The Effect of Methanol on the Self Reaction of HO$_2$ Radicals

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Abstract

The rate constant for the HO$_2$ self reaction has been determined as a function of methanol vapor concentration at 278 K and 299 K. A molecular modulation technique was used in which HO$_2$ radicals were photochemically produced in flowing gas mixtures comprised of Cl$_2$, CH$_3$OH, N$_2$ and O$_2$ with HO$_2$ monitored in the UV at 220 nm. A positive linear dependence of the second order rate constant on methanol concentration was found and this effect increased with decreasing temperature. The rate constant for the HO$_2$ self reaction can be described by

$$k = 9.2 \cdot 10^{-15} \exp(1700/T) + 2.1 \cdot 10^{-34} \exp(3000/T)\,[\mathrm{CH_3OH}]\,\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

in nitrogen at atmospheric pressure and in the methanol concentration range $1 \cdot 10^{16}$ to $3 \cdot 10^{17}$ molecules cm^{-3}.

Introduction

The HO$_2$ radical is an important intermediate in photochemical transformation of air pollutants and combustion chemistry. The self reaction of HO$_2$ radicals [reaction (1)] is often a key process in these systems and consequently the kinetics of this reaction have been the subject of intensive study.

(1) $$\mathrm{HO_2 + HO_2 \longrightarrow H_2O_2 + O_2}$$
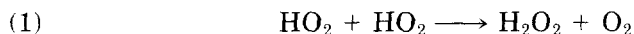
Recent work has shown a positive pressure dependence, a negative temperature dependence, and isotopic effects on the observed second order HO$_2$ self reaction rate constant [1–3]. Also, water and ammonia influence the rate constant observed [4–6]. The effect of water on the HO$_2$ self reaction rate constant is a linear positive dependence. Ammonia has the same effect as water up to a certain concentration level

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but at higher concentrations of ammonia the observed rate constant decreases.

Several different mechanisms have been suggested and there have been at least three attempts to provide a detailed theoretical description of the HO_2 self reaction and the dependence of the reaction rate constant on conditions mentioned above [4–6].

It now seems clear that the reaction must proceed via an association complex or dimer of HO_2 but the exact structure and energetics of the reaction pathways are not clearly defined. The most recent work is by Mozurkewich and Benson [7], 1985, who suggest a mechanism involving doubly hydrogen bonded cyclic dimers of HO_2 as intermediates. They provide a plausible explanation of the observed kinetics, including the effect of water and ammonia. This is in contrast, however, to the earlier calculations of Patrick, Barker, and Golden [8] who favor a loosely bound dimeric intermediate (a linear tetroxide) on the grounds that ring closure cannot compete with re-dissociation of the singly hydrogen bonded dimer, which would rule out the importance of the cyclic structure adopted by Mozurkewich and Benson. The results of matrix isolation studies support the existence of both cyclic [9] and linear tetroxide [10–13] H_2O_4 intermediates.

The effect of water and ammonia on the reaction is believed to result from the formation of a hydrogen bonded complex between the HO_2 radical and the substrate, i.e.

(2) $$HO_2 + H_2O \longrightarrow HO_2 \cdot H_2O$$

(3) $$HO_2 + NH_3 \longrightarrow HO_2 \cdot NH_3$$
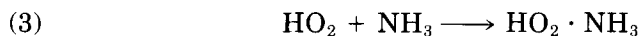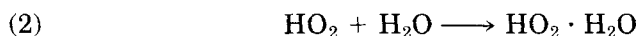
The complex may act as a chaperone in assisting formation of the dimeric intermediate:

(4) $$HO_2 \cdot H_2O + HO_2 \longrightarrow (HO_2)_2 + H_2O$$
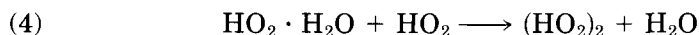
If hydrogen bonded complexes are involved, other species which form hydrogen bonds with HO_2 may also affect the rate. Methanol falls into this category, and since CH_3OH has often been used as a precursor for HO_2 in the study of its gas phase reactions, it is important to evaluate any effect of CH_3OH on HO_2 kinetics. The present work has been undertaken to investigate this possibility.

Experimental

HO_2 kinetics were investigated using the molecular modulation technique, monitoring the HO_2 radical by absorption in the UV at 220 nm ($\sigma = 3.5 \cdot 10^{-18}$ cm^2 molecule^{-1} [4]). The HO_2 radical was generated in flowing gas mixtures by photolysis of chlorine in the presence of methanol and oxygen with nitrogen as the diluent gas, when the

following reactions occur:

(5) $$Cl_2 + h\nu \longrightarrow Cl + Cl$$

(6) $$Cl + CH_3OH \longrightarrow CH_2OH + HCl$$

(7) $$CH_2OH + O_2 \longrightarrow CH_2O + HO_2$$

At the concentrations of methanol and O_2 used in this work, reactions (6) and (7) occur very rapidly and steady state can be assumed for the CH_2OH radicals and Cl atoms. Under these conditions the HO_2 radical production rate, B, can be described by

(I) $$B = 2k_5[Cl_2]$$

where k_5 is the chlorine photolysis rate constant in the system. Clearly the methanol concentration can be increased further without affecting the HO_2 production rate arising from Cl_2 photolysis. The methanol concentration was controlled by a flow of oxygen through a thermostatted bubbler containing methanol (A. R. GRADE, $H_2O \leqslant 1\%$) which was maintained at constant temperature by immersion in a water/ice mixture at 273 K. The methanol concentration was calculated by expression II

(II) $$[CH_3OH] = 2.46 \cdot 10^{19} \cdot \frac{P_v \cdot 273}{760 \cdot T_v} \cdot \frac{P_m}{P - P_m} \cdot \frac{F_{O_2}}{F_{tot}} \text{ molecules cm}^{-3}$$

where P, P_v and P_m are the pressures in the room, the reaction vessel and the methanol vapor pressure in the bubbler respectively. T_v is the reaction cell temperature, F_{O_2} is the flow of oxygen through the bubbler and F_{tot} the total flow of the gas mixture.

In each experiment the total flow was set to 1040 ml/min and the pressure of the reaction cell was atmospheric. The flow of oxygen (Breathing Grade) was varied, in accordance with eq. (II), to obtain the desired methanol concentration. The flow of 5% Cl_2/95% N_2 (B.O.C., Hy-Line Grade) was set to about 30 ml/min in each experiment. Nitrogen (High Purity Grade) was used as a diluent gas. The flows of oxygen and nitrogen were controlled by the use of a MKS mass flow controller. The chlorine concentration was determined in the UV at 330 nm ($\sigma = 2.8 \cdot 10^{-19}$ cm^2 molecule^{-1} [14]). The photolysis rate constant, k_5, was determined to be $1.8 \cdot 10^{-3}$ s^{-1} per lamp in a static system by monitoring the chlorine concentration as a function of light intensity and time, in the same way as described in previous work [4].

The precursor gas mixture flowed through a cylindrical quartz cell, volume 1.2 l and length 1.2 m, which was intermittently illuminated by photolysis lamps (Philips TL40/08 Blacklights, $\lambda_{max} = 350$ nm) driven by a square wave DC power supply. The cell was jacketed and its temperature was controlled by circulating a water/ethylene glycol mixture through the jacket.

Absorption was monitored on a collimated single pass light beam from a stabilized deuterium lamp and detected on a photo multiplier after dispersion on a 0.5 m monochromator (B & M Model BM50). The photomultiplier output was fed to a custom built multichannel signal averager which was linked to a Commodore (PET) microcomputer. This set up made it possible to obtain the averaged time resolved behavior of the HO_2 radical absorption during the photolysis cycle of time τ, where the lamp on period was between $t = 0$ and $t = \tau/2$ and the lamp off period from $t = \tau/2$ to τ. In a typical experiment τ was 1 s and 2000 cycles were averaged. The full details of the experimental set up have been described before [15].

Some experiments were carried out to estimate the H_2O_2 yield. They were conducted under static conditions with the H_2O_2 monitored in the UV at 220 nm ($\sigma = 2.7 \cdot 10^{-19}$ cm^2 molecule^{-1}), in the same way as described previously [4].

The rate constant, k_1, of the second order self decay was determined in the methanol range $1 \cdot 10^{16}$ to $3 \cdot 10^{17}$ molecules cm^{-3} at the temperatures 278 and 299 K.

Analysis of Data and Results

Typical behavior of the HO_2 radical absorption during a photolysis cycle is shown in Figure 1. During illumination, the reaction sequence (5)–(7) operates, and the radical concentration increases until the radical removal rate equals the production rate and a steady state in concentration is achieved. At time $t = \tau/2$ the light is switched off, the radical production rate equals zero, and a decay in concentration is seen.
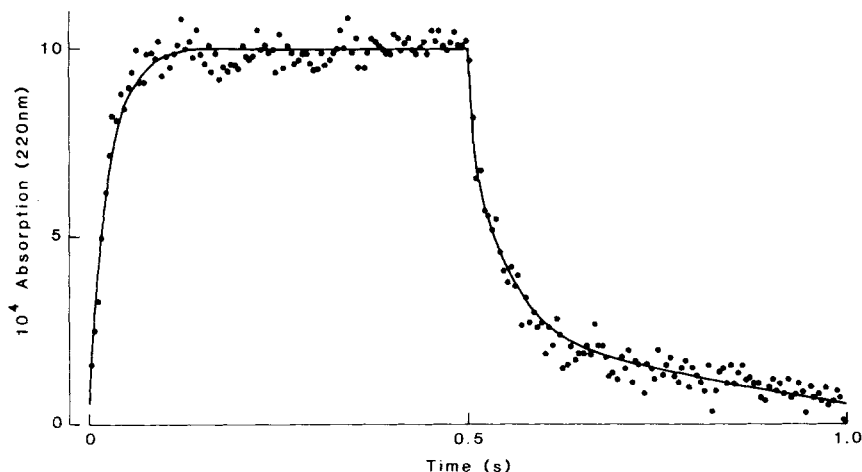

Figure 1. Typical modulated absorption profile for HO_2 ($\tau = 1.0$ s).

If HO_2 is removed only by reaction (1) then its behavior during a modulated photolysis cycle can be described by eq. (III),

$$\text{(III)} \qquad \frac{1}{2} \cdot \frac{dC}{dt} = \frac{B}{2} - k_1 C^2$$

where C is the HO_2 concentration.

When steady state is reached expression III equals zero and

$$\text{(IV)} \qquad B = 2k_1 C_{ss}^2$$

Integration of eq. (III) with eq. (IV) incorporated, yields the following expression for the concentration-time dependence of HO_2 during the "lamp on" period:

$$\text{(V)} \qquad \ln \frac{C_{ss} + C}{C_{ss} - C} = 4k_1 C_{ss}t$$

where a plot of $\ln(C_{ss} + C)/(C_{ss} - C)$ versus time will give a slope equal to $4C_{ss}k_1$ and k_1 can be calculated.

During the "lamp off" period, the rate expression for the HO_2 radical is reduced to

$$\text{(VI)} \qquad -\frac{1}{2} \cdot \frac{dC}{dt} = k_1 C^2$$

which on integration from $t = \tau/2$ becomes:

$$\text{(VII)} \qquad \frac{1}{C} = 2k_1 t + \frac{1}{C_{ss}}$$

A plot of $1/C$ versus time will give the slope $2k_1$.

The measured absorption, A, due to HO_2 is related to the concentration by the expression

$$\text{(VIII)} \qquad A + A_r = \sigma l C$$

where σ is the absorption cross section and l is the absorption path length. A small residual absorption term, A_r, needs to be introduced since the radical concentration does not decay to zero before the illumination restarts, and only the changes in absorption are recorded. The residual absorption can be derived as a function of B, σ, k_1 and the modulation period [16], but in this work the data were analyzed using the eqs. (V) and (VII) which were rewritten in terms of absorption by substitution of eq. (VIII) with A_r as a variable. The value of A_r was varied until linear plots for both rise and fall were obtained. These plots provided values of k_1/σ which could be compared, and since σ was known, k_1 could be calculated.

The value of A_r was always small compared with the steady state absorption (typically 5%). Figure 2 shows plots of eqs. (V) and (VII) for HO_2 corresponding to the build up and decay for different methanol
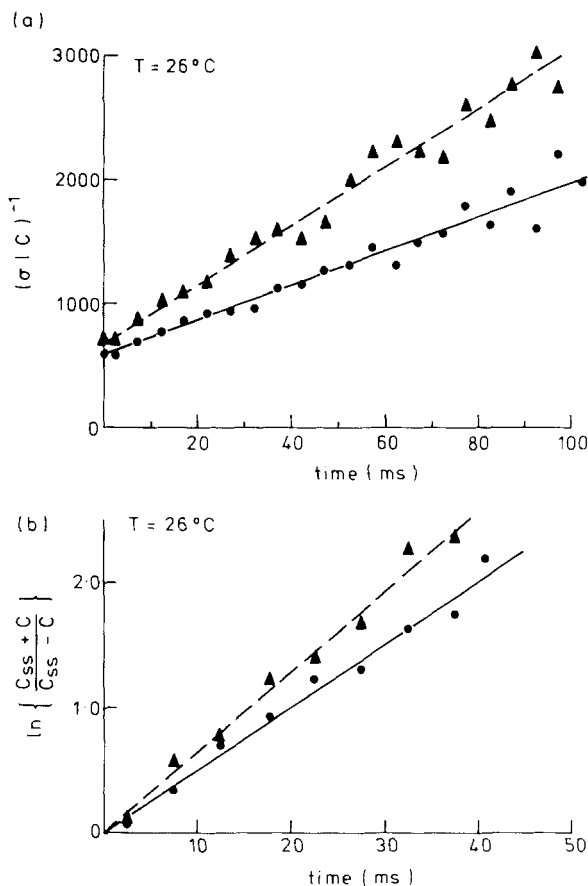
Figure 2.   (a) Plots of decay curves [eq. (VII)]. (b) Plots of build-up curves [eq. (V)].
Lines represent best fits to data with optimized residual absorption included.
(—), [CH$_3$OH] = 4.24 × 10^{16} molecule cm^3; (--), [CH$_3$OH] = 25.4 × 10^{16} mole-
cule cm^{-3}.

concentrations at 26° C. The plots represent 71% and 78% of the decay
and 81% and 85% of the build up curves for the experiments performed
with methanol concentrations of 4.24 × 10^{16} and 25.4 × 10^{16} mole-
cule cm^{-3} respectively. The lines on the graphs are the best fits to the
data after optimization of A_r. In each case the build up and decay
curves show reasonable linearity, with the same value of k_1 concluded
from both plots. No significant deviation from linearity was observed
for any of the conditions used, suggesting that the removal of HO$_2$ was
always second order.

The values of k_1 at varying methanol concentration are shown in
Table I and Figure 3. Within the experimental error the observed rate
constant, k_1, for the HO$_2$ self reaction appears to be a linear function

TABLE I. Experimental values of the HO$_2$ + HO$_2$ reaction rate constant, k_1, at various methanol concentrations and temperatures in nitrogen at atmospheric pressure.

$\dfrac{T}{°C}$	$\dfrac{c_{CH_3OH} \cdot 10^{-16}}{\text{molecules cm}^{-3}}$	$\dfrac{k_1 \cdot 10^{12}}{\text{cm}^3 \text{molecule}^{-1}\text{s}^{-1}}$
	1.29	3.01
	2.58	2.76
	2.61	2.85
	4.24	2.93
	8.59	4.16
26	12.8	4.62
	17.0	3.76
	21.3	5.15
	25.4	4.84
	25.5	5.95
	1.37	4.0
	2.75	4.72
	2.89	4.44
	4.59	6.28
5	9.21	6.69
	13.8	7.30
	18.3	8.21
	27.3	9.57
	27.4	11.88

of methanol concentration. Least square analysis gives the following expressions (IX and X), within a confidence level of 95%.

(IX) $\qquad k_1 = (4.2 \pm 1.0) \cdot 10^{-12} + (2.4 \pm 0.6)$

$\qquad\qquad \cdot 10^{-29}[CH_3OH]cm^3 \text{ molecule}^{-1} s^{-1}, \qquad T = 278 \text{ K}$

(X) $\qquad k_1 = (2.7 \pm 0.6) \cdot 10^{-12} + (1.1 \pm 0.4)$

$\qquad\qquad \cdot 10^{-29}[CH_3OH]cm^3 \text{ molecule}^{-1} s^{-1}, \qquad T = 299 \text{ K}$

Generally the experimental rate constant at each temperature can be expressed by
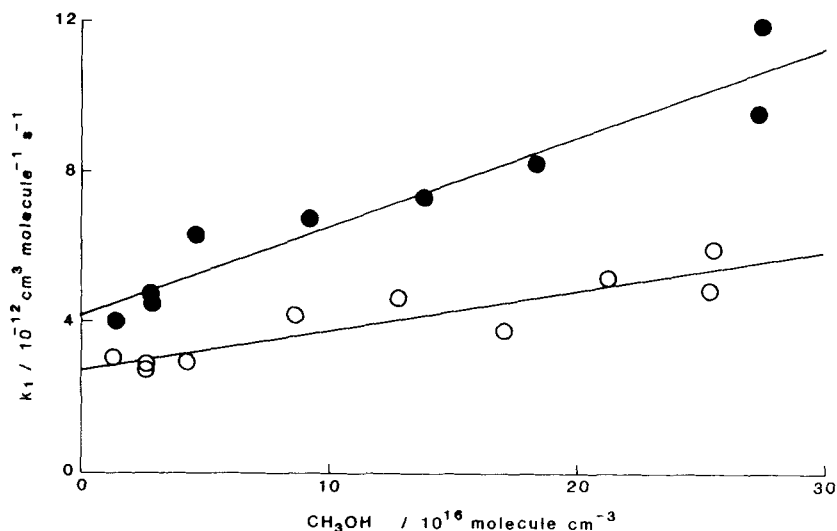
(XI) $\qquad\qquad\qquad k_1 = k_0 + k'[CH_3OH]$

Figure 3.   Measured value of k_1 as a function of [CH$_3$OH].

The corresponding Arrhenius expressions for k_0 and k' from the data at the two temperatures investigated are as follows:

(XII) $k_0 = 9.2 \cdot 10^{-15} \exp(1700/T)$

(XIII) $k' = 2.1 \cdot 10^{-34} \exp(3000/T)$

Owing to the limited amount of temperature dependence data, the uncertainties in these expressions are large, the quoted values of E/R being accurate to $\pm70\%$ and $\pm50\%$ for eqs. (XII) and (XIII) respectively.

All HO$_2$ reacting is expected to give H$_2$O$_2$ and O$_2$ in accordance with reaction (1) and at steady state the rate expression for H$_2$O$_2$ formation is:

(XIV) $\dfrac{d[\text{H}_2\text{O}_2]}{dt} = k_1[\text{HO}_2]^2_{ss} = B/2$

The H$_2$O$_2$ yield, ϕ, then is given by

(XV) $\phi = \dfrac{d[\text{H}_2\text{O}_2]/dt}{B/2}$

At 299 K the yield was 36% at a methanol concentration of $2.8 \cdot 10^{16}$ molecule cm^{-3} and 26% at $2.8 \cdot 10^{17}$ molecule cm^{-3}. At 278 K the yield of H$_2$O$_2$ was about 10% independent of methanol concentration.

Discussion

From Table II it can be seen that the rate constants obtained in this work for the HO$_2$ self reaction at zero methanol concentration are in agreement, within the experimental error, with earlier determinations in the same temperature and pressure region.

Data from this work provides further evidence that strong dipolar hydrogen bonding species influence the second order HO$_2$ self reaction. A linear increase of the rate constant with methanol concentration is found according to eqs. (IX) and (X). The same behavior has been found experimentally for water [4,5]. However, the effect of ammonia [17] is given by an equation of the form:
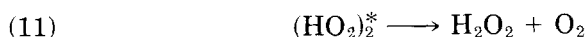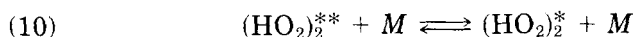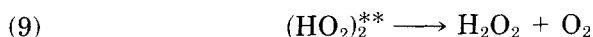
$$k_{exp} = \frac{k_0 + k'[X]}{(1 + K[X]^2)}$$

where X is NH$_3$. If $K[X] \ll 1$ this equation reduces to a linear form as observed for water. Small amounts of water may have been generated in the present system from the wall decomposition of H$_2$O$_2$. The resultant concentrations would be too low, however, to have any effect on reaction (1), based on the previously reported dependences. Similarly, HCl was produced [reaction (6)], and may be expected to form strong dipolar hydrogen bonds with HO$_2$. In these experiments, its concentration was ca. 1×10^{15} molecule cm^{-3} and remained approximately constant for the range of conditions used. Thus the observed changes in the value of k_1 are attributed to the effect of methanol.

TABLE II. Comparison of the HO$_2$ self reaction rate constant, k_o, in nondipolar environments.

Investigator	diluent gas	pressure torr	temperature K	rate constant·10^{12} cm^{3}molecule^{-1}s^{-1}
Hamilton and Lii[17]	H$_2$	1520	298	2.5
Cox and Burrows[4]	N$_2$	760	298	2.35±0.2
	N$_2$	760	273	3.4±0.2
	N$_2$	760	278	3.5±0.2
Sander et.al.[1]	N$_2$	700	298	2.97±0.45
Simonaitis and Heicklen[3]	N$_2$	760	296	2.5±0.1
Kircher and Sander[5]	N$_2$	700	269	3.55±0.24
This work	N$_2$	760	299	2.7±0.6
	N$_2$	760	278	4.2±1.0

Cox [18] and Mozurkewich and Benson [7] have suggested a mechanism for the HO_2 self reaction which proceeds via an excited dimer, $(HO_2)_2^{**}$, which is in equilibrium with HO_2. The excited dimer can either decompose to products directly or can be stabilized to a less excited dimer $(HO_2)_2^*$, which also has no energy barrier to overcome when decomposing to products.

$$(8) \qquad HO_2 + HO_2 \rightleftharpoons (HO_2)_2^{**}$$

$$(9) \qquad (HO_2)_2^{**} \longrightarrow H_2O_2 + O_2$$

$$(10) \qquad (HO_2)_2^{**} + M \rightleftharpoons (HO_2)_2^* + M$$

$$(11) \qquad (HO_2)_2^* \longrightarrow H_2O_2 + O_2$$

In the presence of hydrogen bonding species such as H_2O, CH_3OH and NH_3, HO_2 is in equilibrium with a hydrogen bonded complex according to the equation:

$$(12) \qquad HO_2 + X \rightleftharpoons X \cdot HO_2$$

The equilibrium constant is related to the reaction enthalpy change ΔH_{12}° and the entropy change ΔS_{12}° by the following expression:

$$(XVI) \qquad K_{12} = \frac{[HO_2 \cdot X]}{[HO_2][X]} = \exp(\Delta S_{12}^\circ / R)\, \exp(-\Delta H_{12}^\circ / RT)$$

Here ΔH_{12}° should correspond to the strength of the hydrogen bond. An HO_2 radical may displace the hydrogen bonding species in the complex, giving a stabilized $(HO_2)_2$ dimer

$$(13) \qquad X \cdot HO_2 + HO_2 \rightleftharpoons (HO_2)_2 + X$$
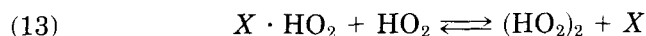
This step is assumed to occur at approximately collision frequency. $(HO_2)_2$ can undergo collisional excitation to become the "less excited" dimer mentioned above, $(HO_2)_2^*$ [reaction (14)], which will decompose to products by reaction (11).

$$(14) \qquad (HO_2)_2 + M \rightleftharpoons (HO_2)_2^* + M$$
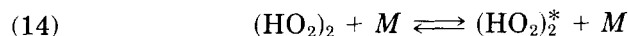
The experimental rate constant for the mechanism as described by Mozurkewich and Benson, can be expressed as

(XVII)

$$k_{exp} = \left[k_{II} + \frac{k_{III}[M] + fk_{13}K_{12}[X]}{1 + (k_{III}[M] + fk_{13}K_{12}[X])/(k_\infty - k_{II})} \right] \Big/ (1 + K_{12}[X])^2$$

where

$$k_{II} = K_8 k_9$$

$$k_{III} = K_8 k_{10}$$

$$k_\infty = (k_9 + k_{11}K_{10})K_8$$

$$f = k_{14}[M]/(k_{14}[M] + k_{-13}[X])$$

The value of f normally equals unity except when the ratio $[X]/[M]$ is very high.

If f equals unity and the expressions $(k_{III}[M] + fk_{13}K_{12}[X])/(k_x - k_{II})$ and $K_{12}[X]$ are much less than unity then (XVII) can be rewritten as

(XVIII) $$k_{exp} = k(P) + k_{13}K_{12}[X]$$

where $k(P)$ is the overall rate constant at a given pressure and in the absence of X. This expression is consistent with the experimentally observed methanol dependence, eq. (XI). Hence, $k(P)$ and $k_{13}K_{12}$ should correspond to k_O and k' respectively.

The methanol dependence can, according to this mechanism, be described by

(XIX) $$k' = k_{13}K_{12} = k_{13} \exp(\Delta S^\circ_{12}/R) \exp(-\Delta H^\circ_{12}/RT)$$

Since k_{13} will have near zero temperature dependence, the observed temperature dependence of k' can be related to the stabilization enthalpy of the hydrogen bonded complex, which should correspond to the strength of the hydrogen bond.

From this work the stabilization energy in the methanol complex is 25 kJ mol^{-1} according to XIII. The uncertainty on this value is large ($\pm 50\%$) since only two temperatures were studied. By fitting the data of Kircher and Sander [5] and Lii et al. [6] to their model, Mozurkewich and Benson derived stabilization energies in the complexes of water and ammonia of 28.0 kJ mol^{-1} and 32.7 kJ mol^{-1} respectively. It appears that the stabilization energies for the HO₂ radical are of comparable magnitude for the three hydrogen bonding species studied, and are about the same as the strength of a normal hydrogen bond in all the complexes. This supports the mechanistic model and the corresponding potential energy surface suggested by Mozurkewich and Benson, where the complex of HO₂ and the hydrogen bonding species is in equilibrium with its precursors and the displacement of the hydrogen bonding species with HO₂ is exothermic with no energy barrier to overcome.

The hydrogen bonds $O-H\cdots O$, $H-O\cdots H$ and $H-N\cdots H$ are strong whereas $N-H\cdots O$ is a weak bond. Since the stabilization energies in the NH₃, H₂O and CH₃OH complexes are similar in magnitude it seems likely, therefore, that the hydrogen in HO₂ is bonded to the nitrogen in ammonia. The same kind of bonding can be assumed for methanol and water, i.e. the oxygen in methanol and water is bonded to the hydrogen in the HO₂ radical.

The largest H₂O₂ yield found in this work was 36%, with the value reducing at higher methanol concentrations and lower temperatures. Cox and Burrows [4] found the yield of H₂O₂ to be about 80% for the HO₂ self reaction in nitrogen at atmospheric pressure. When adding water to the system the yield was only about 40% at 298 K which is about the yield obtained in the methanol environment at the same

temperature. Clearly the presence of strong dipolar hydrogen bonding species significantly affects the observed yield of H_2O_2. This may be explained if the stabilized $(HO_2)_2$ dimer is removed by an additional route not producing H_2O_2 (e.g. wall removal). The low yields may also be explained, however, if H_2O_2 decomposes more readily at the reaction vessel surfaces when strongly adsorbing species such as methanol or water are present in the system. The latter explanation is favored since the lifetime of $(HO_2)_2$ before collisional excitation is almost certainly too short for wall removal to compete.

Conclusion

The data obtained in this work are consistent with the mechanism suggested by Mozurkewich and Benson [7] for the self reaction of HO_2. The calculated energies for the complexes of HO_2 with methanol, water, and ammonia are all comparable with the energy of a normal hydrogen bond. Although this study is in agreement with the reaction scheme suggested by Mozurkewich and Benson for the HO_2 self reaction, more kinetic and thermodynamic data are needed for the reaction in the presence of different hydrogen bonding species. This would give more information about the structure of the hydrogen bonded complexes and the $(HO_2)_2$ dimer. Studies at high and low pressures in hydrogen bonding environments would help to verify the mechanism of the HO_2 self reaction. At the high pressure limit, a depression of the reaction rate by hydrogen bonding species should be seen, and at the low pressure limit, the reaction rate should not be affected by hydrogen bonding species if the mechanism suggested by Mozurkewich and Benson is correct.

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