_2) = 30.9 \pm 0.8 \text{ kcal mol}^{-1,42}$$

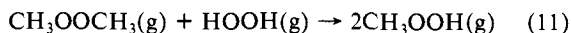
$$\Delta H^\circ_{f,298}(\text{CH}_3\text{O}_2) = 2.7 \pm 0.8 \text{ kcal mol}^{-1,43}$$

$$\Delta H^\circ_{f,0}(\text{CH}_3\text{O}_2) = -0.3 \pm 0.9 \text{ kcal mol}^{-1,42,43}$$

$$DH^\circ_{298}(\text{CH}_3\text{OO-CH}_3) = 67.8 \pm 1.2 \text{ kcal mol}^{-1,44}$$

$\Delta H^\circ_{f,298}(\text{CH}_3\text{O}_2)$ obtained from this study is in reasonable agreement with that calculated from the sum of group contributions [(C(H)₃(O) + O(O)(C) = -10.08 + 14.2 = 4.1 (kcal mol⁻¹)]^{18,20} and is consistent with the upper limit for this quantity determined by Kondo and Benson ($\Delta H^\circ_{f,298}(\text{CH}_3\text{O}_2) < 6.6$ kcal mol⁻¹).²⁵ The value assigned to the heat of formation of the O(O)(C) group requires knowledge of the heat of formation of the HO₂ radical ($\Delta H^\circ_{f,298}(\text{HO}_2) = 2.5$ kcal mol⁻¹ is presumed).²⁰

The most direct calculation of the heat of formation of CH₃O₂ (from experimental $\Delta H^\circ_{f,298}$ values of related compounds) using group additivity principles (particularly the assumption that "next nearest neighbors" do not contribute to bond energies and hence to group heats of formation) begins with the measured heat of formation of CH₃OOCH₃(g)⁴⁵ and presumes the following: first that ΔH° for the reaction



is zero (which provides the heat of formation of CH₃OOH), and second that the CH₃OO-H and HOO-H bond energies are equal. (This assumption yields the heat of formation of CH₃OO since that of HO₂(g) and H₂O₂(g) are known.) There is a small uncertainty in the heat of formation of HO₂. That calculated for CH₃O₂ (at 298 K) is 3.8 kcal mol⁻¹ if Howard's measured heat of formation of HO₂ is used⁴⁶ and is 4.8 kcal mol⁻¹ if that favored by Shum and Benson is chosen.⁴⁷ The agreement with experiment

is again good and well within that expected (2-4 kcal mol⁻¹) considering the possible cumulative uncertainties from the data used and the presumptions needed to obtain this calculated estimate.

II. Thermochemistry of Other R + O₂ ⇌ RO₂ Equilibria. In both experiments of the type reported here and in others from which group contributions to the heats of formation of free radicals are derived, the entropies of both R and RO₂ are generally needed to reduce the data to obtain the desired enthalpies of the radicals or of some of their groups. These entropies are usually calculated since virtually none is available directly from experiment. Different assumptions regarding the unknown portions of the structures and the internal motions of R and RO₂ that are required to calculate these entropies result in different heats of formation. Since there is essentially no uncertainty in the structures and internal motions of CH₃ and CH₃O₂, the close agreement between "experiment" and "calculation" based on group sums is not unexpected. However, for other R groups, there are major uncertainties in the nature of some of the internal motions that contribute significantly to the overall entropy of R and RO₂ (particularly the barriers to internal rotation and the number and nature of low frequency vibrations), uncertainties which become more significant the larger the R group. The nature and magnitude of this problem and its effect on the enthalpies of alkyl radicals reported by various investigators has been discussed in detail by Tsang,⁴⁸ Golden and McMillen,⁴⁹ and Kaplan.⁵⁰

In the case of reaction 4, the *i*-C₃H₇ + O₂ ⇌ *i*-C₃H₇O₂ equilibrium, the magnitude of the disagreement between our measured value of ΔH°_{298} (-37.7 ± 1.8 kcal mol⁻¹) and one calculated using group contributions (-30.7 kcal mol⁻¹) arises in part from these entropy considerations. We have used models for the *i*-C₃H₇ and *i*-C₃H₇O₂ internal motions that result in entropies that are ≈3 cal mol⁻¹ K⁻¹ higher and ≈3 cal mol⁻¹ K⁻¹ lower, respectively, for the two radicals than those derived from the earlier models used by Benson and co-workers for related purposes.^{14,51} The resulting 6 cal mol⁻¹ K⁻¹ difference in ΔS°_{298} for reaction 4 is responsible for ≈4 kcal mol⁻¹ of the 7 kcal mol⁻¹ disparity in ΔH°_{298} values obtained from the two sources. The sources of these two 3 cal mol⁻¹ K⁻¹ entropy differences are discussed in detail by Wagner and Melius.²⁸ They arise basically from the current inclusion into the models for the structures and internal motions of the *i*-C₃H₇ and *i*-C₃H₇O₂ radicals of new knowledge of these subjects derived from both experimental and theoretical studies, particularly by Pacansky and co-workers (on the structure and vibrations of *i*-C₃H₇)⁵²⁻⁵⁴ and by Bair (on the internal rotation barriers about the O-O bond in ROOR compounds).^{27,28,55} As knowledge of the structures and internal motions of R and RO₂ improves, the equilibrium constants measured for reaction 1 (like those given in Table I and in ref 15) can be used to recalculate more accurate heats of formation of the alkylperoxy radicals.

The origin of the remaining 3-4-kcal/mol disparity between the measured and estimated enthalpy change of reaction 4 is still uncertain. It could arise in part or completely from the use of group-derived heats of formation of the larger alkyl radicals (C₂-C₄) that are too low.⁴⁸

With the increased detection sensitivity now at our disposal, we anticipate that we shall now be able to accurately determine ΔH° for R + O₂ ⇌ RO₂ equilibria using the more direct Second Law method for alkyl R groups larger than CH₃ (as was possible in our study of reaction 5).¹⁵ Since such results would be essentially independent of detailed structural knowledge of R and RO₂, we will be able to determine more directly the extent to which

(42) Calculated using the relative enthalpy functions in ref 28.

(43) Calculated using $\Delta H^\circ_{f,298}(\text{CH}_3) = 35.1 \pm 0.1$ kcal mol⁻¹; Heneghan, S. P.; Knott, P. A.; Benson, S. W. *Int. J. Chem. Kinet.* **1981**, *13*, 677-691.

(44) Calculated using $\Delta H^\circ_{f,298}(\text{CH}_3\text{OOCH}_3(\text{g})) = -30.0 \pm 0.3$ kcal mol⁻¹; Baker, G.; Littlefair, J. H.; Shaw, R.; Thynne, J. C. *J. Chem. Soc.* **1965**, 6970-6972.

(45) From the study cited in ref 44.

(46) Howard, C. J. *J. Am. Chem. Soc.* **1980**, *102*, 6937-6941.

(47) Shum, L. G. S.; Benson, S. W. *J. Phys. Chem.* **1983**, *87*, 3479.

(48) Tsang, W. *Int. J. Chem. Kinet.* **1978**, *10*, 821-837.

(49) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493-532.

(50) Kaplan, L. In "Reactive Intermediates"; Jones, M., Moss, R. A., Eds.; Wiley-Interscience: New York, 1985; Vol. 3, Chapter 7.

(51) Hiatt, R.; Benson, S. W. *Int. J. Chem. Kinet.* **1972**, *4*, 151-157.

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

(53) Pacansky, J.; Coufal, H. *J. Chem. Phys.* **1980**, *72*, 3298.

(54) Dupuis, M., private communication.

(55) Bair, R. A., private communication.

R-O₂ bond strengths increase with the size (or perhaps the structure) of the R group, a trend that is suggested by our first two studies of these equilibria, but which is not predicted by group additivity concepts. These additional studies are in progress.

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Complexation of *tert*-Butylammonium Perchlorate by Crown Ethers in Polar Solvents Studied by ¹H NMR Spectroscopy

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Abstract: Association constants of complexes of *tert*-butylammonium perchlorate and 1,3-xylyl-18-crown-5 and 18-crown-6 have been determined by ¹H NMR spectroscopy at various temperatures (240–306.5 K) and in different polar solvents (methanol-*d*₄, acetone-*d*₆, and acetonitrile-*d*₃). For 1,3-xylyl-18-crown-5 the association constants could be determined directly from the observed change of the chemical shifts of the *tert*-butyl protons at increasing crown ether concentration. On the other hand, the association constants with 18-crown-6 were deduced from chemical shift changes of the *tert*-butyl protons in a series of competition experiments. At similar conditions the association constants with 18-crown-6 were always found greater than for 1,3-xylyl-18-crown-5. In general the association constants increase from methanol < acetone < acetonitrile and at decreasing temperature. From this temperature dependence the thermodynamic values of enthalpy and entropy change (ΔH° and ΔS°) upon complexation were derived. The kinetic stability of the complexes between *tert*-butylammonium perchlorate and 18-crown-6 in methanol, acetone, and acetonitrile and with 1,3-xylyl-18-crown-5 in acetone could also be determined at the coalescence temperature T_c . For 1,3-xylyl-18-crown-5-*tert*-butylammonium perchlorate in acetone at $T_c = 183$ K, the Gibbs free energy of activation was found to be $\Delta G^\ddagger = 8.8$ kcal mol⁻¹. The change of kinetic stability of 18-crown-6-*tert*-butylammonium perchlorate in different solvents parallels the observed change of association constants.

Crown ethers can form complexes with inorganic and organic cations¹ and with neutral molecules.² Stabilities of these complexes may vary over a large range and depend on the nature of the guest, the nature of the host, and the solvent. To date the complexation of aryl- and alkylammonium salts by crown ethers in *apolar* solvents has been studied by Cram and co-workers,³⁻⁶ Stoddart and co-workers,⁷⁻⁹ Sutherland and co-workers,¹⁰⁻¹³ Bradshaw and Baxter,¹⁴ and de Jong and Reinhoudt.¹⁵⁻¹⁷ Since

the salts are sparingly soluble in apolar solvents, only indirect methods, e.g., extraction experiments,³⁻⁶ or competition experiments¹⁵⁻¹⁷ can be used. The disadvantage of the extraction method, however, is that for crown ethers with a cavity of ring size larger than 21 ring atoms, water can interfere in the complexation.¹⁶ A ¹H NMR method has been developed to determine the association constant of the 1,3-xylyl-18-crown-5-*t*-BuNH₃PF₆ complex in a *homogeneous* chloroform phase using kinetic techniques.¹⁵ This method is based on the fact that the rate of the exchange of *t*-BuNH₃PF₆ between the 1,3-xylyl-18-crown-5-*t*-BuNH₃PF₆ complex and the kinetically more stable 18-crown-6-*t*-BuNH₃PF₆ complex changes with variation in the concentration. These determinations are possible because of differences in the chemical shift of the *t*-Bu group in the two complexes. Combining these results with the independently determined *relative* association constants of the 18-crown-6-*t*-BuNH₃PF₆ and the corresponding 1,3-xylyl-18-crown-5 complex, the absolute association constant of the 18-crown-6 complex was determined.¹⁷ In polar solvents such as methanol, in which the salts are soluble, the association constants of complexes between crown ethers and alkylammonium salts have been determined directly using calorimetry by Izatt et al.¹⁸ They have studied the effect of the alkyl groups of the

(1) de Jong, F.; Reinhoudt, D. N. *Adv. Phys. Org. Chem.* **1980**, *17*, 279.

(2) de Boer, J. A. A.; Reinhoudt, D. N.; Harkema, S.; Van Hummel, G. J.; de Jong, F. *J. Am. Chem. Soc.* **1982**, *104*, 4073.

(3) Timko, J. M.; Moore, S. S.; Walba, D. M.; Hiberty, P. C.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 4207.

(4) Kyba, E. P.; Helgeson, R. C.; Madan, K.; Gokel, G. W.; Tarnowski, T. L.; Moore, S. S.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 2564.

(5) Newcomb, M.; Timko, J. M.; Walba, D. M.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 6392.

(6) Helgeson, R. C.; Tarnowski, T. L.; Timko, J. M.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 6411.

(7) Coxon, A. C.; Laidler, D. A.; Pettman, R. B.; Stoddart, J. F. *J. Am. Chem. Soc.* **1978**, *100*, 8260.

(8) Laidler, D. A.; Stoddart, J. F. *J. Chem. Soc., Chem. Commun.* **1977**, 481.

(9) Laidler, D. A.; Stoddart, J. F.; Wolstenholme, J. B. *Tetrahedron Lett.* **1979**, 465.

(10) Johnson, M. R.; Sutherland, I. O.; Newton, R. F. *J. Chem. Soc., Perkin Trans. 1* **1979**, 357.

(11) Leigh, S. J.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1089.

(12) Hodgkinson, L. C.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1908.

(13) Hodgkinson, L. C.; Johnson, M. R.; Leigh, S. J.; Spencer, N.; Sutherland, I. O.; Newton, R. F. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2193.

(14) Baxter, S. L.; Bradshaw, J. S. *J. Heterocycl. Chem.* **1981**, *18*, 233.

(15) de Jong, F.; Reinhoudt, D. N.; Smit, C. J.; Huis, R. *Tetrahedron Lett.* **1976**, 4783.

(16) de Jong, F.; Reinhoudt, D. N.; Smit, C. J. *Tetrahedron Lett.* **1976**, 1371.

(17) de Jong, F.; Reinhoudt, D. N.; Smit, C. J. *Tetrahedron Lett.* **1976**, 1375.

(18) Izatt, R. M.; Lamb, J. D.; Izatt, N. E.; Rossiter, B. E., Jr.; Christensen, J. J.; Haymore, B. L. *J. Am. Chem. Soc.* **1979**, *101*, 6273.