REACTIONS OF HO2 WITH NO, OH AND HO2 STUDIED BY EPR/LMR SPECTROSCOPY

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A combined EPR/LMR spectrometer and fast-flow system has been used to investigate the reactions HO₂ + NO(k_1), HO₂ + OH(k_2), HO₂ + HO₂(k_3) at room temperature. The rate constants have been measured: $k_1 = (7.0 \pm 0.6) \times 10^{-12}$ cm³ s⁻¹ (P = 7-10 Torr); $k_2 = (5.2 \pm 1.2) \times 10^{-11}$ cm³ s⁻¹ (P = 8-10 Torr); $k_3 = (1.65 \pm 0.3) \times 10^{-12}$ cm³ s⁻¹ (P = 2.1-24.9 Torr). The conclusion is drawn from analysis of the literature and the present work that k_2 and k_3 do not depend on pressure up to 1 atm.

1. Introduction

The reactions of "odd hydrogen" (H, OH, HO_2) play a central role in combustion [1,2] and in atmospheric chemistry [3]. Therefore studies of the reactions which convert one of these radicals to another, e.g.

$$HO_2 + NO \xrightarrow{\kappa_1} NO_2 + OH,$$
 (1)

and the reactions between these radicals,

$$\mathrm{HO}_{2} + \mathrm{OH} \xrightarrow{k_{2}} \mathrm{H}_{2}\mathrm{O} + \mathrm{O}_{2}, \qquad (2)$$

$$HO_2 + HO_2 \xrightarrow{k_3} H_2O_2 + O_2, \qquad (3)$$

are of considerable interest.

Reaction (1) has been studied very well. Fair agreement in the values of k_1 at room temperature has been obtained in recent works ((7–10) × 10⁻¹² cm³ s⁻¹) [4–9]. Reactions (2) and (3) have been studied much less successfully. The rate constants have an uncertainty of about one order of magnitude. Furthermore a pressure dependence of k_2 and k_3 has been assumed in some papers.

Reactions (1)–(3) were investigated here at room temperature using a combined electron paramagnetic resonance/laser magnetic resonance (EPR/LMR) spectrometer [10,11]. Recently this apparatus was used to study NF₂ reactions with O and N atoms [12].

2. Experimental

The EPR/LMR spectrometer was used in combination with a fast-flow system. The apparatus is shown in fig. 1. The detection section was placed in the EPR cavity and in the optical cavity of a CO_2 laser. The absorption of infrared and 3 cm radiation occurred along a 3 cm zone where the modulation rods were set. The EPR cavity hole was 1.6 cm diameter to register an electric dipole EPR absorption (OH, NO). The reactor was a quartz tube 45 cm long and 2.5 cm inner diameter. The walls were coated with teflon. The radicals were produced in a movable source [13].

The hydroperoxyl radicals were obtained at 2-3Torr in the reaction

$$F + H_2O_2 \rightarrow HF + HO_2 \tag{4}$$



Fig. 1. Experimental apparatus.

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and at 8-25 Torr in the reaction

$$H + O_2 + M \rightarrow HO_2 + M.$$
⁽⁵⁾

H and F atoms were generated in a microwave discharge from H₂ and CF₄ respectively in the presence of a large excess of He (more than one hundredfold). The absolute atom concentrations were measured by means of EPR [14]. A small amount of oxygen molecules ($\approx 10^{15}$ cm⁻³) was admitted into the detection zone to reduce the relaxation times of the magnetic sublevels of H atoms. Under these conditions atomic hydrogen could be detected at a concentration of 10^{11} cm⁻³. The radical injector inner tube was made from teflon for H atoms and from duralumin for F atoms.

Calibration plots of LMR signal versus initial atom concentration $[H]_0$ and $[F]_0$ were made for every run (fixed values of pressure, $[O_2]$ or $[H_2O_2]$). All these plots have linear initial parts. Thus complete atom consumption occurred and secondary reactions

$$H + HO_2 \rightarrow OH + OH,$$

$$\rightarrow H_2 + O_2,$$
 (6)

or

$$F + HO_2 \rightarrow HF + O_2, \tag{7}$$

were absent in these cases. In all our experiments complete atom consumption took place when $[HO_2] \le 10^{12} \text{ cm}^{-3}$.

The OH radicals were obtained in reactions (5) and (6), when the calibration plots showed appreciable curvature. The absolute OH concentration was measured by means of EPR [14]. At the radical injector entrance we observed HO₂ and OH only, and with an uncertainty of 10% the relation $[H]_0 = [HO_2] + [OH]$ was fulfilled.

The purities of gases used were 99.99% (He), 99.98% (O_2), 99.5% (CF_4) and 99.98% (H_2). The concentration of H_2O_2 in solution was 99%. The description of additional purification of the gases, measurements of atom and radical concentrations, etc., is given elsewhere [13].

The kinetics were obtained by varying the distance between the radical injector and the detection zone. The flow velocity was in the range $100-2200 \text{ cm s}^{-1}$. The experiments at low HO₂ concentration (<10¹² cm⁻³) showed that HO₂ wall decay occurred with



Fig. 2. (a) Plot of LMR signal J_{HO_2} versus contact time for the reaction HO₂ + NO. (1) [NO] = 0; (2) [NO] = 1.23 × 10¹³ cm⁻³; (3) [NO] = 2.7 × 10¹³ cm⁻³; (2', 3') accounting the duct velocity (Poiscuille) profile [16]. (b) Plots of [HO₂] (1) and [OH] (2) versus contact time (*P* = 9.6 Torr, [O₂] = 2.1 × 10¹⁷ cm⁻³).

a rate constant $k_{w}^{HO_2} = 2-4 \text{ s}^{-1}$ (see also ref. [15]). Reaction (1) was investigated at pressures 7–10

Torr. Reaction (1) was investigated at pressures 7–10 Torr. Reaction (5) was used as the HO₂ source, and $[HO_2]_0 \le 10^{12} \text{ cm}^{-3}$. Some kinetic curves are shown in fig. 2a. The influence of secondary process (2) was negligible because $k_1 [NO] / k_2 [OH] \ge 1$ and the OH wall decay was large ($k_w^{OH} = 60 \pm 10 \text{ s}^{-1}$). The OH wall decay was measured when the reaction H + NO₂ \rightarrow OH + NO was used as the OH source. A series of seven runs gave an average value of

$$k_1 = (7.0 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$$
.

Reaction (2) was studied at pressures 8-10 Torr. The measurements were carried out at $[HO_2]_0 = (5-9) \times 10^{12}$ cm⁻³ and $[OH]_0 = (3-7) \times 10^{12}$ cm⁻³. Examples of plots of HO₂ concentration (curve 1) and OH concentration (curve 2) versus contact time are given in fig. 2b. The OH and HO₂ concentrations were comparable and therefore the reactions HO₂ + HO₂ and OH + OH can be neglected because reaction (2) is much faster.



Fig. 3. Second-order decay plot for the reaction HO₂ + HO₂ (P = 22.5 Torr, [HO₂]₀ = 1.1 × 10¹³ cm⁻³, v = 194 cm s⁻¹).

Eight pairs of plots (see fig. 2b) were considered. Only reaction (2) and heterogeneous OH decay with $k_w^{OH} = 60 \text{ s}^{-1}$ were taken into account, giving the average value

 $k_2 = (5.2 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

Reaction (3) was investigated when the initial HO₂ concentration, $[HO_2]_0$, was equal to the concentrations of H or F atoms consumed. The typical second-order decay plot for HO₂ is shown in fig. 3. The experiments were carried out at pressures 2.1–24.9 Torr

Table 1 Measurements of rate constant of the reaction $HO_2 + HO_2$ and at $[HO_2]_0 = 4 \times 10^{12} - 6.8 \times 10^{13} \text{ cm}^{-3}$. At the lowest HO₂ concentrations HO₂ wall decay was taken into account. The results are given in table 1. One can see from this table that within the error limits the value of the reaction (3) rate coefficient is contant in the pressure range 2.1–24.9 Torr:

$$k_3 = (1.65 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$$
.

3. Discussion

The value of k_1 obtained in this work is in agreement with the results of recent studies [4-9]. This fact confirms the reliability of information obtained by means of the technique used.

The value of k_2 has been measured earlier at room temperature in many places [7,9,16–32]. The experiments carried out at about 1 atm gave a high value of k_2 = (1-2) × 10⁻¹⁰ cm³ s⁻¹ [16–18,22–24,28,30,32]. At low pressure (1–3 Torr) a low value was obtained, k_2 = (2–7) × 10⁻¹¹ cm³ s⁻¹ [19–21,27,29]. Therefore some authors came to the conclusion that k_2 depended on pressure [22,23]. In only one case was a method for measurement of k_2 at different pressures used; Temps and Wagner obtained k_2 = (6.7 ± 2.3)

Р (Тогг)	HO ₂ source	$10^{-12} [HO_2]_0 (cm^3)$	$10^{12}k_3 (\text{cm}^3 \text{ s}^{-1})$	
 2.1	F + H ₂ O ₂	10	2.1	
2.15	$F + H_2O_2$	68	1.65	
2.7	$F + H_2O_2$	7.5	1.6	
8.5	$H + O_2 + M$	4	1.8	
9.3	$H + O_{2} + M$	6	1.5	
9.8	$H + O_{2} + M$	30 a)	2.0	
12	$H + O_2 + M$	7	1.2	
12.5	$H + O_2 + M$	7.5	2.0	
13.8	$H + O_2 + M$	16	1.2	
15	$H + O_2 + M$	11.5	1.85	
19.6	$H + O_2 + M$	9	1.45	
21.2	$H \div O_2 + M$	17.5	1.9	
20.5	$H + O_2 + M$	15	1.2	
22.5	$H + O_2 + M$	11	1.9	
24.9	$H + O_2 + M$	13	1.7	
		$k_{3,av} = (1.65 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$		

a) HO_2 was measured by means of comparison with the LMR spectrum of NF₂ radicals [13].

 $\times 10^{-11}$ cm³ s⁻¹ at P = 1.6, 5, 10 Torr [31]. Our value of k_2 (8–10 Torr) is in good agreement with this result.

In previous studies relative measurements were made with respect to reference reactions, or computer simulations were used. For example De More [30] has used the value $k_3 = 3.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ to ob $tain k_2 = 1.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ (P = 1 atm). If we assume the more reliable value $k_3 = (1.6-1.8) \times 10^{-12}$ $\text{cm}^3 \text{ s}^{-1}$ then the value from ref. [30] becomes k_2 = 7.7 \times 10⁻¹¹ cm³ s⁻¹. Another example is the lowpressure study of Burrows et al. [7]. The authors of ref. [7] used the value 8×10^{-13} cm³ s⁻¹ for the rate constant of the reference $OH + H_2O_2$ reaction. The value accepted now is $(1.7-1.8) \times 10^{-12} \text{ cm}^3$ s^{-1} [33,34]. Therefore the value 5.1 × 10⁻¹¹ cm³ s⁻¹ obtained in ref. [7] becomes $k_2 = 1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Thus the revision of previous data mixes up the lowpressure and high-pressure results.

The pressure dependence of the rate constant of reaction (2) is doubtful.

The experimental values of k_3 obtained in different studies are given in fig. 4. The data in fig. 4a are related to the low-pressure range (2-25 Torr). The results obtained in this work (O₂ and He as diluent gases) are in good agreement with a recent diode laser study of Thrush and Tyndall (7-20 Torr, O₂ as diluent gas) [26]. Satisfactory agreement is obtained with results of refs. [37,38]. But the value of k_3 obtained in the present work at pressures 2-3 Torr is in substantial disagreement with the results of the early LMR study of Thrush and Wilkinson (2-4 Torr, He and Ar as diluent gases) [39].

The data for the high-pressure range (25-1500Torr) are given in fig. 4b. All these values have been obtained by means of the ultraviolet absorption technique. The ratio of k_3 and the optical absorption cross section σ near 230 nm has been measured in these works. It seems that the large difference in the values obtained $(1.4-4.7) \times 10^{-12}$ cm³ s⁻¹ is connected with uncertainty provoked by the difficulty of the determination of σ . In this pressure range, emphasis on the effect of pressure on k_3 was placed in four works [37,38,40,45]. The weak but evident pressure dependence of k_3 was found in the study of Sander et al. only [40].

We are of the opinion that the combined results given in fig. 4 show that it is likely that the pressure



Fig. 4. Experimental values of the rate constant of the reaction HO₂ + HO₂. (a) Low pressure (2-25 Torr): open area, this work (O₂ and He as diluent gases); counter-hatched area, ref. [36] (O₂); •. ref. [37] (O₂); •, ref. [38] (N₂); •, ref. [39] (He); \triangle , refs. [7,39]; \square , ref. [35]. (b) High pressure (25-1500 Torr): •, ref. [40] (SF₆); •, ref. [40] (He); hatched area and \triangle , ref. [38] (N₂); +, ref. [38] (He); \square , ref. [41] (N₂); •, ref. [22] (O₂ + H₂), ∇ , ref. [42] (N₂); •, ref. [43] (N₂); \square , ref. [44] (H₂); counter-hatched area, ref. [45] (H₂); \times , ref. [46] (H₂); open area, ref. [37] (O₂); *, ref. [47] (He).

dependence of the rate constant of the HO_2 selfreaction in the range 1–1500 Torr is absent.

Nevertheless reaction (3) probably proceeds via an H_2O_4 intermediate. The observed negative temperature dependence of k_3 [37,43,48,49] confirms this assumption. If we assume that k_3 does not depend on pressure until 1500 Torr the lifetime of an intermediate is shorter than the time between collisions, e.g. $\tau < 10^{-10}$ s. FTIR experiments [50] and Nangia and Benson's calculations [51] show that the hydrogen-bonded cyclic dimer $(HO_2)_2$ is the only possible intermediate.

Reaction (3) can proceed along two channels:

HO₂(
$$\tilde{X}^{2}A''$$
) + HO₂($\tilde{X}^{2}A''$)
→ H₂O₂ + O₂($^{3}\Sigma_{g}^{-}$)
+ 37.6 kcal/mole,
(3')
→ H₂O₂ + O₂($^{1}\Delta_{g}$)
+ 15.1 kcal/mole.

(3'')

We believe the (3") channel is dominant. If HO₂ radicals approach on the triplet potential surface, a potential barrier of some kcal/mole must exist, but a negative temperature dependence of k_3 has been observed. If true, it is necessary to take into account the secondary reactions:

HO₂(
$$\widetilde{X}^{2}A''$$
) + O₂($^{1}\Delta_{g}$) $\xrightarrow{k_{8}}$ HO₂($\widetilde{A}^{2}A'$) + O₂($^{3}\Sigma_{g}^{-}$),
(8)
 $k_{8} = 1.7 \times 10^{-12} \text{ cm}^{3} \text{ s}^{-1}$ [52],

$$k_8 = 3.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} [53];$$

HO₂($\widetilde{A}^2 A'$) + M $\xrightarrow{k_9}$ HO₂($\widetilde{X}^2 A''$) + M, (9)

$$k_9 = 2.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} (\text{M} = \text{He}) [54];$$

HO₂($\widetilde{A}^2 A'$) + O₂($^{1}\Delta_g$) $\xrightarrow{k_{10}}$ H + 2O₂($^{3}\Sigma_g^-$), (10)

 $k_{10} = 1.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ [52];

$$HO_{2}(\widetilde{X}^{2}A'') + H \xrightarrow{\kappa_{11}} OH + OH, \qquad (11)$$

$$k_{11} = 3.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ [55]};$$

$$HO_2(\widetilde{X}^2 A'') + OH \xrightarrow{k_{12}} H_2 O + O_2, \qquad (12)$$

$$k_{12} = 5.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ (this work)}.$$

Calculations assuming the scheme (3''), (8)-(12)show that the contribution from processes (8)-(12)is negligible in our experiments due to the fact that $[HO_2]/[M] \leq 1$.

 $O_2({}^{1}\Delta_g)$ EPR detection was impossible because of the relatively low sensitivity ($\approx 5 \times 10^{13} \text{ cm}^{-3}$).

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