Atmospheric Reactions of the HO$_2$ Radical Studied by Laser Magnetic Resonance Spectroscopy

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By J. P. Burrows, D. I. Cliff, G. W. Harris,
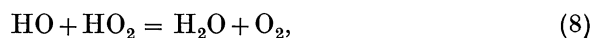B. A. Thrush, F.R.S. and J. P. T. Wilkinson

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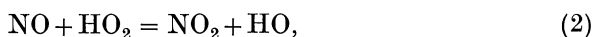Lensfield Road, Cambridge CB2 1EP, U.K.*

Measurement of the rotational spectra of HO_2 and HO by laser magnetic resonance has been used to determine rate coefficients for reactions of HO_2 in a fast flow system at low pressures and ambient temperatures. Processes of atmospheric importance were studied and the rate coefficients obtained were:

$$O + HO_2 = HO + O_2, \tag{4}$$
$$k_4 = (3.1 \pm 1.0) \times 10^{-11} \, cm^3 \, molecule^{-1} \, s^{-1},$$
$$HO + HO_2 = H_2O + O_2, \tag{8}$$
$$k_8 = (5.1 \pm 1.7) \times 10^{-11} \, cm^3 \, molecule^{-1} \, s^{-1},$$
$$NO + HO_2 = NO_2 + HO, \tag{2}$$
$$k_2 = (8.2 \pm 2.4) \times 10^{-12} \, cm^3 \, molecule^{-1} \, s^{-1},$$
$$HO_2 + Cl = HCl + O_2, \tag{17}$$
$$k_{17} = (4.1 \pm 1.4) \times 10^{-11} \, cm^3 \, molecule^{-1} \, s^{-1},$$
$$HO_2 + Cl = HO + ClO, \tag{17a}$$
$$k_{17a} \leqslant 3 \times 10^{-13} \, cm^3 \, molecule^{-1} \, s^{-1},$$
$$HO_2 + SO_2 = HO + SO_3, \tag{21}$$
$$k_{21} \leqslant 2 \times 10^{-17} \, cm^3 \, molecule^{-1} \, s^{-1},$$
$$HO_2 + SO_2 + He = HO_2SO_2 + He, \tag{21a}$$
$$k_{21a} \leqslant 4 \times 10^{-34} \, cm^6 \, molecule^{-1} \, s^{-1},$$
$$HO_2 + CO = HO + CO_2, \tag{22}$$
$$k_{22} \leqslant 2 \times 10^{-17} \, cm^3 \, molecule^{-1} \, s^{-1},$$
$$HO_2 + CO + He = HCO_3 + He, \tag{22a}$$
$$k_{22a} \leqslant 4 \times 10^{-34} \, cm^6 \, molecule^{-2} \, s^{-1}.$$
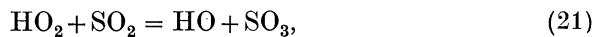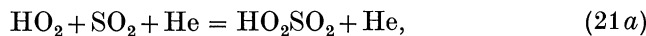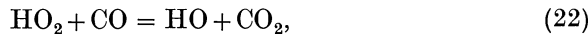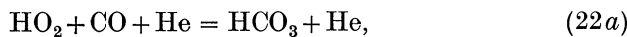
The disproportionation of two HO_2 radicals was shown to proceed more slowly in argon carriers at total pressures around 2 Torr than had been reported at higher total pressures. Upper limits for k_{19} were

$$HO_2 + HO_2 = H_2O_2 + O_2 \tag{19}$$
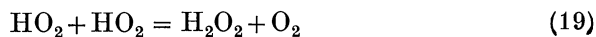
found to lie in the range $(7.5 \pm 5.0) \times 10^{-13} \, cm^3 \, molecule^{-1} \, s^{-1}$.

[463]

INTRODUCTION

The hydrogen containing radicals H, HO, and HO_2, collectively known as HO_x, play a central role in stratospheric chemistry. They are formed mainly by the attack on water vapour of excited oxygen atoms, $O(^1D)$, produced by the short wavelength photolysis of ozone. This process generates HO radicals which are rapidly inter-converted with H and HO_2 by the reactions shown in figure 1. These radicals are removed from the atmosphere by mutual combination reactions of which those between HO and HO_2 and between two HO_2 radicals are believed to be dominant. Thus reactions of the HO_2 radical partly determine the stratospheric densities of HO, a species which plays a major role in ozone removal cycles by converting the active species NO_2 to HNO_3, and reconverting HCl to Cl, which is a chain carrier in the chlorine catalysed decomposition of ozone.

$$O(^1D) + H_2O, CH_4, H_2 \longrightarrow HO, H$$

$$H_2O + h\nu \longrightarrow HO, H$$

$$HO + HO_2 = H_2O + O_2$$
$$HO_2 + HO_2 = H_2O_2 + O_2$$
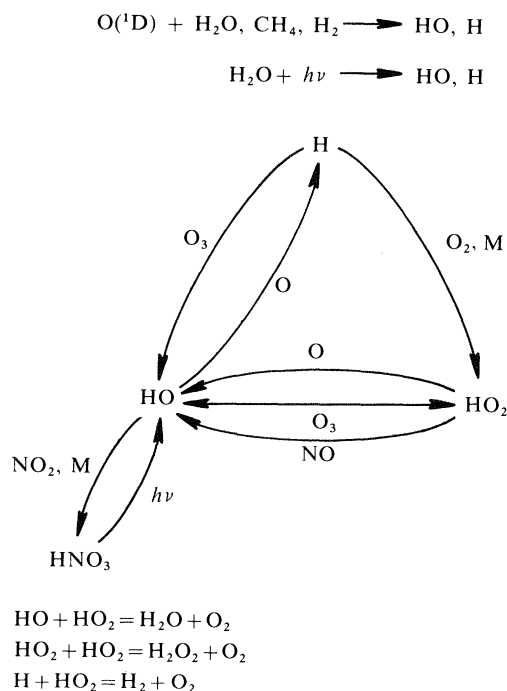$$H + HO_2 = H_2 + O_2$$

FIGURE 1. The role of HO_2 in the chemistry of the atmosphere.

Direct measurements of reaction rates for HO_2 have, until comparatively recently, been rendered difficult by the lack of a sensitive and unequivocal method for detecting this species. In the pioneering mass spectrometric studies of Foner & Hudson (1953, 1962) it was difficult to determine the absolute sensitivity, and formation of HO_2^+ from other sources could cause interference. Leu & DeMore (1976) estimate a factor of 2 uncertainty in the absolute sensitivity of a mass spectro-meter for HO_2. The modulated photolysis studies of Paukert & Johnston (1972), the

pulse radiolysis studies of Hochanadel *et al.* (1972) and the shock tube studies of Troe (1970) all relied on the strong continuous absorption of HO_2 near 230 nm. Other species present in the system may absorb in this region, the absorption coefficient may change with temperature, and recently Hamilton & Lii (1977) have shown that HO_2 forms a hydrate which also absorbs in this spectral region and can react at different rates from free HO_2.

The near infrared electronic spectrum of HO_2, studied by Becker *et al.* (1974), and by Freedman & Jones (1976), is very weak and lies in an awkward region for the photoelectric measurement needed for kinetic studies (1.2 μm). The observation of the rotational spectrum by laser magnetic resonance spectroscopy (Radford *et al.* 1974) provides a very sensitive method for detecting HO_2, since the intensity of such spectra is proportional to the square of components of the dipole moment which is large for HO_2 (Buenker & Peyerimhoff 1976; S. Saito 1978, personal communication).

Preliminary measurements using this technique have already been reported (Burrows, *et al.* 1977) and its independent use in studies of the reactions of HO_2 with NO and NO_2 has been reported (Howard & Evenson 1977; Howard 1977).
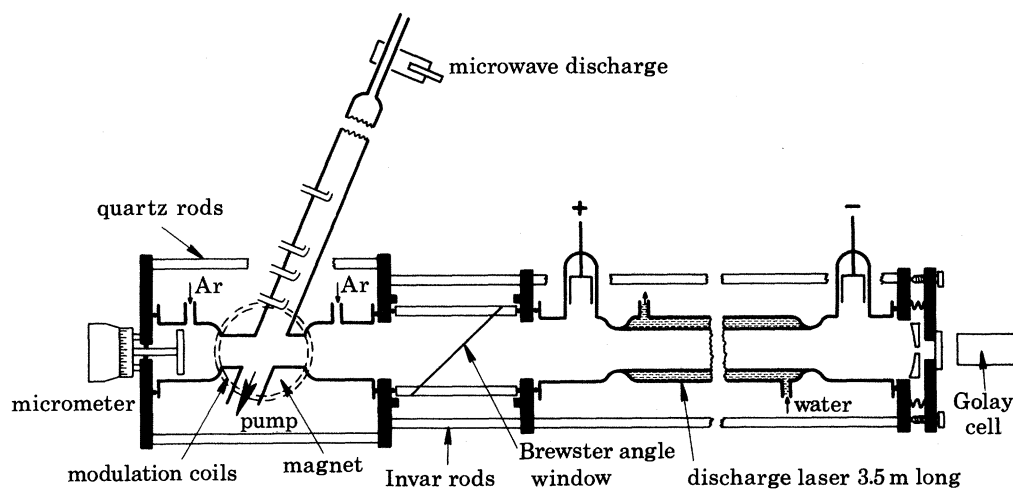

FIGURE 2. Laser magnetic resonance spectrometer for kinetic studies.

EXPERIMENTAL

Figure 2 is a cross sectional diagram of the experimental apparatus. HO and HO_2 radicals, generated in a conventional discharge-flow system, are monitored by using a strong magnetic field to bring Zeeman components of their rotational transitions into resonance with a water vapour laser. Sensitivity is enhanced by detecting the free radicals within the laser cavity, and physical separation of the reaction and laser sections was achieved by an 8 μm thick polypropylene film set at the Brewster

angle, in a mount that could be rotated to achieve the desired orientation between the magnetic field and the electric vector of the laser radiation.

The laser cavity, which was 5.5 m long and approximately 50 mm in diameter, was formed by two gold coated Pyrex mirrors with radius of curvature of 6 m giving a confocal arrangement. The laser was normally operated on the 118.6 µm line of water vapour obtained by a current stabilized d.c. discharge, typically of 2 kV at 1 A, between a stainless steel anode and a water-cooled copper cathode, approximately 3.5 m apart. Water vapour at a pressure of about 50 Pa flowed slowly through this section. It was found that the addition of hydrogen to the lasing gas or the use of an argon or helium carrier did not give any consistent improvement in signal : noise ratio. The laser line was identified by using the micrometer to move one mirror through successive mode maxima. A small proportion of the laser radiation passed through a 1 mm diameter hole in the other mirror to the detector. This was normally a Unicam Golay cell, but in some experiments a Molectron Germanium bolometer operating at 1.5 K was substituted.

The 400 mm Bruker electromagnet gave magnetic fields up to 22 kG with a 60 mm air gap. It was fitted with 300 mm diameter external modulation coils. Because of the slow response of the Golay cell a modulation frequency of 35 Hz was used. The detector output passed through a Brookdeal amplifier and phase sensitive detector and the spectra were displayed as a function of magnetic field in differential form by using an X–Y recorder.

Two flow tubes were used in the experiments, both of which were approximately 70 cm in length and 2.5 cm in diameter. One flow tube was constructed with fixed inlet jets for reagents at 5 cm intervals and the other had a sliding injector of 0.6 cm internal diameter.

Both HO and HO_2 were detected by perpendicular transitions at fairly high fields using the 118.6 µm transition of water vapour. For HO the $|\frac{5}{2}, \frac{3}{2}, \frac{1}{2}\rangle \leftarrow |\frac{3}{2}, \frac{3}{2}, -\frac{1}{2}\rangle$ transition at 13.65 kG was used. With HO_2, the maximum sensitivity was achieved by using two overlapping transitions with unresolved hyperfine splittings at 15.49 kG. In the notation of Hougen (1975), these were the $M_J = -1.5 \leftarrow -2.5$ of $4_{3,2} \leftarrow 5_{2,3}$ and $M_J = 3.5 \leftarrow 4.5$ of $4_{3,1} \leftarrow 5_{2,4}$ rotational transitions both between lower levels of their spin doublets. Comparison of the intensity of this line with that of corresponding nearby unoverlapped transitions of HO_2 with $M_J = 3.5 \leftarrow 4.5$ and $M_J = -1.5 \leftarrow -2.5$ respectively over a range of conditions showed that no detectable errors were introduced by using an overlapped line.

The absolute sensitivity was determined by using the very rapid reaction

$$H + NO_2 = HO + NO \tag{1}$$

to generate known concentrations of HO radicals by adding small measured flows of NO_2 to excess atomic hydrogen obtained by a microwave discharge through H_2–Ar or H_2–He mixtures. In these experiments, it was established that the peak-to-peak height of the HO spectrum was directly proportional to the HO concentration over three orders of magnitude (figure 3). The relative sensitivities for HO_2 and HO were

determined by using chemical methods to convert HO_2 into HO and vice versa by the comparatively fast reactions

$$HO_2 + NO = HO + NO_2, \tag{2}$$
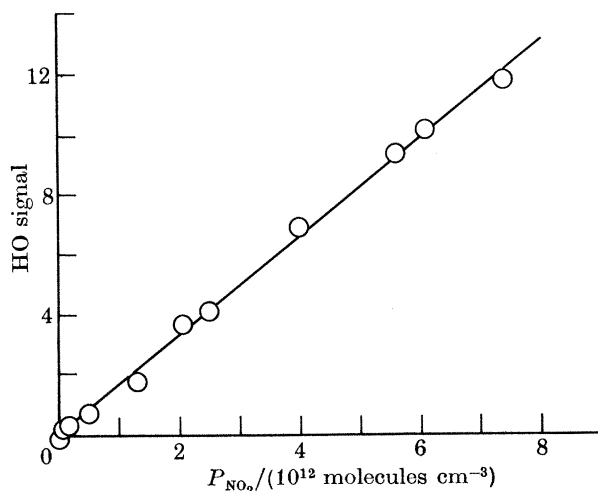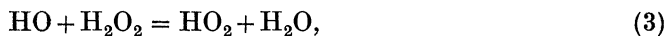
$$HO + H_2O_2 = HO_2 + H_2O, \tag{3}$$

FIGURE 3. Peak-to-peak height of 15.49 kG HO line plotted against HO concentration.

which are discussed in the Results section. In these experiments, excess nitric oxide was added to HO_2 produced by a Tesla discharge through H_2O_2 in an argon carrier, or alternatively excess H_2O_2 was added to HO radicals produced by reaction (1). In both cases, the ratio of sensitivities for HO and HO_2 in terms of peak-to-peak height under defined modulation conditions, etc., was found to be $(50 \pm 5) : 1$ for lines mentioned above with either helium or argon carriers at total pressures between 100 and 400 Pa. These ratios were not affected significantly by surface recombination of HO or of HO_2. For HO, this corresponded to a first order rate coefficient between 30 and 70 s^{-1} giving γ_{HO} of $3-6 \times 10^{-3}$. Surface recombination of HO_2 was much slower with a surface decay rate of 5–10 s^{-1} corresponding to $\gamma_{HO_2} \approx 3 \times 10^{-4}$. All the quoted error limits correspond to two standard deviations of the experimental measurements. Uncertainties in the rate coefficients determined by others for the reference reactions are not included.

Helium carrier gas (B.O.C.) was purified by passage, at 1 atm†, over heated Cu_2O at 725 K to remove any traces of H_2 present. Argon (B.O.C.) carrier, at 1 atm, was passed over Cu turnings at 725 K to remove any O_2 present. Oxygen (B.O.C.) and hydrogen (B.O.C.) were dried by flowing them through a column containing P_2O_5. Nitric oxide (Matheson, 99.5 %) was purified by passage through molecular sieve 13 X at 195 K, followed by repeated freeze–pump–thaw cycles. Any NO impurity in

† 1 atm $\approx 10^5$ Pa.

NO_2 (Matheson, 99.9 %) was removed by mixing samples with oxygen, leaving them for several hours, and then pumping off the unreacted oxygen after freezing out the NO_2 at 195 K. Chlorine (Matheson, 99.5 %) was purified by passage through a trap at 195 K followed by repeated freeze–pump–thaw cycles at 77 K.

RESULTS

(i) *The reaction* $O + HO_2 = HO + O_2$. $\qquad$ (4)

In this system oxygen atoms, produced by passing a flow of approximately 1 % of O_2 in a helium or argon carrier through a microwave discharge, were reacted with hydrogen peroxide. The concentrations of HO and HO_2 produced in this system were monitored as a function of reaction time by varying the point of addition of hydrogen peroxide with a sliding injector.

The concentrations of oxygen atoms, which fell within the range 10^{13}–10^{14} molecules cm^{-3}, for total pressures of *ca.* 1 Torr, were measured by titrating them upstream using the rapid stoichiometric reaction

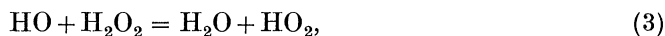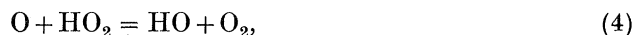$$O + NO_2 = O_2 + NO, \qquad (5)$$

and then adding H_2O_2 just above the monitoring region and using the HO produced by the reaction

$$O + H_2O_2 = HO + HO_2 \qquad (6)$$

to monitor the consumption of O atoms by reaction (5). Thus the O atom concentration was determined by adding just enough NO_2 to make the HO signal disappear.

The concentrations of H_2O_2 used, which lay within the range 10^{14}–10^{15} molecules cm^{-3}, were determined by trapping out the H_2O_2 at 77 K just beyond the observation region and then titrating against standard potassium permanganate solutions. The reaction between O and H_2O_2 can be described by the elementary processes:

$$O + H_2O_2 = HO + HO_2, \qquad (6)$$

$$O + HO = O_2 + H, \qquad (7)$$

$$O + HO_2 = HO + O_2, \qquad (4)$$

$$HO + H_2O_2 = H_2O + HO_2, \qquad (3)$$

$$HO + HO_2 = H_2O + O_2. \qquad (8)$$

The HO and HO_2 concentrations in this system rose to simultaneous maxima, at which point

$$d[HO_2]/dt - d[HO]/dt = 0,$$

giving $\qquad 0 = 2k_3[HO][H_2O_2] + k_7[O][HO] - 2k_4[O][HO_2]$

$$[HO_2]/[HO] = k_7/2k_4 + k_3[H_2O_2]/k_4[O].$$

A plot of $[HO_2]/[HO]$ against $[H_2O_2]/[O]$, shown in figure 4, was linear and the ratio of slope to intercept of 0.042 was in good agreement with the literature value (Hampson & Garvin 1978) of 0.039. From this plot the desired rate coefficient k_4 can be determined from both the slope and intercept. These were

$$k_4/k_7 = 0.83 \quad \text{and} \quad k_4/k_3 = 37,$$

which, using the values of k_3 and k_7 from Hampson & Garvin (1978), give $k_4 = 3.24 \times 10^{-11} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ and $k_4 = 2.94 \times 10^{-11} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ respectively. Combining these values gives a mean value of k_4 of $(3.1 \pm 1.0) \times 10^{-11} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at 298 K. This is a slightly lower than the value of $(3.5 \pm 1.0) \times 10^{-11} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ reported from the preliminary experiments (Burrows *et al.* 1977). The uncertainty limits quoted do not include those of the reference reactions (3) and (7).
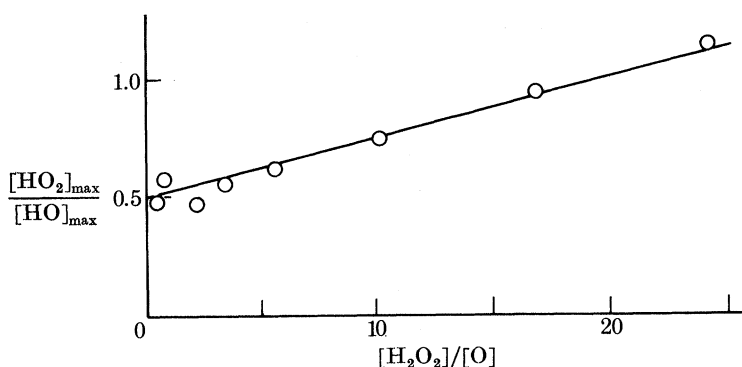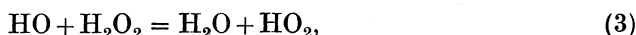

FIGURE 4. Plot of $[HO_2]_{max}/[HO]_{max}$ against $[H_2O_2]/[O]$ for the reaction $O + HO_2 = HO + O_2$.

(ii) *The reaction* $HO + HO_2 = H_2O + O_2$. (8)

The rate of this reaction was determined by generating HO_2 in systems where its concentration is determined by the competing reactions:

$$HO + H_2O_2 = H_2O + HO_2, \tag{3}$$

$$HO + HO_2 = H_2O + O_2. \tag{8}$$

If these two reactions reach a steady state, then

$$k_8/k_3 = [H_2O_2]/[HO_2].$$

For the true stationary state in HO_2 to be attained the initial ratio, $[H_2O_2]/[HO]$, must be less than 10. Otherwise HO is preferentially consumed in (3) and the measured concentration of HO_2 is less than for the true stationary state (Benson 1960). Three methods were used to achieve this condition. In the first method the fast reaction

$$H + NO_2 = HO + NO \tag{1}$$

was used to generate HO which was then reacted with H_2O_2. This method is complicated by the need to use large initial flows of HO, as a result of which the following occur:

$$HO + HO = H_2O + O, \tag{9}$$

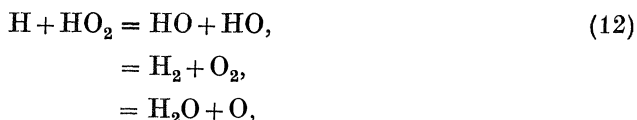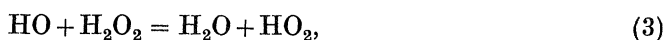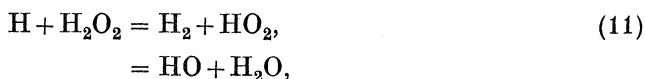$$O + HO_2 = HO + O_2, \tag{4}$$

$$NO + HO_2 = NO_2 + HO. \tag{2}$$

These might affect the determination of k_8.

The second method overcame this potential difficulty by generating both HO and HO_2 using the reaction between H atoms and hydrogen peroxide. If ozone is then added to this system any residual H atoms are converted to HO by the very rapid reaction

$$H + O_3 = HO + O_2, \tag{10}$$

and the concentration of HO_2 then reaches a steady state as defined above.

In the absence of O_3 the kinetics of the $H + HO_2$ system are complicated, some of the more important reactions being:

$$H + H_2O_2 = H_2 + HO_2, \tag{11}$$
$$= HO + H_2O,$$

$$HO + H_2O_2 = H_2O + HO_2, \tag{3}$$

$$H + HO_2 = HO + HO, \tag{12}$$
$$= H_2 + O_2,$$
$$= H_2O + O,$$

$$HO + HO_2 = H_2O + O_2. \tag{8}$$

Its kinetic analysis is difficult because the branching ratios and rate coefficients of (11) and (12) are uncertain. This complication is avoided by using O_3 to remove H atoms from the system rendering reactions (11) and (12) inoperative.

In the third method HO and HO_2 were generated as before by the reaction between H atoms and H_2O_2 but NO_2 rather than O_3 was added to convert H into HO. In the second and third methods, the O_3 or NO_2 was added approximately 20 ms reaction time before the observation region to allow time for mixing and for the concentration of HO_2 to reach a new steady state. The results are presented in table 1. Using the value of k_3 of 8×10^{-13} cm^{-3} molecule^{-1}s^{-1} recommended by Hampson & Garvin (1977) the desired rate coefficient k_8 is found to be:

$$k_8 = (5.1 \pm 1.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1} \text{ at } 298 \text{ K},$$

with total pressures of about 2 Torr. (1 Torr $\approx$ 133 Pa.)

This value lies between the two previous determinations of k_8. Hochanadel et al. (1972) studied the reaction by monitoring HO_2 by its continuous u.v. spectrum around 205 nm in the pulse radiolysis of water in the presence of oxygen. They

suggested that the reaction goes at the collision frequency of $(2.0 \pm 0.3) \times 10^{-10}\ cm^3$ molecule^{-1} s^{-1} at 298 K. However, there is now clear evidence that a significant proportion of HO_2 is present as a monohydrate in the presence of water vapour near its saturation vapour pressure, and that this hydrate differs in reactivity from HO_2 (Hamilton 1975). Furthermore, insufficient information is given to permit a re-analysis of their data. Friswell & Sutton (1972) studied radical recombinations in H_2–O_2–N_2 flames at 2130 K and deduced a value of $k_8 = (2 \pm 0.6) \times 10^{-11}\ cm^3$ molecule^{-1} s^{-1}. Since radical recombination reactions often have negative temperature coefficients, the disproportionation of HO and HO_2 may behave similarly.

TABLE 1. DATA FOR $HO + HO_2 = H_2O + O_2$, AT 298 K

H_2O_2/molecule cm^{-3}	$\dfrac{[H_2O_2]}{[HO_2]}$	$10^{11}k$/(cm^3 molecule^{-1}s^{-1})	reaction system
3.2×10^{14}	73.4	5.87	$H + H_2O_2$, then NO_2
3.2×10^{14}	64.25	5.14	$H + NO_2$, then H_2O_2
4.2×10^{14}	65.5	5.24	$H + H_2O_2$, then O_3
1.5×10^{14}	59.4	4.75	$H + H_2O_2$, then O_3
1.6×10^{14}	69	5.52	$H + H_2O_2$, then NO_2
3.9×10^{14}	54.4	4.35	$H + H_2O_2$, then NO_2
5.0×10^{14}	59.4	4.75	$H + H_2O_2$, then NO_2
mean		(5.1 ± 1.7)	

(iii) *The reaction* $NO + HO_2 = NO_2 + HO$.   (2)

The reaction was studied under conditions where the reactions

$$NO + HO_2 = HO + NO_2, \qquad (2)$$

$$HO + H_2O_2 = H_2O + HO_2, \qquad (3)$$
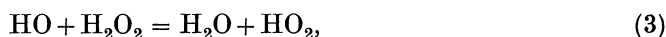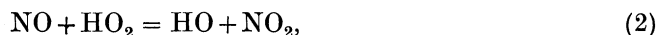
generated a steady state concentration of HO radicals given by:

$$[HO_2]/[HO] = k_3[H_2O_2]/k_2[NO].$$

Two separate sources of HO_2 were used in these experiments. (*a*) The majority were performed by using a Tesla discharge through a mixture of approximately 1 % H_2O_2 in argon to generate HO_2 radicals in the presence of excess H_2O_2. This novel source of HO_2 was initially investigated to determine the nature of the products from the discharge. With excess H_2O_2, significant concentrations of HO_2 were generated in the absence of detectable amounts of HO. As the proportion of H_2O_2 was reduced, the HO_2 signals diminished and small HO signals appeared. Additions of NO_2 were made, but resulted in no detectable change in the concentrations of HO or HO_2. Because the rapid reactions

$$H + NO_2 = HO + NO, \qquad (1)$$

$$O + NO_2 = NO + O_2, \qquad (5)$$
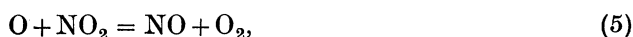
would remove any H and O that were present in the system and these species react very rapidly with HO_2, we conclude that H and O have negligible concentrations in the products of a Tesla discharge through H_2O_2.

Reaction (2) was investigated by introducing NO, at concentrations in the range 10^{12}–10^{14} molecules cm^{-3}, to the flowing gases which contained excess H_2O_2 and concentrations of HO_2 in the range 10^{11}–10^{13} molecules cm^{-3}. The signals due to HO_2 were reduced and signals due to HO appeared. The concentrations of both species were governed by the steady state equation given above, as is apparent from the plot of $[HO_2]/[HO]$ against $[H_2O_2]/[NO]$ shown in figure 5. The gradient of this plot gives $k_2/k_3 = 11.1$, which, with the value of k_3 adopted above gives $k_2 = 8.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(b) In the second method HO_2 was generated by the reaction of F atoms with excess H_2O_2. F atoms were generated by passing CF_4 in a helium carrier at a total pressure of about 2 Torr through a microwave discharge. Strong signals from HO_2 were obtained in this way, associated with the reactions
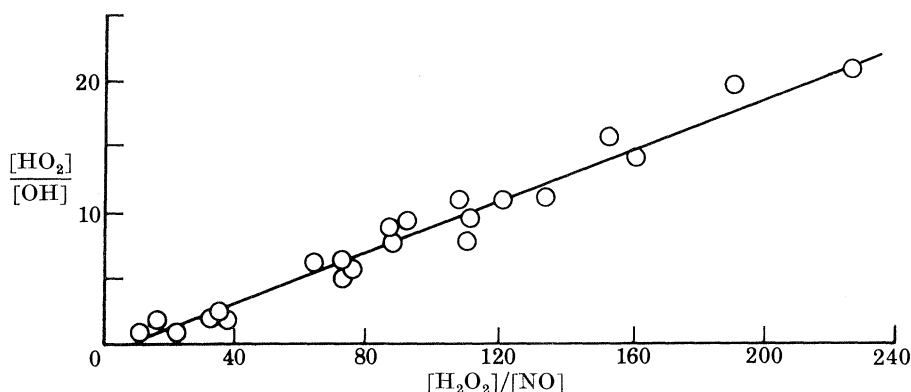
$$F + H_2O_2 = HF + HO_2, \tag{13}$$

$$F + HO_2 = HF + O_2. \tag{14}$$

FIGURE 5. Plot of $[HO_2]/[HO]$ against $[H_2O_2]/[NO]$ for the reactions $HO_2 + NO = HO + NO_2$ and $HO + H_2O_2 = H_2O + HO_2$.

For a given flow of H_2O_2 the concentration of CF_4 was adjusted so as to maximize the HO_2 signals, and on addition of NO the HO_2 signals were attenuated and HO signals appeared. Plots of $[HO_2]/[HO]$ against $[H_2O_2]/[NO]$ were again found to be linear, with a gradient (k_2/k_3) of 9.4, which gives $k_2 = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Combination of the results of both (a) and (b) gave

$$k_2/k_3 = 10.3 \pm 3.0.$$

Using this ratio and the value for k_3 adopted above, we obtain a value of k_2 of $(8.2 \pm 2.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K; the uncertainty does not include that of k_3.

Before the development of l.m.r. as a method for measuring reaction rates of HO_2, the rate coefficient of reaction (2) had been determined indirectly, by competition with the reaction

$$HO_2 + HO_2 = H_2O_2 + O_2, \tag{19}$$

with the use of an assumed mechanism.

Such studies gave much lower values of k_2, than those found here or by Howard & Evenson (1977), who also used direct detection with l.m.r. The latter obtained values of $k_2 = (7.7 \pm 0.8)$ and $(8.3 \pm 0.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} from the first order decay of HO_2 in excess NO. They obtained $k_2 = (8.4 \pm 0.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} from the rate of formation of NO_2 in a system that resembled ours in that reactions (2) and (3) maintained a steady state ratio of HO_2 and HO. The excellent agreement of these values establishes the validity of kinetic studies of HO_2 by l.m.r. and confirms the reliability of the calibration procedures used. Recent indirect determinations of k_2 have used resonance fluorescence to detect the HO produced when NO is added to a discharge flow system in which HO_2 is generated by the reaction

$$H + O_2 + M = HO_2 + M. \tag{15}$$

Preliminary values of k_2 of $(8.0 \pm 0.8) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Kaufman & Riemann 1978 *a*) and $(7 \pm 3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Margitan & Anderson 1978) have been obtained by this technique.

(iv) *The reactions* $HO_2 + Cl = HCl + O_2$ (17)

    and $HO_2 + Cl = HO + ClO.$ (17*a*)

The reaction between Cl atoms and HO_2 was studied by establishing stationary concentrations of HO_2 governed by the reactions

$$Cl + H_2O_2 = HCl + HO_2, \tag{16}$$

$$Cl + HO_2 = HCl + O_2. \tag{17}$$

Chlorine atoms were generated in two ways.

(*a*) A flow of about 1 % Cl_2 in about 2 Torr of helium was passed through a microwave discharge and into the reaction tube.

(*b*) Approximately 1 % of H_2 in about 2 Torr of helium was passed through a microwave discharge and into the reaction tube. The H atoms produced were reacted with an excess of Cl_2, where the fast reaction

$$H + Cl_2 = Cl + HCl \tag{18}$$

rapidly converts H atoms to Cl atoms.

The experiments were carried out by using a flow tube coated with a halocarbon wax or teflon, which was conditioned by flowing Cl atoms over it for 10 h. H_2O_2 was then added through a sliding injector and concentrations of HO_2 generated in the

$Cl + H_2O_2$ system were monitored as a function of reaction time. The concentrations used were

$$H_2O_2: 10^{14}\text{--}10^{15} \text{ molecules cm}^{-3},$$

$$Cl: 10^{13}\text{--}10^{14} \text{ molecules cm}^{-3},$$

$$HO_2: 10^{12}\text{--}10^{13} \text{ molecules cm}^{-3}.$$

The HO_2 concentration rose very rapidly to a maximum which decayed slowly with time. This decay appeared to be due to the recombination of HO_2, and is discussed below. The true steady state of HO_2 was obtained by adjusting the concentration of Cl atoms for a given concentration of H_2O_2 such that the concentration of HO_2 was maximized. This ensured that the initial value of the ratio, $[H_2O_2]/[Cl]$, was less than 10 and thus that the true stationary state for HO_2 was obtained.
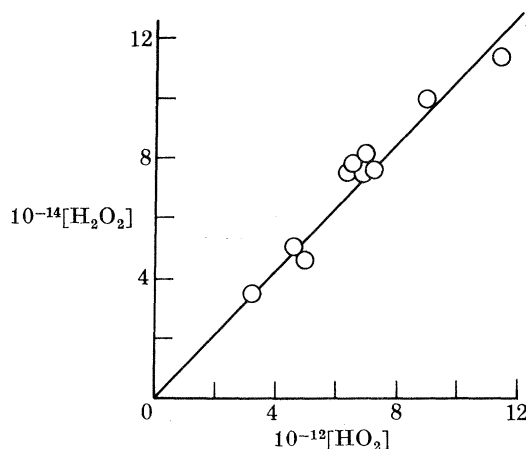

FIGURE 6. Plot of $[H_2O_2]$ against $[HO_2]$ for the $Cl + H_2O_2$ chemical system.

A plot of H_2O_2 against HO_2 (see figure 6) was linear, and at the stationary state

$$[HO_2] = k_{16}[H_2O_2]/k_{17}.$$

From the gradient $\qquad [H_2O_2]/[HO_2] = k_{16}/k_{17} = 108 \pm 12.$

There have been two recent determinations of k_{16}, by Poulet *et al.* (1978) and by Michael *et al.* (1977), which agree quite well. Taking the mean value of $(3.8 \pm 0.8) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$ at 298 K we obtain a value of k_{17} of $(4.1 \pm 1.4) \times 10^{-11} \text{ cm}^3$ molecule^{-1}s^{-1} at 298 K.

There have been three recent investigations of this reaction. Leu & Demore (1976) investigated the $Cl + H_2O_2$ system by mass spectrometry. They obtained a value of k_{16} by observing the pseudo-first order decay of H_2O_2 in the presence of excess Cl atoms, and determined k_{17} by observing the steady state of HO_2 produced by having Cl atoms in large excess over H_2O_2. This method yields

$$k_{17} = (3^{+4.5}_{-1.8}) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1} \text{ at 298 K.}$$

This result is based on the value of k_{16} found in their studies; with the value adopted here it becomes

$$k_{17} = (2^{+3}_{-1.2}) \times 10^{-11}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}\ \mathrm{at}\ 298\ \mathrm{K}.$$

The large uncertainty limits arise from the unknown sensitivity of their mass spectrometer for HO_2. Poulet *et al.* (1978) also studied reaction (17) in the same way as Leu & Demore (1976), obtaining a higher value of

$$k_{17} = (6.8 \pm 2.5) \times 10^{-11}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}\ \mathrm{at}\ 298\ \mathrm{K}.$$

The scatter of their data is large and the error represents only one standard deviation. Cox & Derwent (1975) studied the chlorine photosensitized oxidation of H_2 at 1 atm total pressure and 306 K in a stopped flow system. A computer analysis was necessary to determine a value of k_{17} of $(2.5 \pm 1) \times 10^{-11}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ at 298 K. The value obtained depended upon several rate coefficients which have since been redetermined, changing the value of k_{17} in a non-trivial manner.

In these experiments an attempt was made to measure the extent of the thermodynamically feasible alternative reaction

$$\mathrm{Cl + HO_2 = ClO + HO.} \tag{17a}$$

Presumably any HO produced in the above reaction would be consumed by

$$\mathrm{HO + H_2O_2 = H_2O + HO_2.} \tag{3}$$

Thus, assuming a stationary state,

$$k_{17a} = k_3\,[\mathrm{HO}]\,[\mathrm{H_2O_2}]/[\mathrm{HO_2}]\,[\mathrm{Cl}].$$

In the experiments performed, no measurable concentrations of HO were produced. This leads to an upper limit on k_{17a} of

$$k_{17a} \leqslant 3 \times 10^{-13}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}.$$

Thus less than 1 % of the reaction proceeds via the second pathway. Since this work was performed a new assessment of $\Delta H^{\circ}_{f_{298}}(\mathrm{HO_2}) = 2 \pm 9\,\mathrm{kJ\,mol^{-1}}$ has been made by Wagman (1978). On this basis, reaction (17a) becomes $18 \pm 10\,\mathrm{kJ\,mol^{-1}}$ endothermic and the upper limit obtained for its rate coefficient is only significant if the endothermicity is close to its lower bound, since the higher values for the heat of reaction would give an Arrhenius factor smaller than the ratio of the upper bound of k_{17a} to the collision number.

(v) *The reaction* $\mathrm{HO_2 + HO_2 = H_2O_2 + O_2}$. $\hfill$ (19)
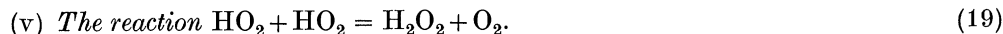
It was noted in the previous section that the HO_2 generated in the $Cl + H_2O_2$ system decayed slowly. The observed decays were slower than could be attributed to the combination reaction of two HO_2 radicals, for which the accepted rate coefficient is $(2.4 \pm 0.9) \times 10^{-12}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ at 298 K, determined in experiments where the total pressure is near atmospheric. Possible explanations of the observed slow decay are that HO_2 may be generated in some heterogenous process, or that it may be due to some artefact of the $Cl + H_2O_2$ reaction.

Experiments were performed by using several wall surfaces, including hydro-fluoric acid cleaned pyrex, teflon, and a halocarbon wax. The $F + H_2O_2$ system described above was also used as a source of HO_2. In all cases a similar behaviour was observed. Unfortunately, HO_2 decayed by only a factor of about 2 over the available reaction time of 60 ms, and it was therefore impossible to distinguish between first order and second order kinetic processes:

$$HO_2 + HO_2 = H_2O_2 + O_2, \tag{19}$$

$$HO_2 = \text{wall}. \tag{20}$$

A computer simulation of the $Cl + H_2O_2$ system was undertaken with the reaction scheme

$$Cl + H_2O_2 = HCl + HO_2, \tag{16}$$

$$Cl + HO_2 = HCl + O_2, \tag{17}$$

$$HO_2 + HO_2 = H_2O_2 + O_2. \tag{19}$$

The simulated profile of HO_2 gave good agreement with experimentally determined profiles. Analysis of the experimental data, assuming all the measured decay is due to reaction (19), yields the values shown in table 2. Upper limits for k_{19} in the table lie in the range $k_{19} = (7.5 \pm 5.0) \times 10^{-13} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ and thus we conclude that

$$k_{19} \leqslant 1.2 \times 10^{-12} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1} \text{ at } 298 \, \text{K},$$

at pressures around 2 Torr in argon carrier.

This result suggests that k_{19} may be pressure dependent. However, this reaction shows other unexpected features; previous determinations of k_{19} are listed in table 3. Paukert & Johnston (1972) determined $k_{19} = (3.6 \pm 0.5) \times 10^{-12} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at 298 K, using the molecular modulation technique by producing concentrations of HO_2 by photolysis of H_2O_2 at 253.7 nm in the presence of 1 atm of helium, and by photolysing Cl_2/H_2O_2 mixtures, also in 1 atm of helium, at 330 nm. HO_2 was detected by its u.v. absorption around 220 nm. Around the same time Hochanadel et al. (1972) obtained $k_{19} = (9.5 \pm 1.0) \times 10^{-12} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at 298 K by studying the pulse radiolysis of H_2O–He–O_2–H_2 mixtures; they obtained apparent second order decays of HO_2 by measuring its u.v. absorption around 205 nm. The discrepancy between these two values was explained by Hamilton & Lii (1977), who showed that the presence of water vapour leads to a faster rate coefficient. They also showed this to be true for NH_3 in place of water vapour, and showed a similar effect in DO_2 chemistry. They proposed that such behaviour may be explained by the formation of the adducts $HO_2 \cdot H_2O$ and $HO_2 \cdot NH_3$, which react more rapidly than free HO_2 with other free HO_2 radicals, but which have similar u.v. absorption spectra. Using the absorption cross section given by Paukert & Johnston (1972), they deduced a value of k_{19} of $(2.5 \pm 0.8) \times 10^{-12} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at 298 K.

More recently Cox (1978) and Cox & Burrows (1979) have studied the photolysis of Cl_2–H_2–O_2 mixtures by molecular modulation. This work confirms that the

addition of water vapour does increase the apparent second order rate coefficient but it does not confirm nor disprove Hamilton's and Lii's proposition of adduct formation. The temperature dependence of the HO_2 recombination reaction was also measured and shown to correspond to a negative activation energy of aproximately 10 kJ mol^{-1} in the region of 273–338 K.

TABLE 2. UPPER LIMITS FOR THE RATE COEFFICIENT OF THE REACTION
$HO_2 + HO_2 = H_2O_2 + O_2$ AT 298 K

chemical system	pressure Torr	$10^{13}k/(\text{cm}^3 \text{ molecule}^{-1}\text{s}^{-1})$
$Cl + H_2O_2$ on pyrex walls	2.15	6.3
$Cl + H_2O_2$ on pyrex walls	1.92	10.0
$Cl + H_2O_2$ on pyrex walls	1.92	5.23
$Cl + H_2O_2$ on halocarbon walls	2.08	10.2
$Cl + H_2O_2$ on halocarbon walls	2.15	L4.0
$Cl + H_2O_2$ on halocarbon walls	2.0	5.54
$Cl + H_2O_2$ on halocarbon walls	2.0	7.9
$F + H_2O_2$ on pyrex walls	2.85	6.4
$F + H_2O_2$ on pyrex walls	2.85	5.4
$F + H_2O_2$ on pyrex walls	2.3	4.0
$F + H_2O_2$ on pyrex walls	4.99	12.5
$F + H_2O_2$ on teflon walls	2.2	6.1
$F + H_2O_2$ on teflon walls	2.2	5.54
mean upper limit		(7.5 ± 5.0)

Overall at 2 Torr $k_{HO_2+HO_2} < (7.5 \pm 5) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

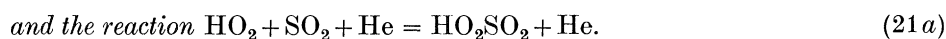TABLE 3. RECENT MEASUREMENTS FOR $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ AT 298 K

reference	technique	pressure Torr	$k/(\text{cm}^3 \text{ molecule}^{-1}\text{s}^{-1})$
Foner & Hudson (1962)	mass spectrometry	*ca* 0.5	*ca.* 3×10^{-12}
Paukert & Johnston (1972)	molecular modulation	760	$(3.6 \pm 0.5) \times 10^{-12}$
Hochanadel *et al.* (1972)	flash photolysis	760	$(9.5 \pm 1.0) \times 10^{-12}$
Hamilton (1975)	pulsed radiolysis	1520	$(2.5 \pm 0.5) \times 10^{-12}$
Cox & Burrows (1979)	molecular modulation	760	$(2.3 \pm 0.8) \times 10^{-12}$
Cox & Burrows (1979)	molecular modulation	30	1.6×10^{-12}
this work (upper limits)	l.m.r.	2	$(7.5 \pm 5) \times 10^{-13}$

One simple mechanism which may explain the unusual behaviour of reaction (19) is

$$HO_2 + HO_2 \underset{b}{\overset{a}{\rightleftharpoons}} H_2O_4^* \xrightarrow[\text{M}]{c} H_2O_4 \xrightarrow[\text{M}]{d} H_2O_2 + O_2$$
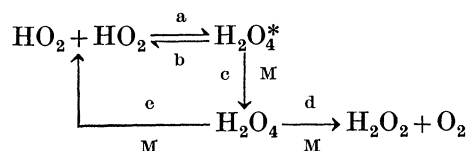
In this scheme, competition between the two unimolecular paths for the decomposition of H_2O_4 can give the required temperature and pressure dependence since path (e) to $HO_2 + HO_2$ would have a high A factor whereas path (d), which involves a cyclic transition state, would have a low one. The difference in activation energies for these two processes would then give the observed negative temperature coefficient for the overall combination reaction, and the ratio of their pre-exponential factors would prevent any difficulty as to the ratio of the rates of the two processes.

(vi) *The reaction* $HO_2 + SO_2 = HO + SO_3$ $\hspace{2cm}$ (21)

$\hspace{1cm}$ *and the reaction* $HO_2 + SO_2 + He = HO_2SO_2 + He.$ $\hspace{1cm}$ (21a)

This reaction was studied in a manner similar to that used for the investigation of the $HO_2 + NO$ reaction. HO_2 was generated either by reaction of F atoms with excess hydrogen peroxide, or by a Tesla discharge through H_2O_2, and was then mixed with SO_2 in an attempt to observe the possible chain reaction

$$HO_2 + SO_2 = HO + SO_3, \hspace{2cm} (21)$$

$$HO + H_2O_2 = HO_2 + H_2O. \hspace{2cm} (3)$$

If these two reactions reach a steady state, then

$$k_{21} = k_3 [OH] [H_2O_2] / [SO_2] [HO_2].$$

In all experiments additions of SO_2 failed to produce any diminution of the HO_2 signals or appearance of HO signals; the only effect seen was a damping of laser action at high concentrations of SO_2. This yields an upper limit for the rate of reaction (21) of

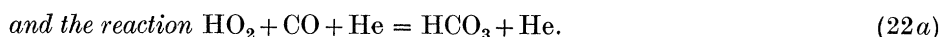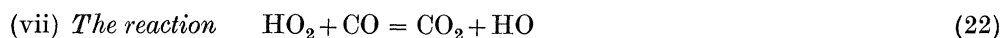$$k_{21} \leqslant 2 \times 10^{-17} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1} \text{ at 298 K.}$$

Davis *et al.* (1973) measured the rate of reaction (21) indirectly by a competitive method based on $^{18}O_2$ labelling; they obtained a value of $k_{21} = (8.7 \pm 1.8) \times 10^{-16}$ $\text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at 300 K.

Having found no evidence for any second order reaction between HO_2 and SO_2, a brief investigation of the possible third order reaction, (21a), was undertaken:

$$HO_2 + SO_2 + He = HO_2SO_2 + He. \hspace{2cm} (21a)$$
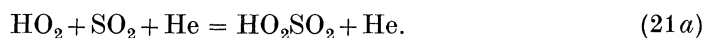
The time dependent study of the reaction of fixed concentrations of SO_2 with HO_2, generated by the same methods as above, was studied but no third order reaction could be detected, even at partial pressures of SO_2 of 3 Torr. This study yielded an upper limit on the rate of reaction (21a) to be set at

$$k_{21a} \leqslant 4 \times 10^{-34} \, \text{cm}^6 \, \text{molecule}^{-2} \, \text{s}^{-1} \quad \text{at} \quad 298 \, \text{K.}$$

(vii) *The reaction* $HO_2 + CO = CO_2 + HO$ $\hspace{2cm}$ (22)

$\hspace{1cm}$ *and the reaction* $HO_2 + CO + He = HCO_3 + He.$ $\hspace{1cm}$ (22a)

This reaction was studied in an entirely analogous fashion to reaction (21), i.e. CO was added to HO_2 in the presence of excess H_2O_2 and the signals due to HO_2 and

HO were monitored for any change. If HO_2 undergoes a transfer reaction with CO the reaction scheme would be

$$CO + HO_2 = CO_2 + HO, \tag{22}$$

$$HO + H_2O_2 = HO_2 + H_2O, \tag{3}$$

$$CO + HO = CO_2 + H. \tag{23}$$
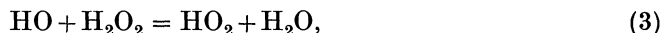
Assuming a stationary state in HO, the rate coefficient for reaction (22) is given by

$$k_{22} = [HO]\{k_3[H_2O_2] + k_{23}[CO]\}/[CO][HO_2].$$

No change in the HO_2 and HO signals could be observed on addition of CO. This allowed an upper limit of the rate coefficient of reaction (22) to be set at

$$k_{22} \leqslant 2.0 \times 10^{-17} \, cm^3 \, molecule^{-1} \, s^{-1} \, at \, 298 \, K.$$

This upper limit is consistent with previous studies of reaction (22).

An investigation of any possible third order reaction was attempted, in a manner analogous to that for reaction (21a), and again no reaction as detected. This leads to an upper limit of

$$k_{22a} \leqslant 4 \times 10^{-34} \, cm^6 \, molecule^{-2} \, s^{-1} \, at \, 298 \, K.$$

DISCUSSION

The comparisons made above between the present results and previous studies using less direct methods of identifying the reactions of the HO_2 radical emphasizes the importance of direct observation of a transient species when there is any doubt as to its reaction mechanism.

One point of particular interest is the dissimilar behaviour of the radical disproportionation reactions.

$$HO + HO = H_2O + O, \tag{9}$$
$$k_9 = 1.6 \times 10^{-12} \, cm^3 \, molecule^{-1} \, s^{-1},$$

$$HO + HO_2 = H_2O + O_2, \tag{8}$$
$$k_8 = 5.1 \times 10^{-11} \, cm^3 \, molecule^{-1} \, s^{-1},$$

$$HO_2 + HO_2 = H_2O_2 + O_2, \tag{19}$$
$$k_{19} = 2.5 \times 10^{-12} \, cm^3 \, molecule^{-1} \, s^{-1}.$$

The observed pressure dependence of k_{19} shows that this reaction, unlike (8) and (9), is not simply a hydrogen atom transfer process, and that it must involve an initial association step to form an energized H_2O_4 species. For this reason it cannot be expected that the radicals HO_2 and HO will obey the commonly assumed

geometric mean rule that the rate coefficient for a reaction between two dissimilar radicals is twice the geometric mean of those for the reactions with themselves.

$$ClO + ClO = Cl_2 + O_2, \tag{23}$$

$$k_{23} = 2.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$HO_2 + ClO = HOCl + O_2, \tag{24}$$

$$k_{24} = 4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

(Kaufman & Reimann 1978b; Watson 1977).

For HO_2 and ClO the direct comparison is again vitiated because it is between a hydrogen atom transfer reaction (24) and two processes (19) and (23), which proceed by complex mechanisms where the role of the intermediates has not been fully established. For instance there is evidence that the initial step in reaction (23) yields $Cl + ClOO$ and that the overall reaction has a positive temperature dependence and some pressure dependence (Clyne *et al.* 1974).

Thus any attempt to extend the well known similarities between the reactivities of HO and Cl to the species HO_2 and ClO, as suggested by the rapidity of the atmospherically important reactions

$$HO_2 + NO = HO + NO_2, \tag{2}$$

$$ClO + NO = Cl + NO_2, \tag{25}$$
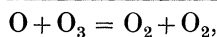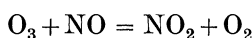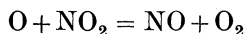
and by the similar rate coefficients of their combination reactions with NO_2,

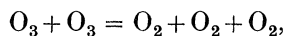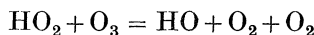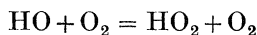$$HO_2 + NO_2 + M = HO_2NO_2 + M, \tag{26}$$

$$ClO + NO_2 + M = ClONO_2 + M, \tag{27}$$
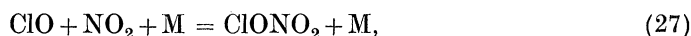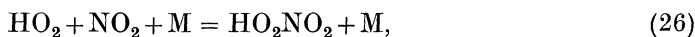
must be viewed with caution.
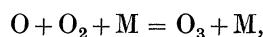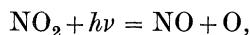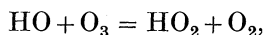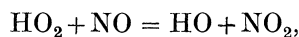
The atmospheric implications for the rate coefficients of HO_2 reactions reported here, particularly those with NO and HO have been discussed extensively elsewhere (Broderick 1977). Reaction (2) strongly couples together the 'odd oxygen' (ozone) destruction cycles due to nitrogen oxides and to hydrogen radicals:

$$O + NO_2 = NO + O_2$$
$$O_3 + NO = NO_2 + O_2$$
$$\overline{O + O_3 = O_2 + O_2,}$$

and

$$HO + O_2 = HO_2 + O_2$$
$$HO_2 + O_3 = HO + O_2 + O_2$$
$$\overline{O_3 + O_3 = O_2 + O_2 + O_2,}$$

to give a cycle

$$HO_2 + NO = HO + NO_2,$$
$$HO + O_3 = HO_2 + O_2,$$
$$NO_2 + h\nu = NO + O,$$
$$O + O_2 + M = O_3 + M,$$

which does not remove odd oxygen, and the new higher values for k_2 virtually eliminate the projected depletions of odd oxygen by NO and NO_2 derived from exhausts of stratospheric aircraft or from increased N_2O due to greater use of nitrogenous fertilizers.

The low pressure fall-off in the rate coefficient of reaction (19), which is considered to be the main source of H_2O_2 in the stratosphere, is also of interest since the pressure used in our experiments corresponds to altitudes of about 50 km. This observation may partly explain past failures to detect H_2O_2 in the stratosphere by infrared spectroscopy (Thrush 1979).

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