should be given by k_f[terphenyl]. The observed and calculated values (k_f[terphenyl]) together with the differences are given in Table IV. All systems show a positive residual difference. Similar analysis of k_f vs. hydrocarbon pressure at constant rare gas pressure yields a similar result i.e., a positive residual rate.

The differences are of the order of $(1 \pm 0.6) \times 10^8$ s^{-1}, but nevertheless significant since in all cases they are positive. These differences are large compared to k_f[terphenyl] which is typically $\sim 3 \times 10^7$ s^{-1}. This implies that there is an electron energy loss process which is independent of rare gas or hydrocarbon pressure. A similar observation was made in our earlier study[2] of Ne/N_2 and He/N_2 systems using a completely different pulse radiolysis system. We are unable to propose a reasonable explanation for this effect.

Conclusions. The excitation of aromatic hydrocarbons by electron irradiation of rare gas–hydrocarbon mixtures proceeds by a subexcitation electron mechanism. The rate constants for excitation are very high, i.e., about 10^{13} dm^3 mol^{-1} s^{-1}; a secondary and weak effect is attributable to electron energy loss to rare gas atoms by momentum transfer (about 10^9 dm^3 mol^{-1} s^{-1}).

In all systems, a residual electron energy loss rate is observed which is independent of rare gas or hydrocarbon pressure. The mechanism of this latter process is not understood.

Acknowledgment. R.C. acknowledges support from the Australia Research Grants Scheme (A.R.G.S.). R. C. and L. D. also wish to acknowledge the support of ANL for maintenance and support costs at ANL during their stay.

Temperature Dependence of the Reaction $HO_2 + HO_2$ at Low Pressures

Gerald A. Takacs[†] **and Carleton J. Howard***

Aeronomy Laboratory, NOAA-R/E/AL2, Environmental Research Laboratories, Boulder, Colorado 80303

(Received: July 1, 1985)

The temperature dependence of the self-reaction of HO_2, $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (k_1) (1), was investigated by detecting HO_2 with laser magnetic resonance in a low-pressure flow tube coated with halocarbon wax. Two independent chemical reactions ($CH_2OH + O_2$ and $F + H_2O_2$) were used to produce HO_2 and two calibration procedures were used to determine the concentration of HO_2. With 95% confidence limits, $k_1(T) = (2.0 \pm 0.6) \times 10^{-13} \exp\{(595 \pm 120)/T\}$ cm^3 molecule^{-1} s^{-1} for the pressure-independent bimolecular channel of reaction 1 from 253 to 390 K, where $-d[HO_2]/dt = 2k_1[HO_2]^2$.

Introduction

The only significant source of gaseous atmospheric hydrogen peroxide is the reaction of two HO_2 radicals:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (1)$$

The concentrations of atmospheric HO_2 and H_2O_2 are dependent on the rate of reaction 1 and the rates of destruction of H_2O_2:[1,2] by photodissociation

$$H_2O_2 + h\nu \rightarrow OH + OH \qquad (2)$$

by reaction with OH

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \qquad (3)$$

and by the heterogeneous processes involved in rainout. Accurate values for the rate coefficient of reaction 1 as a function of temperature are therefore needed for the assessment of HO_x removal and for comparison with measurements of H_2O_2 concentration levels.

The rate constant of the self-reaction of HO_2 has been investigated extensively at high pressures ($\sim$1 atm) and shows a pressure dependence[3,4] and a negative temperature coefficient.[5-7] These observations have been explained by a mechanism consisting of a termolecular component involving an H_2O_4 intermediate, in addition to the pressure-independent bimolecular disproportionation, reaction 1.

Room temperature measurements of the rate coefficient for the bimolecular pathway that have been obtained by using UV,[3-5] IR,[8,9] laser magnetic resonance (LMR)[10] absorption of HO_2, and mass spectrometry[11] are in good agreement. In this paper, we have extended our earlier room temperature study[10] to investigate the temperature dependence of k_1 with a low-pressure discharge-flow system equipped with LMR detection.

Experimental Section

The flow tube reactor and the LMR technique for detecting HO_2, OH, and NO_2 with the 118.6-μm line of the water vapor laser have been described in detail previously.[10,12]

Temperature control of the 2.54-cm-i.d. Pyrex flow tube was achieved by circulating either dibutyl phthalate (300–450 K) or ethanol (250–300 K) from a thermoregulated reservoir through a condenser-like jacket surrounding the flow tube. The inside surface of the flow tube was coated with a halocarbon wax and baked under vacuum up to the wax melting point of 405 K.

Hydroperoxyl radicals were produced by the appropriate source reactions 4–6

$$F + H_2O_2 \rightarrow HF + HO_2 \qquad (4)$$

[†] NOAA-NRC Senior Research Associate, 1982–83, on leave from Department of Chemistry, Rochester Institute of Technology, Rochester, NY.

[*] Also affiliated with the Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, and to whom correspondence should be addressed.

(1) Howard, C. J. In "Proceedings of the NATO Advanced Study Institute on Atmosphere Ozone", Aikin, A. C., Ed.; U.S. Department of Transportation: Washington, DC, 1979; Report No. FAA-EE 80-22, 409.

(2) DeMore, W. B.; Molina, M. J.; Watson, R. T.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R. Jet Propulsion Laboratory: Pasadena, CA, 1983; JPL Publication 83-62.

(3) Sander, S. P.; Peterson, M.; Watson, R. T.; Patrick, R. *J. Phys. Chem.* **1982**, *86*, 1236.

(4) Simonaitis, R.; Heicklen, J. *J. Phys. Chem.* **1982**, *86*, 3416.

(5) Cox, R. A.; Burrows, J. P. *J. Phys. Chem.* **1979**, *83*, 2560.

(6) Lii, R-R.; Gorse Jr., R. A.; Sauer Jr., M. C.; Gordon, S. *J. Phys. Chem.* **1979**, *83*, 1803.

(7) Patrick, R.; Pilling, M. J. *Chem. Phys. Lett.* **1982**, *91*, 343.

(8) Thrush, B. A.; Tyndall, G. S. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 1469.

(9) Thrush, B. A.; Tyndall, G. S. *Chem. Phys. Lett.* **1982**, *92*, 232.

(10) Takacs, G. A.; Howard, C. J. *J. Phys. Chem.* **1984**, *88*, 2110.

(11) Sander, S. P. *J. Phys. Chem.* **1984**, 88, 6018.

(12) Howard, C. J.; Evenson, K. M. *J. Chem. Phys.* **1974**, *61*, 1943; Zahniser, M. S.; Howard, C. J. *J. Chem. Phys.* **1980**, *73*, 1620.

$$Cl + CH_3OH \rightarrow HCl + CH_2OH \tag{5}$$

$$CH_2OH + O_2 \rightarrow CH_2O + HO_2 \tag{6}$$

in the last 5 cm of a 7.0-mm-i.d. movable injector as described in the room temperature study of reaction 1.[10] Some details of the conditions in the source injector are given in Table I. Fluorine and chlorine atoms were made in a microwave discharge containing dilute mixtures of F_2 in He and Cl_2 in He, respectively. The conditions in the source injector were adjusted so that the source reactions would go to completion within the 5-cm source reaction zone. Although the flow velocity, $\bar{v}$, in the injector was relatively high, a large concentration of the source reactant, either H_2O_2 or CH_3OH, assured that no significant amounts of atomic F or Cl escaped into the flow tube reaction zone. Calculations based on the published rate coefficients $k_4 = 8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} [13] and $k_5 = 6.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [14] indicated that the number of halogen atoms leaving the source was $<10^{-6}$ times their initial concentrations. The $[O_2]$ in the Cl/CH_3OH source was also adjusted so that >99.9% of the CH_2OH was removed by reaction 6, taking $k_6 = 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[15] The experimental conditions in the flow tube during the kinetic investigation are shown in Table II.

To obtain the rate constant for reaction 1, absolute concentration calibrations for the LMR signal are required. For the Cl + CH_3OH + O_2 source, HO_2 was converted to NO_2 according to reaction 7, by the addition of excess NO, and the LMR signal

$$HO_2 + NO \rightarrow OH + NO_2 \tag{7}$$

of NO_2 was measured. To prevent the OH produced in reaction 7 from making CH_2OH by reaction 8 and subsequently producing

$$OH + CH_3OH \rightarrow H_2O + CH_2OH \tag{8}$$

more HO_2 by reaction 6, C_2F_3Cl was added to the system to scavenge OH radicals:[12]

$$OH + C_2F_3Cl \rightarrow \text{products} \tag{9}$$

where $k_9 = 6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Then the microwave discharge that produced the Cl atoms was turned off and known amounts of NO_2 were flowed into the flow tube to determine the sensitivity of the LMR spectrometer to NO_2. Similar calibrations with the F + H_2O_2 source could not be carried out accurately, because significant amounts of HO_2 and OH were observed in undischarged mixtures of F_2–NO–H_2O_2 and F_2–C_2F_3Cl–H_2O_2. This was apparently due to a thermal reaction initiated by F_2.

For both the Cl + CH_3OH + O_2 and F + H_2O_2 sources, calibrations were also done using OH as the calibrating gas. Low concentrations of HO_2 were made from reaction 10 by discharging

$$H + O_2 + M \rightarrow HO_2 + M \tag{10}$$

a trace amount of H_2 in He and reacting the H atoms with O_2 in a high-pressure cell that was located on the upstream end of the flow tube.[12] The HO_2 was then stoichiometrically converted to OH by the addition of excess NO through the injector (reaction 7), when the injector was positioned just above the detection volume. In separate experiments using conditions identical with the conversion experiments, the LMR calibration for OH was determined by producing known amounts of OH from the reaction of excess H atoms with measured amounts of NO_2 that were added through the injector.[10]

$$H + NO_2 \rightarrow OH + NO \tag{11}$$

This method takes advantage of the large dynamic range and linearity of LMR detection as described in the appendix of the previous study.[10]

The first-order wall loss of HO_2

$$HO_2 + \text{wall} \xrightarrow{k_w} \text{products} \tag{12}$$

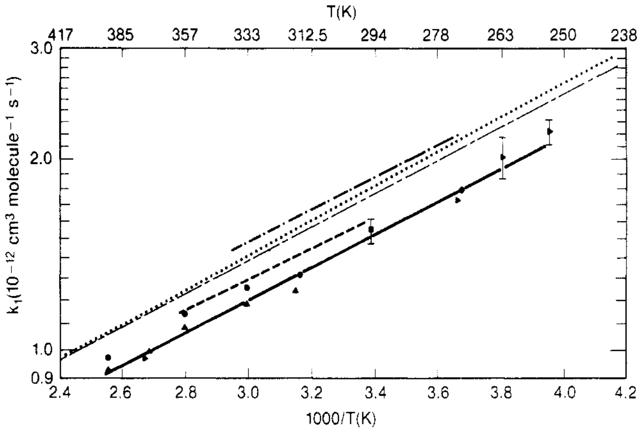

Figure 1. Semilog plot of k_1 vs. 1000/T: (–·–·) Cox and Burrows; (····) Kircher and Sander (M = N_2);[17] (–·–) Kircher and Sander (M = Ar);[17] (– – –) Thrush and Tyndall;[9] (—) this work: ■, room temperature data from ref 10; ●, Cl + CH_3OH + O_2, NO_2 calibration; ▶, Cl + CH_3OH + O_2, OH calibration; and ▲, F + H_2O_2, OH calibration. Error bars are one standard deviation of the mean.

was measured daily throughout the study at HO_2 concentration levels for which reaction 1 would not contribute to HO_2 loss. For the temperatures ≥272, 263 and 253 K, k_w typically was ≤0.4, 0.8 and 1.1 s^{-1}, respectively. Sahetchchian et al.[31] have reported a larger increase in the wall loss rate with decreasing temperature than we observe, but surface reactions are expected to be dependent on the nature of the reactor wall. We have seen no evidence of a second-order wall reaction, as observed earlier[10] on phosphoric acid coated walls, and assume that it was not significant. Computer simulation of the kinetic experiments, using a GEAR program[10,16] for numerical integration of the differential equations arising from HO_2 loss by reactions 1 and 12, showed that wall loss contributed about ≤5, 8, and 11%, respectively, to the HO_2 decay at ≥272, 263, and 253 K. These corrections were made to the measured rate constants at 263 and 253 K.

A discussion of chemical purities and other details on experimental procedures were given in our room temperature study of reaction 1.[10]

Results

The observed changes in $[HO_2]$ in the rate coefficient measurements were between a factor of 2.5 and a factor of 6.7. The F + H_2O_2 source gave somewhat higher initial $[HO_2]$ which permitted larger decays to be measured with that source. The ranges of experimental conditions are summarized in Table II. The temperature range of the F + H_2O_2 source was limited by the melting point of the halocarbon wax (405 K) and possible condensation of H_2O_2 in the injector (295 K). The use of the Cl + CH_3OH + O_2 source below room temperature was restricted to temperatures greater than 252 K, where HO_2 wall loss did not make a substantial contribution to the overall HO_2 loss. At lower temperatures the first-order wall loss of HO_2 increased sharply and large corrections, i.e. >11%, would be required.

The rate coefficients, k, defined by $-d[HO_2]/dt = 2k_1[HO_2]^2$, are tabulated in Table III and are shown in a semilog plot as a function of $1/T$ (K) in Figure 1. A weighted least-squares fit to this data gives $k_1(T) = (2.0 \pm 0.6) \times 10^{-13} \exp\{(595 \pm 91)/T\}$ cm^3 molecule^{-1} s^{-1} where the error bars are for 95% confidence limits and include a factor for systematic errors as described below.

Discussion

Chemical Sources of HO_2. The temperature dependence of the rate constant for F + H_2O_2, reaction 4, is not known. However, E/R for the reactions Cl + H_2O_2 and Br + H_2O_2 are 980 ± 500 and >2500 K,[2] respectively, and the H abstraction by F from H_2O_2 may be expected to have a small positive activation energy. The

---

(13) Smith, D. J.; Setser, D. W.; Kim, K. C.; Bogan, D. J. *J. Phys. Chem* **1977**, *81*, 898.

(14) Michael, J. V.; Nava, D. F.; Payne, W. A.; Stief, L. J. *J. Chem. Phys.* **1979**, *70*, 3652.

(15) Radford, H. E. *Chem. Phys. Lett.* **1980**, *71*, 195.

(16) Hindmarch, A. C. "GEAR: Ordinary Differential Equation Solver"; Lawrence Livermore Laboratory: University of California, Livermore, CA, 1972; Report No. UCID-30001, Rev. 1.

TABLE I: Experimental Conditions in the Injector Source[a]

source	$[X_2]$, 10^{14} cm^{-3}	$[H_2O_2]$, 10^{15} cm^{-3}	$[CH_3OH]$, 10^{14} cm^{-3}	$[O_2]$, 10^{15} cm^{-3}	[He], 10^{16} cm^{-3}	$\bar{v}$, cm s^{-1}	T, K	$[X]/[X]_0$[b]	$[CH_2OH]/[CH_2OH]_0$[c]
$X + H_2O_2$ (X = F)	3.7–8.3	1.0–1.7			3.1–19.2	1294–2848	295–389	$<6 \times 10^{-7}$	
$X + CH_3OH + O_2$ (X = Cl)	0.5–1.8		1.6–18.9	2.5–8.0	2.2–12.8	1182–3522	252–391	$<8 \times 10^{-7}$	$<9 \times 10^{-4}$

[a] Experimental conditions in the last 5 cm of the 7.0-mm i.d. tube of the injector. [b] $[X]/[X]_0$ = fraction of halogen atoms injected into the flow tube. [c] $[CH_2OH]/[CH_2OH]_0$ = fraction of CH_2OH injected into the flow tube.

TABLE II: Flow Tube Experimental Conditions

source	$[X_2]$, 10^{14} cm^{-3}	$[H_2O_2]$, 10^{15} cm^{-3}	$[CH_3OH]$, 10^{14} cm^{-3}	$[O_2]$, 10^{15} cm^{-3}	[He], 10^{16} cm^{-3}	$\bar{v}$, cm s^{-1}	T, K	$[HO_2]$, 10^{12} cm^{-3}	$[HO_2]_i/[HO_2]_f$[a]
$X + H_2O_2$ (X = F)	2.0–2.7	0.5–0.7			3.2–19.6	334–364	295–389	1.6–19.8	3.9–6.7
$X + CH_3OH + O_2$ (X = Cl)	0.3–0.7		1.1–5.0	1.8–3.1	3.0–12.9	321–367	252–391	1.2–12.5	2.5–4.6

[a] Ratio of initial to final HO_2 concentration that was observed over a 40-cm reaction distance.

TABLE III: Rate Constant Measurements of the $HO_2 + HO_2$ Reaction as a Function of Temperature

T, K	source	calibration method	no. of measurements	k_1, 10^{-12} cm^3 molecule^{-1} s^{-1}
253	$Cl + CH_3OH + O_2$	OH	5	(2.22 ± σ = 0.10)
263	$Cl + CH_3OH + O_2$	OH	4	(2.01 ± σ = 0.16)
272	$Cl + CH_3OH + O_2$	NO_2	1	1.78
273	$Cl + CH_3OH + O_2$	OH	1	1.71
294 ± 1	$Cl + CH_3OH + O_2$, $F + H_2O_2$	OH, NO_2	13	(1.54 ± σ = 0.07)[a]
316	$Cl + CH_3OH + O_2$	NO_2	1	1.32
317	$F + H_2O_2$	OH	1	1.24
332	$Cl + CH_3OH + O_2$	NO_2	1	1.26
333	$F + H_2O_2$	OH	1	1.18
356	$Cl + CH_3OH + O_2$	NO_2	1	1.15
356	$F + H_2O_2$	OH	1	1.09
372	$F + H_2O_2$	OH	1	1.01
373	$Cl + CH_3OH + O_2$	OH	1	0.98
389	$F + H_2O_2$	OH	1	0.94
390	$Cl + CH_3OH + O_2$	NO_2	1	0.98

[a] Data from previous study reported in ref 10.

temperature-independent value, 8×10^{-12} cm^3 molecule^{-1} s^{-1},[13] was used for the rate constant of reaction 4 in calculating that the fraction of F atoms entering the flow tube was $<6 \times 10^{-7}$ (Table I). A positive activation energy for reaction 4 would only decrease this number for all the measurements except those at room temperature. Therefore we believe it is unlikely that any significant amount of F could escape into the reaction zone.

The rate constant for $Cl + CH_3OH$, reaction 5, has been investigated by Michael et al.[14] using the flash photolysis-resonant fluorescence technique from 200 to 500 K. They found k_5 to be 6.3×10^{-11} cm^3 molecule^{-1} s^{-1} with no significant temperature dependence. With this value, reaction 5 was shown to be complete within the injector, and, for our experiments, $<8 \times 10^{-7}$ of the Cl atoms exited the injector into the flow tube. With deuterated methanols, Radford[15] has shown that, at room temperature, the Cl atom in reaction 5 selectively abstracts an H atom from the CH_3 group to produce CH_2OH and not CH_3O:

$$Cl + CH_3OH \rightarrow CH_3O + HCl \tag{13}$$

Reaction 13 is endothermic by only about 1 kcal/mol.[18] The branching for reactions 5 and 13 may change with temperature. For example, Hägele et al.[19] studied the reaction of OH with CH_3OH and reported that the fraction of CH_3O product increased from 0.11 at 298 K to 0.22 at 393 K. CH_2OH rapidly reacts with O_2 at room temperature to form HO_2 by reaction 6, $k_6 = 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1},[15] in contrast to CH_3O which reacts with O_2 slowly

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \tag{14}$$

$k_{14} = 1.3 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1},[2] at 298 K. Three-body association of oxygen to CH_2OH has been shown to be negligible at 301 ± 2 K.[20] If k_6 is taken to be invariant with temperature, $<9 \times 10^{-4}$ of the CH_2OH should enter the flow tube during our experiments (Table I). Because of the slowness of reaction 14[2] ($k_{14} = 1.2 \times 10^{-13} \exp\{-1350 \pm 500/T\}$), ≥98% of any CH_3O that may be produced by the $Cl + CH_3OH$ reaction in our 298 to 390 K experiments would enter the flow tube and possibly cause complications in the kinetic measurements because of the occurrence of reactions such as (15) and (16). Reaction 15 followed

$$CH_3O + CH_3OH \rightarrow CH_3OH + CH_2OH \tag{15}$$

$$CH_3O + HO_2 \rightarrow CH_3OH + O_2 \tag{16}$$

by reaction 6 would make HO_2, while reaction 16 would destroy HO_2 in the flow tube. No interference by CH_3O is expected in the calibration experiments, since during HO_2 conversion with NO to NO_2 the termolecular reactions of CH_3O with NO and NO_2 are insignificant under our experimental conditions. In fact, no change in the $[NO_2]$ that was produced during the calibration was observed over a 40-cm change in reaction distance. All of the kinetic plots were linear and showed no curvature as might be expected if reactions 15 or 16 were occurring in the system. Furthermore the data taken with the $F + H_2O_2$ source were consistent with those from the $Cl + CH_0OH + O_2$ source in the temperature region where CH_3O was most likely to be formed. Therefore we believe that there are no significant complications in our kinetic study due to reactions 15 and 16. It should be noted that the studies of Thrush and Tyndall[9] and Kircher and Sander[17] relied exclusively on the $Cl + CH_3OH + O_2$ source.

Temperature Dependence of the $HO_2 + HO_2$ Reaction at Low Pressures. The precision of a single rate coefficient measurement at the 95% confidence level is about 20% as calculated by using the standard propagation of error analysis[21] with the following error estimates: gas flow rates, ±3%; flow tube pressure, ±2%, flow tube temperature, ±1%, flow tube radius, ±1%, decay plot slope, ±5%, and HO_2 concentration calibration, ±15%. With the inclusion of possible systematic errors, ±10%, in the weighted least-squares fit of the plot of $\ln k_1$ against $1/T$, the recommended temperature dependence for k_1 at low pressures is $k_1(T) = (2.0 \pm 0.6) \times 10^{-13} \exp\{(595 \pm 120)/T\}$ cm^3 molecule^{-1} s^{-1} at the 95% confidence level.

Cox and Burrows[5] were the first to report values for k_1 as a function of temperature at low pressures. They formed HO_2 mainly from reaction 17 by photolysis of Cl_2 in the presence of

$$CHO + O_2 \rightarrow HO_2 + CO \tag{17}$$

---

(17) Kircher, C. C.; Sander, S. P. *J. Phys. Chem.* **1984**, *88*, 2082.

(18) Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1976; 2nd ed, Tables A.8 to A.12.

(19) Hägele, J.; Lorenz, K.; Rhäsa, D.; Zellner, R. *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 1023.

(20) Ohta, T.; Bandow, H.; Akimoto, H. *Int. J. Chem. Kinet.* **1982**, *14*, 173.

(21) Cvetanovic, R. J.; Singleton, D. L.; Paraskevopoulos, G. *J. Phys. Chem.* **1979**, *83*, 50.

TABLE IV: Temperature Dependence of the $HO_2 + HO_2$ Reaction at Low Pressures

$k_1(T)$, 10^{-13} cm^3 molecule^{-1} s^{-1}	T range, K	method[a]	ref
$(2.0 \pm 0.6) \exp\{(595 \pm 120)/T\}$	253–390	FT/LMR	this work
$(2.6 \pm 0.4) \exp\{(581 \pm 44)/T\}$	274–339	MM/UV	5
$(2.4) \exp\{(560 \pm 200)/T\}$	298–358	FP/IR	9
$(2.3) \exp\{(600 \pm 130)/T\}$	240–417	FP/UV (Ar)	17
$(2.2) \exp\{(620 \pm 60)/T\}$	241–417	FP/UV (N_2)	17

[a] MM = molecular modulation, UV = ultraviolet absorption, FP = flash photolysis, IR = infrared absorption, FT = flow tube, LMR = laser magnetic resonance absorption in halocarbon wax coated flow tube.

formaldehyde and O_2. With single measurements at 274, 298, and 339 K for a total pressure of 10 torr of N_2, they found $k_1(T) = (2.6 \pm 0.4) \times 10^{-13} \exp\{(581 \pm 44)/T\}$ using the molecular modulation/UV absorption technique. This result is in good agreement with our study. Thrush and Tyndall[8] questioned the validity of the Cox and Burrows findings because they ignored a reaction between HO_2 and formaldehyde in their kinetic analysis.

Thrush and Tyndall[9] flash photolyzed Cl_2–CH_3OH–O_2 mixtures in order to produce HO_2 by reaction 6 and followed HO_2 decay by IR absorption with a diode laser. They investigated reaction 1 between 6 and 13 torr of N_2 or SF_6 at 298, 323, 333, and 359 K and reported $k_1(T) = 2.4 \times 10^{-13} \exp\{(560 \pm 200)/T\}$ cm^3 molecule^{-1} s^{-1}, which is in excellent agreement with our results.

Recently Kircher and Sander,[17] who made HO_2 by flash photolysis of mixtures of Cl_2–CH_3OH–O_2 and used the UV absorption spectrum of HO_2 to determine its concentration, studied reaction 1 in the presence of the diluent gases Ar and N_2 from 80 to 992 torr and from 100 to 700 torr, respectively. Extrapolating to low pressures, they obtained $k_1(T) = 2.3 \times 10^{-13} \exp\{(600 \pm 130)/T\}$ and $2.2 \times 10^{-13} \exp\{(620 \pm 60)/T\}$ cm^3 molecule^{-1} s^{-1} for Ar and N_2, respectively, from 240 to 417 K which are also in very good agreement with our findings. Their pressure-dependent component was reported to be about 3.4×10^{-32} cm^6 molecule^{-2} s^{-1} at 298 K in argon. If one assumes a similar value for M = He, the termolecular reaction contributes <0.5% to the measured k_1 at the highest pressure, 6 torr, in our study.

A comparison of all the investigations of k_1 at low pressure is shown in Figure 1 and in Table IV. The agreement among the four studies is extremely good, considering the variety of experimental methods employed.

Bimolecular reactions with negative sloped or curved Arrhenius plots in general,[22-25] and the $HO_2 + HO_2$ reaction in particular,[17,26] have been recently the subject of much theoretical investigation and speculation. The observed temperature, pressure, and isotopic behavior of the $HO_2 + HO_2$ reaction rate coefficient has been successfully modled by Patrick et al.[26] and Kircher and Sander[17] using RRKM theory to describe the two-channel decomposition of an energetic, loosely bound H_2O_4 intermediate complex. The structure of this intermediate and its energy levels are key ingredients and are major uncertainties in the models. The models possess too many adjustable parameters to provide a definitive picture of the reaction mechanism. One structure, a cyclic double hydrogen-bonded form, was investigated by Fitzgerald and Schaefer[27] who computed dimerization energies in the range 4.5–4.9 kcal mol^{-1} using DZ SCF and DZ + P SCF basis sets. This result indicates that the binding of two monomers as a double-bonded six-membered ring is much weaker than one would predict for two hydrogen bonds between highly polar molecules. Although this structure provides a minimum on the H_2O_4 potential energy hypersurface, it may not be the lowest minimum. It is interesting that the ground-state structure of the H_2O_2 product requires that the hydrogen atoms are oriented on opposite sides of the O–O bond with a dihedral angle of $\simeq 120°$.[28,29] A transition state for the product channel which has a structure similar to the H_2O_2 molecule supports the model predictions of a tight transition state for this channel.[25,26] It would be very valuable to have further theoretical studies of the $HO_2 + HO_2$ reaction surface to improve our understanding of the mechanism.

A new study of the products of the $HO_2 + HO_2$ reaction by Glinski and Birks[30] indicates that H_2 is formed in less than 1% of the reactions at low pressures and 298 K. A study at higher temperatures by Sahetchian et al.[31] reported significant amounts of H_2, so it is possible that a small amount of H_2 is formed under those conditions.

Acknowledgment. This work was supported in part by the Chemical Manufacturers Association Technical Panel on Fluorocarbon Research and by NOAA as part of the National Acid Precipitation Assessment Program.

Registry No. HO_2, 3170-83-0.

---

(22) Golden, D. M. *J. Phys. Chem.* **1979**, *83*, 108.

(23) Fontijn, A.; Zellner, R. "Reactions of Small Transient Species, Kinetics and Energetics", Fontijn, A., Clyne, M. A. A., Eds.; Academic: New York, 1983; p 1.

(24) Marinelli, W. J.; Johnston, H. S. *J. Chem. Phys.* **1982**, *77*, 1225.

(25) Mozurkewich, M.; Benson, S. W. *J. Phys. Chem.* **1984**, *88*, 6429. See also Mozurkewich, M.; Lamb, J. J.; Benson, S. W. *J. Phys. Chem.* **1984**, *88*, 6435. Lamb, J. J.; Mozurkewich, M.; Benson, S. W. *J. Phys. Chem.* **1984**, *88*, 6441.

(26) Patrick, R.; Barker, J. R.; Golden, D. M. *J. Phys. Chem.* **1984**, *88*, 128.

(27) Fitzgerald, G.; Schaefer III, H. F. *J. Chem. Phys.* **1984**, *81*, 362.

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

(29) Cremer, D.; Christen, D. *J. Mol. Spectrosc.* **1979**, *74*, 480.

(30) Glinski, R. J.; Birks, J. W. *J. Phys. Chem.* **1985**, *89*, 3449.

(31) Sahetchian, K. A.; Heiss, A.; Rigny, R. *Can. J. Chem.* **1982**, *60*, 2896.