J. Chem. Soc., Faraday Trans. 2, 1982, **78**, 1469–1475

Reactions of HO_2 Studied By Flash Photolysis with Diode-laser Spectroscopy

BY BRIAN A. THRUSH* AND GEOFFREY S. TYNDALL
Department of Physical Chemistry, University of Cambridge, Lensfield Road,
Cambridge CB2 1EP

Received 22nd February, 1982

Tunable diode lasers make it possible to record the infrared spectra of transient species at Doppler-limited resolution on time-scales of <1 ms. This technique has been combined with flash photolysis to study reactions of the HO_2 radical. Studies of the recombination of HO_2 radicals at total pressures between 7 and 20 Torr† give rate coefficients in the range $(1.5–2.0)\times 10^{-12}\ cm^3\ s^{-1}$ at 305 K for oxygen carriers. These values are significantly lower than other workers have found near atmospheric pressure. They support the view that this reaction yields $H_2O_2+O_2$ by two parallel paths, one a direct disproportionation the other involving an H_2O_4 intermediate.

The technique of flash photolysis[1,2] has provided much information about the reactions of free radicals which have identifiable spectra in the visible or ultraviolet regions. The extension of this technique to the infrared offers the advantage that all transient species and their reaction products (other than free atoms or homonuclear diatomic molecules) have characteristic spectra in this region. However, few such studies have been made[3] owing to the lack of variable frequency infrared sources with high spectral brightness. Tunable diode lasers now provide such a source. Although the output is typically <1 mW, their linewidth is $<10^{-3}\ cm^{-1}$, which is less than the Doppler width of individual vibration–rotation transitions. Furthermore, they can be scanned rapidly by varying the excitation current so that it is possible to record high-resolution spectra of narrow regions of the infrared with repetition times ≪1 ms.

We report here the construction of a flash-photolysis apparatus with such a detection system and its use to study reactions of HO_2 radicals in the gas phase. These are monitored by observing individual rotation lines of the ν_3 band near $1100\ cm^{-1}$ with a time resolution of 200 μs. The first reaction studied has been the disproportionation of HO_2 radicals

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

where evidence from the pressure and temperature dependence of the overall rate coefficient suggests that the reaction proceeds wholly or partly *via* an H_2O_4 intermediate:

$$HO_2+HO_2 \underset{M}{\overset{M}{\rightleftharpoons}} H_2O_4 \rightarrow H_2O_2+O_2. \qquad (2)$$

To summarise, studies of reaction (1) at pressures near atmospheric using pulse radiolysis,[4] molecular modulation[5,6] or flash photolysis[7] have monitored HO_2 by its continuous u.v. abosrption spectrum near 230 nm. These measurements give $k_1=(2–3)\times 10^{-12}\ cm^3\ s^{-1}$, but they might be affected by other substances which

---

† 1 Torr ≡ 101 325/760 Pa.

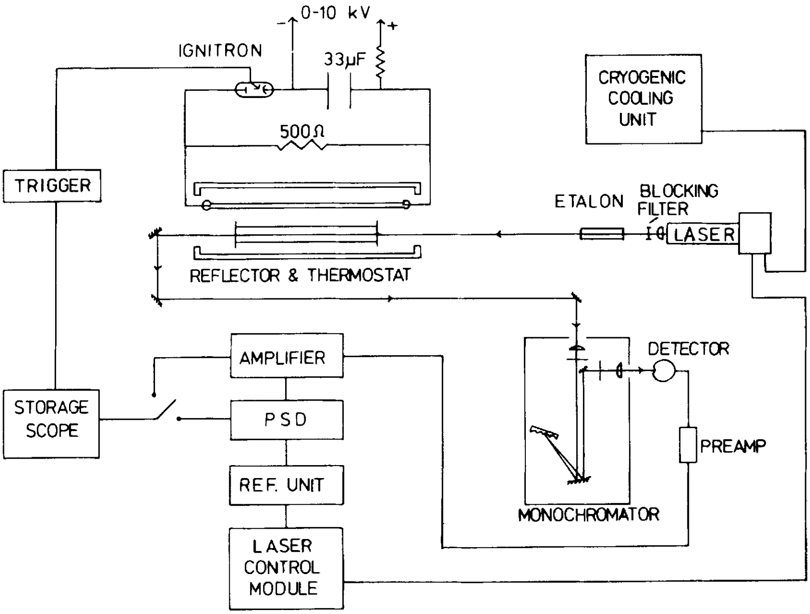

FIG. 1.—Apparatus used for flash-photolysis experiments with detection by tunable diode-laser spectroscopy.

absorb in the same region. In particular, Hamilton[4] has shown that HO_2 forms strongly hydrogen-bonded adducts with H_2O and with NH_3, which have unchanged u.v. spectra but recombine much more rapidly than free HO_2.

Cox and Burrows[6] used molecular modulation to study this reaction at total pressures down to 3 Torr. They observed a decrease in the overal rate of decay of HO_2 consistent with mechanism (2). However, their kinetic analysis assumed that the rate coefficient for the removal of HO_2 by bimolecular reaction with formaldehyde was $<1\times10^{-15}$ cm^3 s^{-1} whereas Su *et al.*[8] have reported a rate constant of 1×10^{-14} cm^3 s^{-1} and unpublished measurements with our apparatus give values of $(2\text{–}4)\times10^{-14}$ cm^3 s^{-1}, values which would provide an alternative explanation of the observed pressure-dependent decay of HO_2. The observation of a strong negative temperature coefficient for the disproportionation of HO_2 radicals[6,9] also favours mechanism (2).

Recent flash-photolysis studies by Sander *et al.*[10] show that the rate of recombination of HO_2 radicals depends on the pressure and nature of the carrier gas for total pressures between 100 and 700 Torr. Their work favours the simultaneous occurrence of the disproportionation mechanism (1) and the combination mechanism (2) with $k_1 = 1.6\times10^{-12}$ cm^3 s^{-1}. In contrast, studies by laser magnetic resonance spectroscopy at total pressures between 2 and 4 Torr gave much lower rate coefficients for this reaction which were proportional to the total pressure and depended on the nature of the carrier gas involved.[11]

Unlike their u.v. spectra, the i.r. spectra of HO_2 and its hydrate will be completely different at high resolution. Diode-laser spectroscopy is particularly suitable for studying reactions of HO_2 at total pressures of 4–30 Torr, the upper limit being governed by loss of sensitivity due to pressure broadening. This is clearly the most important region for determining the mechanism of disproportionation of HO_2

radicals. It also corresponds to altitudes of 25–40 km in the stratosphere, where unsuccessful attempts have been made to detect the H_2O_2 which is formed by reactions (1) and/or (2).

EXPERIMENTAL

HO_2 radicals were generated by the flash photolysis of $Cl_2+CH_3OH+O_2$ or $Cl_2+H_2CO+O_2$ mixtures:

$$Cl_2+h\nu \rightarrow Cl+Cl$$

$$Cl+CH_3OH \rightarrow HCl+CH_2OH$$

$$CH_2OH+O_2 \rightarrow H_2CO+HO_2$$

$$Cl+H_2CO \rightarrow HCl+HCO$$

$$HCO+O_2 \rightarrow CO+HO_2.$$

In both cases, monitoring the change in formaldehyde concentration (amount formed or removed, respectively) by diode-laser spectroscopy provided a direct measure of the amount of HO_2 generated.

The experiments were carried out in a quartz reaction vessel, 500 mm long and 24 mm internal diameter, fitted with barium fluoride windows. A single quartz flash lamp, 600 mm between electrodes, containing 30 Torr of pure argon was used. This was connected through a BK476 ignitron to a 33 μF condenser which stored 600 J at the normal working voltage of 6 kV. A series resistor of 0.33 Ω was included to minimise electrical interference produced by the flash discharge. Both the lamp and the reaction vessel were supported inside a cylinder coated with magnesium oxide, which served as a reflector and a thermostat. This part of the apparatus was surrounded by a wire cage of $\frac{1}{2}$ in.† mesh to minimise radiated interference.

The gases were stored and premixed using a conventional glass vacuum system. Total pressures up to 100 Torr were measured with an MKS Baratron gauge. A glass spiral gauge was used up to 500 Torr. Chlorine (Matheson) was purified by several freeze–pump–thaw cycles and then used as a 6% mixture in oxygen (B.O.C., White Spot). Methanol was distilled from an A.R. sample which had previously been degassed and its vapour stored as an 8% mixture in oxygen. Formaldehyde was obtained by warming paraformaldehyde to 50 °C. Because the maximum pressure used was 0.3 Torr polymerisation was not a problem, although some losses due to adsorption occurred over longer periods of time.

The Laser Analytics model LOA source was fitted with a laser diode which could be tuned between 1090 and 1200 cm^{-1}. An *f*/1 ZnSe collimating lens was placed immediately in front of it, followed by an InSb blocking filter to cut out scattered light of wavelengths <7 μm from the flash which might bleach the centres in the diode with loss of laser action.

Absolute frequency calibration was obtained from known line positions for NH_3[12] and H_2CO[13] interpolated with a 10 cm air-spaced etalon (free spectral range = 0.05 cm^{-1}). Laser modes were selected using a modified Grubb Parsons GS2 monochromator fitted with a 75 line mm^{-1} Bausch and Lomb grating blazed at 12 μm. This gave a resolution of 1.5 cm^{-1} with a 1 mm slit-width. For kinetic measurements, it proved possible to operate the laser diode on a single mode and the monochromator was bypassed giving an improved signal-to-noise ratio.

Laser radiation was observed with a Plessey LXC1000S PbSnTe detector operated at 77 K and fitted with a matched VAB1000 preamplifier. This was followed by a Brookdeal 9452 amplifier, the output of which was displayed on a Telequipment DM64 storage oscilloscope. For measurement of transient species, sawtooth modulation at 5–8 kHz was applied to the laser so that the laser scanned *ca.* 0.01 cm^{-1} every 125–200 μs. Five or six scans covering a decay time of the order of 1 ms were photographed or measured directly

---

† 1 in. $\equiv 2.54\times10^{-2}$ m.

from the oscilloscope screen. The first scan after the flash was not used because of the possible effect on the measured signal of interference picked up by the detector. Flash energies up to 600 J did not cause the laser frequency to move significantly from its preset value.

The spectra of stable reagents and products were measured by passing the amplifier output through a Brookdeal 9412A + 9422 phase-sensitive detector to a chart recorder or the storage oscilloscope. Because the decay of HO_2 radicals obeys second-order kinetics, it is necessary to determine their initial concentration. This was determined with an estimated accuracy of 10% by measuring the amount of formaldehyde destroyed in the flash photolysis of a $Cl_2 + H_2CO + O_2$ mixture. For 0.25 Torr Cl_2, 0.2 Torr H_2CO and 4–6 Torr O_2 and a flash energy of 600 J, *ca.* 4% of the chlorine was dissociated, giving initial concentrations of HO_2 in the range 6×10^{14}–1×10^{15} cm^{-3}. Computer modelling showed that formation of HO_2 was complete in 20 μs in such systems.

The region of the HO_2 spectrum scanned included an unresolved triplet of lines; $F_2(10_{1,10} \leftarrow 9_{1,9})$, $F_2(10_{3,7} \leftarrow 9_{3,6})$ and $F_2(10_{3,8} \leftarrow 9_{3,7})$ at 1117.538 cm^{-1} and a single line $F_1(10_{1,10} \leftarrow 9_{1,9})$ at 1117.543 cm^{-1}. The positions calculated for these lines[14] from observation of the ν_3 band[15] and of the rotational spectrum[16] by laser magnetic resonance are, respectively, 1117.552, 1117.540, 1117.540 and 1117.561 cm^{-1}. Our measurements are precise to ± 0.003 cm^{-1}. The small discrepancy for the lines with $K_a = 1$ is not unexpected, because these levels show the largest asymmetry splitting and are least well predicted from observations on other lines. These lines showed strictly parallel kinetic behaviour and the unresolved triplet being stronger it was used for kinetic measurements, giving a signal-to-noise ratio of 5 : 1 associated with the detector noise for a bandwidth of 100 kHz. Low-frequency noise (*ca.* 3 Hz) due to the vibration generated by the cryopump was not a significant problem in our work.

RESULTS

The rate of reaction between HO_2 radicals was measured at total pressures between 7 and 20 Torr using initial concentrations of HO_2 in the range 5×10^{14}–1.6×10^{15} molecule cm^{-3}. Typical second-order decays of HO_2 are shown in fig. 2.

For a series of experiments at a given pressure, second-order curves were superimposed and gave consistent intercepts which were proportional to $[HO_2]_0^{-1}$.

The results of all kinetic experiments are summarised in table 1. The rate coefficient does not show any systematic dependence on the total pressure, or on initial radical concentration. All these results were taken using methanol as substrate, since large excess concentrations of formaldehyde introduced some curvature into the decays owing to its reaction with HO_2.

The errors shown are 95% confidence limits including all random errors. The value of k is based on the measured value of $[Cl]_0 = 7.7 \times 10^{-2} [Cl_2]$ and the assumption that all chlorine atoms are converted to HO_2. A further systematic error of up to 10% is possible here.

The estimated temperature rise in these experiments was 10–15 K. The rates are therefore given as measured at 305–310 K.

DISCUSSION

The experiments reported here show that flash photolysis combined with diode-laser spectroscopy is potentially a powerful technique for the direct study of free-radical reactions in the gas phase. The limited frequency range (*ca.* 0.1 cm^{-1}) which can be used in a given experiment requires an accurate knowledge or prediction of the frequencies of the lines in a transient spectrum. However, this

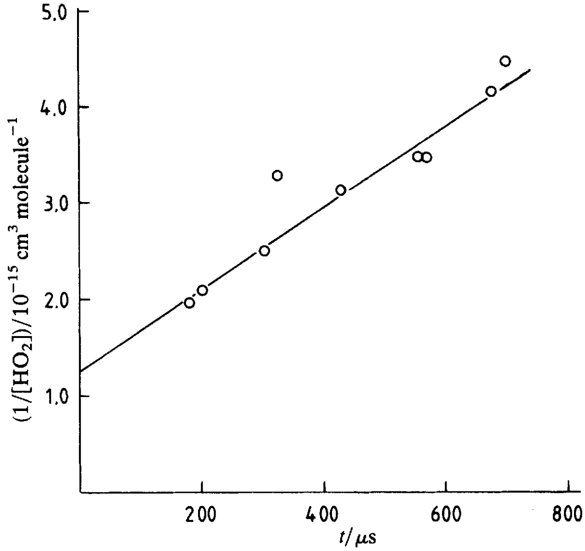

FIG. 2.—Second-order decay of HO_2. $[HO_2]_0 = 7.8 \times 10^{14}$ molecule cm^{-3}. Total pressure = 10.7 Torr.

TABLE 1.—MEASUREMENTS OF RATE COEFFICIENT FOR $HO_2 + HO_2$ AT 305 K

p /Torr	$[Cl_2]$ /Torr	$[CH_3OH]$ /Torr	$[HO_2]_0/10^{14}$ molecule cm^{-3}	$k/10^{12}$ cm^3 molecule^{-1} s^{-1}	no. of determinations
7.1	0.22	0.27	5.4	2.0±0.1	6
7.0	0.26	0.22	6.5	1.9±0.2	7
7.1	0.29	0.19	7.3	1.85±0.1	3
10.7	0.31	0.45	7.8	1.9±0.2	9
10.7	0.34	0.40	8.6	1.9±0.1	8
9.7	0.39	0.27	10.0	1.6±0.1	7
13.8	0.33	0.67	8.2	1.5±0.1	4
14.1	0.41	0.58	10.3	1.8±0.1	7
19.4	0.61	0.75	15.3	1.65±0.15	8
18.3	0.66	0.6	16.5	1.9±0.1	4

limitation can be overcome by observing the time-resolved formation of a stable product from the free-radical reaction, providing that it is not an atom or a homonuclear diatomic molecule. In the present apparatus, where species are detected near 1000 cm^{-1}, maximum sensitivities are obtained at total pressures up to 20 Torr, where pressure broadening begins to be important. Working above 3000 cm^{-1} where the H-stretching modes lie would increase the pressure at which line broadening becomes significant by a factor of three.

Our rate coefficients for the disproportionation of HO_2 radicals lie in the range $(1.5\text{–}2.0) \times 10^{-12}$ cm^3 s^{-1} at 300 K and show no discernible trend with pressure for oxygen carriers over the range 7–20 Torr. These values are significantly lower than the accepted value of 2.5×10^{-12} cm^3 s^{-1} for total pressures near atmospheric.[17] Recently, Sander *et al.*[10] used flash photolysis combined with u.v. absorption

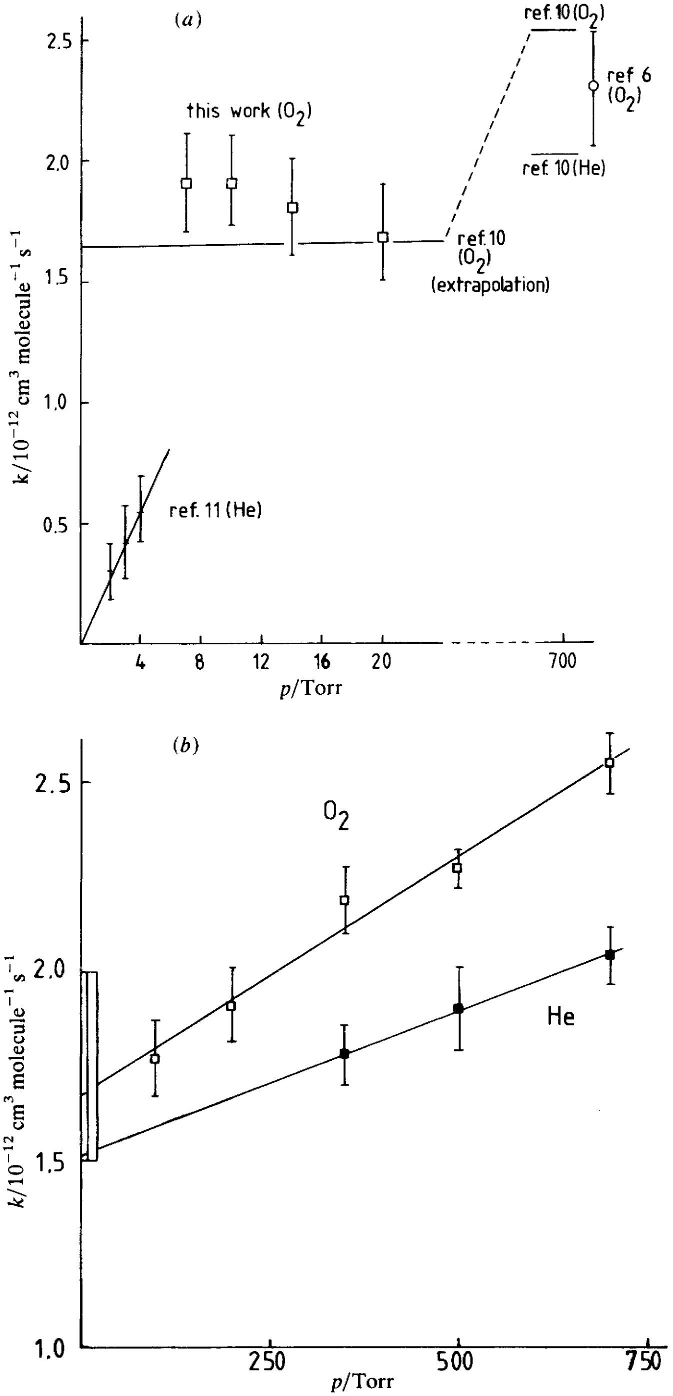

FIG. 3.—Dependence of rate coefficient for $HO_2 + HO_2$ on total pressure for helium and oxygen carriers. References as in text. (*a*) Pressure range 0–20 Torr; (*b*) comparison with data of Sander *et al.*[10] over pressure range 0–700 Torr.

spectroscopy to study this reaction with a variety of carriers at total pressures between 100 and 700 Torr. Their rate coefficients showed a relatively small increase with pressure and extrapolated to a value of $k_1 \approx 1.6 \times 10^{-12}$ cm^3 s^{-1}, as shown in fig. 3. Combining our preliminary data with theirs yields a low-pressure limit of $k_1 = 1.7 \times 10^{-12}$ cm^3 s^{-1}. Thus the present evidence favours the simultaneous occurrence of a bimolecular disproportionation mechanism

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

and of a pressure-dependent associative mechanism also yielding $H_2O_2 + O_2$

$$HO_2 + HO_2 \underset{M}{\overset{M}{\rightleftharpoons}} H_2O_4 \rightarrow H_2O_2 + O_2. \qquad (2)$$

The latter is believed to proceed *via* a hydrogen-bonded cyclic intermediate,[18] a view supported by the absence of O—O bond rupture in the overall reaction.[19] The overall reaction has a strong negative temperature dependence,[6,9] which is expected for a combination mechanism (2) rather than for a relatively slow hydrogen abstraction, reaction (1). It is therefore important to study the pressure dependence of this reaction over a range of temperatures.

We thank the N.E.R.C. for a research grant. G.S.T. thanks A.E.R.E. Harwell and the S.E.R.C. for a CASE award. Helpful discussions with Dr R. A. Cox are gratefully acknowledged.

[1] G. Porter, *Proc. R. Soc. London, Ser. A*, 1950, **200**, 284.
[2] R. G. W. Norrish and B. A. Thrush, *Quart. Rev. Chem. Soc.*, 1956, **10**, 149.
[3] L. Y. Tan, A. M. Winer and G. C. Pimentel, *J. Chem. Phys.*, 1972, **57**, 4028.
[4] E. J. Hamilton Jr and R-R. Lii, *Int. J. Chem. Kinet.*, 1977, **9**, 875.
[5] T. T. Paukert and H. S. Johnston, *J. Chem. Phys.*, 1972, **56**, 2824.
[6] R. A. Cox and J. P. Burrows, *J. Phys. Chem.*, 1979, **83**, 2560.
[7] C. J. Hochanadel, T. J. Sworski and P. J. Ogren, *J. Phys. Chem.*, 1980, **84**, 3274.
[8] F. Su, J. G. Calvert and J. H. Shaw, *J. Phys. Chem.*, 1979, **83**, 3185.
[9] R-R. Lii, R. A. Gorse Jr, M. C. Sauer Jr and S. Gordon, *J. Phys. Chem.*, 1979, **83**, 1803.
[10] S. P. Sander, M. Peterson, R. T. Watson and R. Patrick, *J. Phys. Chem.*, in press.
[11] B. A. Thrush and J. P. T. Wilkinson, *Chem. Phys. Lett.*, 1979, **66**, 441.
[12] Š. Urban, V. Špirko, D. Papoušek, J. Kauppinen, S. P. Belov, L. I. Gershtein and A. F. Krupnov, *J. Mol. Spectrosc.*, 1981, **88**, 274.
[13] M. Allegrini, J. W. C. Johns and A. R. W. McKellar, *J. Mol. Spectrosc.*, 1977, **67**, 476.
[14] A. R. W. McKellar, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 63.
[15] J. W. C. Johns, A. R. W. McKellar and M. Riggin, *J. Chem. Phys.*, 1978, **68**, 3957.
[16] J. T. Hougen, H. E. Radford, K. M. Evenson and C. J. Howard, *J. Mol. Spectrosc.*, 1975, **56**, 210.
[17] *Chemical Kinetic and Photochemical Data for Use in Stratospheric Modelling*, evaluation no. 4, NASA (U.S. Govt. Printing Office, Washington D.C., 1981).
[18] B. A. Thrush, *Acc. Chem. Res.*, 1981, **14**, 116.
[19] H. Niki, P. D. Maker, C. M. Savage and L. P. Breitenbach, *Chem. Phys. Lett.*, 1980, **73**, 43.

(PAPER 2/329)