Reactions of HO₂ with NO and NO₂ studied by Mid-infrared Laser Magnetic Resonance

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The technique of mid-infrared laser magnetic resonance spectroscopy combined with a discharge-flow system has been used to study reactions of the HO₂ radical at total pressures up to 13 Torr, corresponding to conditions in the middle stratosphere.

The validity of the technique was confirmed by the determination of a rate coefficient of $(8.5 \pm 1.3) \times 10^{-12}$ cm³ molec⁻¹ s⁻¹ at 297 K for the reaction

 $HO_2 + NO \rightarrow OH + NO_2$

in excellent agreement with previous studies. The reaction

 $HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$

was also studied. For M = He, the rate coefficient is $(6.0 \pm 1.5) \times 10^{-32}$ cm⁶ molec⁻² s⁻¹ at 297 K, while the data for M = Ar were fitted by the expression 1.24×10^{-31} (T/300)^{-2.37±0.16} cm⁶ molec⁻² s⁻¹ between 275 and 326 K.

Reactions of the HO_2 radical play a crucial role in the chemistry of the (non-polar) stratosphere.¹ This arises because the concentrations of HO_2 and OH radicals are strongly coupled by rapid reactions such as

$$HO_2 + NO \rightarrow OH + NO_2$$
 (1)

and OH radicals determine the balance between ozone destruction by nitrogen oxides and that by chlorine radicals. The precise measurements of reaction rate coefficients needed for stratospheric modelling have established unexpected pressure dependences in the rates of some reactions of HO₂ and OH such as

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2. \tag{2}$$

Previous laboratory studies of the reactions of HO₂ radicals have used pulsed photolysis, usually at total pressures between 100 and 760 Torr^{+2.3} which correspond to the troposphere, although with laser flash photolysis total pressures as low as 25 Torr can be used without excessive temperature rise.⁴ In such experiments the concentration of HO₂ is normally determined from its continuous absorption near 230 nm, a measurement which could be affected by the presence of vibrationally excited HO₂ or by peroxy species, such as the known hydrogen-bonded adducts of HO₂.⁵

Studies of HO₂ in discharge-flow systems have generally been conducted at total pressures around 1 Torr, corresponding to the top of the stratosphere. There have been both indirect studies,⁶ using reaction (1) to convert HO₂ into the readily detected OH, and direct studies using the technique of far-infrared laser magnetic resonance spectroscopy (LMR) to measure a rotational transition of HO₂ near 100 μ m.^{7.8} Here, pressure broadening is significant even at a total pressure of 1 Torr,⁹ and with increasing pressure the sensitivity falls off as approximately the inverse square of the total pressure.

The vibration-rotation spectrum of HO_2 has considerable potential for studying reactions of HO_2 at total pressures that pertain in the stratosphere because pressure broadening becomes significant only above 10 Torr. A further advantage is that this technique is specific and would not suffer interference from such species as HO_2 hydrates. We have reported¹⁰ measurements of the rate coefficient of reaction (2) using flash photolysis and time-resolved tunable diode laser spectroscopy of the v_3 band of HO₂ near 1120 cm⁻¹. Similar measurements of the corresponding reaction of DO₂⁻¹¹ monitored its v_2 band at 1020 cm⁻¹.

Here we describe the use of mid-infrared laser magnetic resonance spectroscopy to measure the rate coefficients of reactions (1) and

$$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$$
(3)

at total pressures up to 13 Torr.

Although it is possible to detect the LMR spectrum of the v_3 band of HO₂ with a normal CO₂ laser¹² and a preliminary report¹³ of the use of a CO₂ laser to study reactions of HO₂ makes no mention of the use of isotopic CO₂, none of the observed resonances proved strong and stable enough for kinetic studies and it was necessary to use an isotopic ${}^{12}C{}^{18}O_2$ laser, where particular care was needed to prevent drift of the laser output due to contamination by the normal isotope.

Experimental

The experimental arrangement is shown schematically in fig. 1. The water-cooled Pyrex laser tube is 1.4 m long and has an internal diameter of 1.5 cm with ZnSe windows mounted at Brewster's angle. The laser cavity length of 3.3 m was determined by Invar rods in the pre-magnet section and quartz rods where the cavity passed between the poles of the electromagnet. The ends of the cavity were defined by a gold-coated diffraction grating (150 grooves mm⁻¹, blazed at 10.6 µm in the first order) and by a ZnSe output coupler with a radius of curvature of 10 m and a reflectivity of 82% at 9.1 µm. Within the laser tube the discharge was struck between two molybdenum anodes and a central, water-cooled, nickel cathode using a Wallis type OL153/30N LR2 power supply.

The continuous wave ${}^{12}C^{18}O_2$ laser was operated in a sealed-off mode. The composition and pressure of the gases in the laser tube had a marked effect on both laser stability and power output. The optimum laser gas mixture was found to be ${}^{12}C^{18}O_2$, N₂, He, Xe and H₂ with partial pressures of 1.2, 1.7, 4.7, 0.5 and 0.11 Torr, respectively, giving a total pressure of 8.2 Torr. The presence of H₂ in the mixture was particularly important as it catalysed the regeneration of ${}^{12}C^{18}O_2$ from the dissociation products formed in the discharge and hence prolonged the lasing lifetime.

^{† 1} Torr 101 325/760 Pa.



Fig. 1. The mid-IR LMR system.

The laser radiation emerging from the end of the cavity was split by a KBr disc. Most of the output passed through this beam-splitter to the power meter (Photon Control Ltd, model 11S). The rest of the beam was directed on to an Hg-Cd-Te detector (Laser Monitoring Systems Ltd) cooled to 77 K. The mechanical chopper facilitated the tuning of the laser and it was always switched off during kinetic experiments. The laser was manually tuned, the desired ${}^{12}C^{18}O_2$ laser line being observed on a spectrum analyser (Optical Engineering Inc.). The strongest HO₂ transitions were found at 8.90 kG on the ${}^{12}C^{18}O_2$ R(20) laser line at 1097.15 cm⁻¹, and at 3.21 kG on the ${}^{12}C^{18}O_2$ R(14) laser line at 1093.53 cm⁻¹. These peaks were used in the kinetic experiments.

The flow cell was located within the laser cavity and between the pole faces of a 15 in† Varian electromagnet (model no. V-4502-15). The magnetic field was controlled using a Hall probe attached to one pole face. The magnet control unit was calibrated using an ERO35 NMR Gaussmeter. The magnetic field experienced by the sample was modulated at 10 kHz using series-tuned subsidiary coils, each supplied by one output of a Marantz PM 750DC amplifier. The signal from the Hg-Cd-Te detector passed through a Plessey CA5100 pre-amplifier and a Brookdeal 9452 amplifier to a Brookdeal 9412A phase-sensitive detector. The output in first-derivative form, was then displayed on a Bryans 29000 XY chart recorder.

For the HO₂ + NO experiments, two different Pyrex flow tubes were used: a 70 cm long tube of internal diameter (i.d.) 1.832 cm, the inside surface of which was coated with Teflon (Du Pont FEP-120); and an 80 cm long tube of 2.570 cm i.d. which was left uncoated. For brevity, these tubes are designated the '3/4 in' and '1 in' flow tubes, respectively. Only the '3/4 in' flow tube was used in the HO₂ + NO₂ + He experiments.

For the $HO_2 + NO_2 + Ar$ experiments in which the temperature dependence of the reaction was studied, a Pyrex jacket (57 cm long) was attached to an 85 cm long, boric acid coated flow tube of 1.940 cm i.d. The outside of the Pyrex jacket was thermally insulated using a 1 cm thick layer of Triton Kaowool Ceramic Fibre which was in turn covered

with a layer of aluminium foil. For experiments at 275 K, a water-ethylene glycol mixture was circulated through the jacket of the flow tube using an Emscope Water Cooler (model MS16). For experiments at 326 K, water was heated in a thermostat bath and pumped through the jacket of the flow tube. Temperatures were measured using chromel-alumel thermocouples attached to the outside of the Pyrex jacket. The digital temperature readout was calibrated before use. The temperature gradient along the length of the flow tube was checked during the experiments at 275 and 326 K, and was found to be less than 0.5 K over the 57 cm jacket length. The total error in temperature measurement was estimated to be ± 2 K.

 HO_2 was generated in a fixed side port near the top of the flow tube by passing a trace of CF_4 in an Ar or He carrier through a 50 W 2450 MHz microwave discharge and reacting the F atoms thus produced with H_2O_2 ,

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

The CF_4 and H_2O_2 flow rates were adjusted to give the maximum $[HO_2]$.

A Teflon-coated double-inlet system was used in all experiments. The 0.88 cm o.d. outer inlet tube was of fixed length and extended from just above the flow tube to ca. 10 cm downstream of the side port to which the HO₂ source was attached. The outer inlet presented a surface that had not been in contact with the atmosphere outside the flow tube to the HO₂ radicals emerging from the source. It effectively prevented contact between the part of the movable inner inlet that was regularly exposed to the atmosphere, and the HO_2 radicals, hence reducing HO₂ radical destruction on the outer surface of the movable inner inlet. Using this sytem, the wall loss of HO₂ radicals on the inner inlet (k_{iw}) was too small to be measured, *i.e.* $k_{iw} < 1 \text{ s}^{-1}$. The reactant gas (NO or NO₂) was added to the flow tube through the 0.45 cm o.d. movable inner inlet. Four 1 mm diameter holes were drilled at the tip of the movable inlet to promote rapid mixing of the reactant with the carrier gas.

The flow rates of all gases, apart from NO_2 , were measured using mass-flow controllers [Advanced Semiconductor Materials (ASM), type AFC-260]. Before employing these flow controllers in the experimental flow system, they were

 $^{+ 1 \}text{ in} = 2.54 \text{ cm}.$

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each calibrated by allowing gas to flow through the controllers into a bulb of known volume, and measuring the rate of change of pressure with time of the gas in that known volume. Almost all of the ASM flow controllers were found to have a zero error. Hence by plotting calibration graphs for each controller, set gas flows could be measured accurately. ASM flow controllers were found to be unsuitable for measuring NO₂ flow rates. NO₂ flow rates were therefore measured using a glass capillary flow meter in which the pressure drop across a constricted tube was measured using a silicone oil manometer. This capillary flow meter was calibrated before use, allowance being made for the $2NO_2 \rightleftharpoons N_2O_4$ equilibrium which is rapidly established and significant in the storage bulb and flow meter. Total pressures were measured using a Baratron gauge (type 22BHS) attached to the horizontal part of the flow cell. From these pressures, the pressures at any other points along the flow tube could be determined using the Poiseuille equation. The applicability of this equation was verified by connecting a second Baratron pressure gauge to one of the side ports near the top of the flow tube, excellent agreement being obtained. In kinetic experiments, the calculated pressure at the mid-point of the reaction length was used in the analyses.

The manufacturers' stated minimum purity levels for the gases used were Ar (Air Products, 99.998%), He (British Oxygen Company, 99.999%), CF₄ (B.O.C., 99.7%) and NO₂ (Cambrian Gases, 99.5%). The Ar and He gas cylinders were found to contain significant amounts of water vapour and so Ar and He were each passed through silica gel traps cooled to 195 K and 77 K, respectively, before entry to the flow tube. CF_4 was also purified by passage through a silica gel trap cooled to 195 K. The nitrogen dioxide reactant was purified by adding excess O₂ (B.O.C., 99.97%) to the NO₂ (Cambrian Gases, 99.5%) in a 10 dm³ bulb and leaving the gases to mix for at least 12 h to eliminate the NO impurity. The gaseous NO₂ was then frozen at 195 K and any unreacted O₂ was pumped off. The purified NO₂ appeared as a white solid. After thawing, this purification process was repeated. The purified NO₂ was stored in a 5 dm³ bulb in the dark. The amount of NO impurity still remaining in the NO₂ bulb was determined to be <0.1%, using far-IR LMR.

The NO reactant was supplied as a 5% NO in Ar mixture (B.O.C.). This mixture was used without further purification, although for some of the kinetic runs more dilute NO/Ar mixtures were made up from it by adding Ar (B.O.C., research grade, 99.9995%). The most dilute mixture prepared in this way was 1.3% NO/Ar.

Hydrogen peroxide (Interox Chemicals Ltd) was supplied in an 86% by weight mixture with water. Before use, the H_2O_2 was purified in a vacuum system by sucking argon through it for several hours until the solution had diminished to about one-third of its original volume. This residual solution was analysed by removing a small sample (*ca.* 0.7 g), diluting it to 500 cm³ acidifying it with H_2SO_4 , and then titrating a 25 cm³ aliquot of the diluted sample with standardised 0.1 mol dm⁻³ KMnO₄. In this way the weight percent of purified H_2O_2 was found to be better than 98%.

All kinetic runs were carried out under pseudo-first-order conditions where the concentrations of NO or NO₂ were in large excess over the concentration of HO₂. Pseudo-first-order rate coefficients, ¹k, were obtained from plots of $\ln(h/h_0)$ against the reaction distance, z,

$$\ln(h/h_0) = -\frac{1}{kz/v}$$

where h is the HO₂ peak height in first derivative form, and v is the mean flow velocity. At each reaction distance at least two HO₂ peaks were recorded and then averaged. Reference HO₂ peak heights (h_0) were recorded at the beginning and

end of each kinetic run, and kinetic runs were only deemed valid if the two values of h_0 were in good agreement.

The measured values of ${}^{1}k$ were corrected for axial and radial diffusion, using the equation¹⁴

$${}^{1}k_{c} = {}^{1}k(1 + {}^{1}kD_{eff}/v^{2}).$$

 $D_{\rm eff}$ is the effective diffusion coefficient, given by

$$D_{\rm eff} = D + r^2 v^2 / 48D$$

where D is the molecular diffusion coefficient. The corrected values, ${}^{1}k_{e}$, were up to 5% higher than the measured values ${}^{1}k$.

Results

$HO_2 + NO \rightarrow OH + NO_2$ at 297 K

The first set of rate coefficients determined for reaction (1) were low and not very reproducible owing to the regeneration of HO₂ by the reaction of OH produced in reaction (1) with excess H_2O_2

$$OH + H_2O_2 \rightarrow HO_2 + H_2O.$$
 (5)

Varying the flow rates of H_2O_2 and CF_4 was found to alter only the initial concentrations of HO_2 and did not eliminate the effects of reaction (5). C_2F_3Cl (Argo International Ltd, 99.0%) was therefore added to scavenge the OH produced in reaction (1). The rate coefficient of the reaction between OH and C_2F_3Cl has been determined by Howard¹⁵ to be 6×10^{-12} cm³ molec⁻¹ s⁻¹ in He buffer gas in the range 0.7–7 Torr at 296 K.

One potential drawback of using C_2F_3Cl is that it absorbs strongly in the region 1050–1100 cm^{-1,16} a frequency range that includes the ${}^{12}C{}^{18}O_2$ laser lines at 1093.5 cm⁻¹ [R(14)] and 1097.2 cm⁻¹ [R(20)] used here. To investigate the effect of laser-line absorption, various flows of C_2F_3Cl were added to He in the flow tube. Changes in laser output were monitored using the power meter. It was found that adding C_2F_3Cl reduced the laser output linearly for both the R(14) and R(20) laser lines of ${}^{12}C{}^{18}O_2$ with the effect being more dramatic on the former of these lines and at lower laser powers (fig. 2).

In most of the experiments where C_3F_3Cl was employed to scavenge OH, the less strongly absorbed R(20) laser line was used. However, in experiments involving lower concentrations of C_2F_3Cl where either the R(20) or R(14) laser line could be employed, the use of the R(14) laser line made no difference to the kinetic results obtained. In other words, the absorption of ${}^{12}C{}^{18}O_2$ laser radiation by C_2F_3Cl did not affect the values of the rate coefficients determined.

The reaction between HO_2 and C_2F_3Cl was studied by adding C₂F₃Cl through the Teflon-coated inner inlet tube at various reaction distances. Seven sets of measurements were made over the pressure range 2.3-12.7 Torr at 297 K. Firstorder decay coefficients in HO₂ were found to be low, ${}^{1}k_{c} < 6$ s⁻¹, for concentrations of C_2F_3Cl as high as 1.7×10^{16} molec cm⁻³. An average of the seven sets of measurements gave an upper limit of $k \leq 3.3 \times 10^{-16}$ cm³ molec⁻¹ s⁻¹ for the bimolecular reaction between HO₂ and C₂F₃Cl. In all of the experiments involving NO, the C₂F₃Cl was added through the fixed-length Teflon-coated outer inlet tube, the tip of which was situated 10 cm downstream of the HO₂ source and at least 10 cm upstream from the tip of the movable NO injector. A total of 46 kinetic runs were carried out in the study of the $HO_2 + NO$ reaction in the presence of C_2F_3Cl scavenger, the concentration of which was typically $(1-3) \times 10^{15}$ molec cm⁻³. All experiments were performed at 297 ± 2 K and over the pressure range 0.8–13 Torr. The flow

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Fig. 2. A plot of % attenuation of laser power against $[C_2F_3Cl]$ for the ${}^{12}C^{18}O_2$ laser lines at 1093.5 cm⁻¹ [R(14)] and 1097.2 cm⁻¹ [R(20)]. Initial laser power: (\triangle) 70 mW [R(14)]; (\bigcirc) 475 mW [R(14)]; (\bigcirc) 150 mW [R(20)]; (\bigtriangledown) 700 mW [R(20)].

conditions and results are summarised in table 1. Experiments 1–12 were carried out in the uncoated 1 in flow tube and experiments 13–46 were performed in the Teflon-coated 3/4 in flow tube. Decay plots such as those shown in fig. 3 yielded pseudo-first-order rate coefficients. Their corrected values, ${}^{1}k_{e}$, were plotted against NO concentration as illustrated in fig. 4. The linearity of this plot shows the validity of the pseudo-first-order kinetic analysis and the insignificance of secondary reactions. The gradient in fig. 4 intersects the ${}^{1}k_{e}$ axis at 2.6 s⁻¹. This small value might be attributed to a



Fig. 3. HO₂ + NO(+C₂F₃Cl scavenger). Typical first-order decay plots. (\bigcirc) [NO] = 3.33 × 10¹² molec cm⁻³; (\square) [NO] = 6.03 × 10¹² molec cm⁻³; (\bigcirc) [NO] = 12.7 × 10¹² molec cm⁻³. P = 3.65 Torr and v = 2390 cm s⁻¹.



Fig. 4. $HO_2 + NO(+C_2F_3Cl$ scavenger). A plot of the corrected pseudo-first-order rate coefficient against the NO concentration. (Δ) Experiments carried out in the 1 in diameter flow tube. (\bigcirc) Experiments carried out in the 3/4 in diameter flow tube.

small additional first-order wall loss of HO₂ on the walls of the flow tube, or it could be attributed to uncertainties since least-squares analysis gave a standard error in the mean of $\pm 2.3 \text{ s}^{-1}$.

Individual values of k_1 were calculated by dividing each value of ${}^{1}k_{c}$ by the [NO] used. These are plotted against pressure in fig. 5. No pressure dependence of k_1 was found over the range 0.8–13 Torr. Therefore, any termolecular reaction channel involving the stabilisation of HOONO or its partial stabilisation as an intermediate cannot be significant in this pressure range.

Fig. 4 and 5 also show that there is good agreement between the measurements carried out in the 1 in and 3/4 in flow tubes, confirming that the kinetics are not dependent upon the reactor surface. In addition, when the NO flow was stopped after a kinetic run, the HO₂ signal immediately returned to its initial value. This implies that the reaction between HO₂ and NO does not take place on the reactor surface, since no induction period was observed. Nor was there any systematic variation of the values of k_1 with the linear flow velocity in either tube.

From the 46 separate determinations of k_1 , a mean value of $k_1 = (8.51 \pm 0.84) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \text{ at } 297 \text{ K was}$



Fig. 5. $HO_2 + NO(+C_2F_3Cl$ scavenger). Plot of k_1 vs. pressure. (\triangle) Experiments carried out in the 1 in diameter flow tube. (\bigcirc) Experiments carried out in the 3/4 in diameter flow tube.

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Table 1. Flow conditions and results for $HO_2 + NO(+C_2F_3Cl scavenger)$

1 2	·		/cm s	$/10^{12}$ molec cm ⁻³	/s ⁻¹	$/10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	
1 2	1 in flow tube ($r = 1.285$ cm)						
2	0.87	283	868	6.17	58.57	9.49	
	1.16	468	1076	9.60	91.19	9.50	
3	1.60	747	1244	8.29	72.66	8.76	
4	1.86	961	1374	7.49	72.13	9.63	
5	1.87	980	1403	7.37	60.30	8.18	
6	1.99	1038	1386	6.06	48.85	8.06	
7	2.01	1051	1390	9.95	89.35	8.98	
8	2.03	1051	1375	7.50	65.32	8.71	
9	2.03	1045	1368	7.54	61.60	8.17	
10	2.03	1044	1367	7.55	66.79	8.85	
11	2.05	1065	1381	7.45	59.05	7.92	
12	3.09	1933	1668	6.19	57.71	9.32	
3/4 in flow tube (r = 0.916 cm)							
13	1.63	739	2378	8 54	77 56	9.08	
13	1.63	737	2373	8.56	71.04	8 80	
15	2.12	1089	2696	7 54	62.13	8 24	
15	2.12	1051	2504	7.83	55 77	7 12	
10	2.12	1072	2554	3 38	30.53	9.02	
17	2.15	1072	2648	1 00	15 01	7 00	
10	2.10	2162	2040	1.33	10.19	8 22	
20	3.63	1168	1546	11.24	97.10	8 30	
20	3.64	1808	2387	3 33	34 47	10.40	
21	3.04	1845	2307	5.55	40.53	8 41	
22	3.65	1836	2423	6.13	48.10	7 85	
23	3.65	1837	2417	12.66	102.61	8 11	
25	3.66	1807	2412	603	60.02	9.95	
25	3.66	1315	1726	10.49	87 38	8 32	
20	3.67	1834	2401	196	19.48	9.94	
28	J.07	1076	1345	15.10	126.70	8 39	
20	5.02	1967	2048	644	57.95	9.00	
30	5.02	1955	2070	9.09	84.60	9 31	
31	5 30	1244	1230	640	43 74	683	
32	625	1560	1199	11 93	91 24	7 67	
33	6.25	1535	1175	12 19	97.91	8.03	
34	7.11	2197	1620	4.86	42.73	8 79	
35	717	2193	1604	8 22	62.40	7 59	
36	7.25	1974	1425	9.23	74 97	8 12	
37	7 33	2013	1425	916	76.87	8 39	
38	8 11	2566	1660	5 32	49.98	9 39	
39	847	2162	1343	5.82	44 50	7 58	
40	8 4 4	2182	1357	5 79	41.07	7.09	
41	9.16	2234	1280	6.16	50.34	8.17	
42	9.83	3735	1990	4 4 3	40.72	9.19	
43	10.52	2960	1476	5.99	38.90	6.50	
44	11.43	4123	1888	5 56	53 71	9.66	
45	12.72	3465	1426	618	48 44	7 84	
46	12.97	5906	2389	4.41	40.37	9.15	

 $a \ 1 \ \text{sccm} = 1 \ \text{cm}^3 \ \text{min}^{-1}$ at 273 K and $1.01 \times 10^5 \ \text{Pa}$.

obtained. The uncertainty represents one standard deviation of the measurements but does not include the contributions of systematic errors. If systematic errors of $\pm 1\%$ in absolute pressure and temperature measurements, and $\pm 2\%$ in total flow rate and NO flow rate measurements, are allowed for, then the overall uncertainty is estimated at *ca*. 15% which gives

$$k_1 = (8.5 \pm 1.3) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \text{ at } 297 \text{ K}.$$

This value is in excellent agreement with the NASA Panel's recommended value of $(8.3 \pm 1.2) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 298 K.¹⁷

$HO_2 + NO_2 + He \rightarrow HO_2NO_2 + He at 297 K$

A total of 36 kinetic runs were carried out over the pressure range 1.5–10 Torr. Pseudo-first-order decays of HO₂ were measured for NO₂ concentrations between 1.2 and 3.7×10^{15} molec cm⁻³. The flow velocities were between 9.7 and 14 m s⁻¹.

The corrected first-order decay coefficient, ${}^{1}k_{c}$, should be proportional to $[NO_{2}]$ [He]. Fig. 6 shows it to be strictly proportional to $[NO_{2}]$ for a constant helium pressure of 3.4 Torr. In fig. 7, the quantity ${}^{1}k_{c}/[NO_{2}]$ is plotted against total pressure giving a plot with excellent linearity. Although the carrier was predominantly helium (95–99.5%), NO₂ might be expected to have a much higher efficiency than He as a third body. The value of ${}^{1}k_{c}/[NO_{2}]$ at constant total pressure was plotted against $[NO_{2}]$. Fig. 8 has no discernible slope, showing that the role of NO₂ as a third body is not significant in these experiments. From the slope of the graph in fig. 7, a value of the termolecular rate coefficient was obtained of

$$k_3(M = He)$$

$$= (6.0 + 1.5) \times 10^{-32} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1} \text{ at } 297 \text{ K}$$

The quoted error is the estimated total error at the 1σ level.

The intercept on the ordinate axis in fig. 7 corresponds to a second-order rate coefficient of 2.8×10^{-15} cm³ molec⁻¹



Fig. 6. $HO_2 + NO_2 + He$ at 297 K. A plot of the corrected pseudofirst-order rate coefficient against the NO₂ concentration. P = 3.4Torr.

 s^{-1} . This represents an upper limit for the reaction

$$HO_2 + NO_2 \rightarrow HONO + O_2.$$
 (6)

However, although the intercept in fig. 7 agrees well with that obtained by Howard¹⁸ in discharge-flow experiments over a smaller pressure range, our value was found to depend on the number of cooled silica gel traps present in the helium supply lines. The above value was obtained with four cooled traps in the system. When the number of cooled traps was reduced to two, its value increased by a factor of *ca*. 4 to 1.2×10^{-14} cm³ molec⁻¹ s⁻¹. This is probably due to an increased con-



Fig. 7. $HO_2 + NO_2 + He$ at 297 K. A plot of the pseudo-secondorder rate coefficient against the total pressure. The dotted line shows Howard's¹⁸ results.



Fig. 8. $HO_2 + NO_2 + He$ at 297 K. A plot of the pseudo-second-order rate coefficient against the NO₂ concentration. P = 3.4 Torr.

centration of H_2O in the flow tube, conditioning the flowtube surface so as to make it more active in the heterogeneous reaction between HO₂ and NO₂. The value obtained for $k_3(M = He)$ did not depend upon the number of cooled traps present.

$HO_2 + NO_2 + Ar \rightarrow HO_2NO_2 + Ar$ between 275 and 326 K

These experiments with argon were carried out in the same manner as for helium, but with three cooled silica gel traps present. Twenty-eight kinetic runs were made with Ar as third body at 297 K and over the pressure range 1.5-10.1 Torr. NO₂ concentrations were in the range $(0.69-2.5) \times 10^{15}$ molec cm⁻³ and flow velocities were between 6.1 and 13.5 m s^{-1} . The pseudo-first-order rate coefficients corrected for diffusion effects, ${}^{1}k_{c}$, had values between 12 and 50 s⁻¹. Plots of ${}^{1}k_{c}$ against [NO₂] for eight runs at a constant total pressure of 3.53 Torr were strictly linear. The quantity ${}^{1}k_{c}/[NO_{2}]$ at constant pressure was independent of [NO₂] up to the highest value used, $[NO_2] = 2.5 \times 10^{15}$ molec cm⁻³, which represented 2.2% of the total flow. This showed that NO₂ played no significant role as a third body, and with the corresponding plot for the helium carrier, places an upper limit of 8×10^{-31} cm⁶ molec⁻² s⁻¹ on the rate coefficient of reaction (3) with M = NO₂. Fig. 9 shows the plot of ${}^{1}k_{c}/[NO_{2}]$ against the total pressure. The computed best fit to the points was a straight line, the slope of which gives a value for the termolecular rate coefficient of

$$_{3}(M = Ar)$$

k

$$= (1.27 \pm 0.32) \times 10^{-31} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1} \text{ at } 297 \text{ K}.$$

The estimated total error is quoted. The intercept on the ordinate axis has a value of 3.5×10^{-15} cm³ molec⁻¹ s⁻¹ which is close to that obtained in the HO₂ + NO₂ + He experiments at 297 K with four cooled traps in the pre-flow tube gas lines.

Twenty-one kinetic runs were carried out at 326 K, covering the pressure range 1.7-10.1 Torr. The reaction was slower than it was at 297 K requiring higher concentrations of NO₂ to achieve a satisfactory decay in HO₂ signal. Increased HO₂ destruction was observed on the flow tube surface at 326 K compared to 297 K. The importance of this was verified by recording HO₂ signals, in the absence of NO₂, with the water in the flow tube jacket at room temperature while the water in the bath was heated to 326 K. When the pump connecting the bath to the flow tube jacket was switched on, the flow tube reached a temperature of 326 K within 1 min. This caused the HO_2 peak height to decrease by ca. 30% on average and then stay steady. Without a boric acid coating on the flow tube this decrease was nearer 60%. The reduced initial HO₂ concentrations for the kinetic runs limited values of the corrected pseudo-first-order rate coefficient to below 30 s^{-1} . Nevertheless, the results were reproducible and a graph



Fig. 9. $HO_2 + NO_2 + Ar$ at 297 K. A plot of the pseudo-second-order rate coefficient against the total pressure.

was plotted of the pseudo-second-order rate coefficients against pressure (fig. 10). The slope of this graph gives a value for the termolecular rate coefficient of

$$k_3(M = Ar) = (1.00 \pm 0.25) \times 10^{-31} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$$

at 326 K.

The intercept on the ordinate axis is very small giving an apparent second-order rate coefficient of -0.3×10^{-15} cm³ molec⁻¹ s⁻¹.



Fig. 10. $HO_2 + NO_2 + Ar$ at 326 K. A plot of the pseudo-second-order rate coefficient against the total pressure.

Twenty-four kinetic runs were carried out at 275 K over the pressure range 1.6–10.1 Torr. The reaction was found to be faster than it was at 297 K. The corrected pseudo-firstorder rate coefficients took values in the range $13-43 \text{ s}^{-1}$. The destruction of HO₂ on the flow tube walls was found to be even greater than it was at 326 K, with reductions in the initial HO₂ signals of up to 50%, in the absence of NO₂, when the temperature was changed from 297 to 275 K. Nevertheless, the sensitivity of the detection apparatus was high enough to enable fairly reproducible measurements to be made. Fig. 11 shows the plot of ${}^{1}k_{e}/[\text{NO}_{2}]$ against pressure, the slope of which gives a value for the termolecular rate coefficient of

$$k_3(M = Ar) = (1.49 \pm 0.37) \times 10^{-31} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$$

at 275 K.

The rate coefficients for M = Ar at 275, 297 and 326 K yield a temperature dependence of

$$k_3(M = Ar)$$

$$= 1.24 \times 10^{-31} (T/300)^{-2.37 \pm 0.16} \text{ cm}^{6} \text{ molec}^{-2} \text{ s}^{-1}.$$

The alternative Arrhenius expression is

$$k_3(M = Ar) = (1.14 \pm 0.36) \times 10^{-32}$$

 $\times \exp[(710 \pm 66)/T] \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}.$

Both expressions fitted the data equally well. The temperature dependence found here is somewhat smaller than the value of $T^{-3.2\pm0.4}$ recommended by the NASA Panel¹⁷ for the low-pressure rate coefficient on the basis of measurements^{3.4} for $M = N_2$, O_2 which should show a similar temperature coefficient.

The intercept on the ordinate axis in fig. 11 corresponds to a second-order rate coefficient of 8.9×10^{-15} cm³ molec⁻¹ s⁻¹. Comparing the intercepts of fig. 9–11, it can be seen that the apparent bimolecular reaction between HO₂ and NO₂ has a strong negative temperature dependence. This excludes the possibility that it is in fact a true homogeneous bimolecular reaction, such as reaction 6, between HO₂ and NO₂.



Fig. 11. $HO_2 + NO_2 + Ar$ at 275 K. A plot of the pseudo-second-order rate coefficient against the total pressure.

In experiments with a helium carrier it was noted that this apparent second-order rate coefficient was reduced considerably by further purification of the carrier by passage through cold traps. This process was clearly removing water from the carrier, and it is concluded that this second-order rate coefficient is associated with a heterogeneous reaction between HO_2 and NO_2 which is catalysed by the presence of adsorbed water molecules. In this connection, it should be noted that HO_2 forms a strong hydrogen bond to the water molecules.

Discussion

 $HO_2 + NO$

Precise laboratory measurements of the rates of reaction of OH and HO_2 made to assist modelling of stratospheric chemistry have found unexpected increases in the second-order rate coefficient with total pressure. In some cases such as the very rapid reaction

$$OH + HO_2 \rightarrow H_2O + O_2 \tag{7}$$

Keyser¹⁹ has shown that this effect was not real and was caused by discrepancies between discharge-flow studies at low pressures and the use of other techniques at higher total pressures. In other cases such as reaction (2) and the reaction

$$OH + HNO_3 \rightarrow H_2O + NO_3 \tag{8}$$

careful measurements have confirmed the pressure dependence of the rate coefficient,¹⁷ which, taken with the overall negative temperature coefficient, must arise from the presence of a minimum in the potential surface for the reaction. As in the case of reaction (2), the pressure dependence of the rate coefficient arises because collisional relaxation of systems in the region of this minimum increases the probability of its decomposition to products rather than to reactants.¹⁰ The $HO_2 + NO$ reaction (1) is unexpectedly fast for a process which is only 31 kJ mol⁻¹ exothermic and has a negative temperature coefficient. It therefore must proceed via an attractive potential surface which is expected to have a minimum corresponding to pernitrous acid (HOONO), a species that has been observed in aqueous solution^{20,21} but not yet in the gas phase. Although there is excellent agreement between the measurements of the rate coefficient of reaction (1) around 1 Torr, there are insufficient data at higher total pressures to establish whether k_1 increases with total pressure. Our experiments show that there is no detectable pressure dependence up to 13 Torr (i.e. over the range of conditions encountered in the upper stratosphere), but further experiments at much higher total pressures are needed as the rate coefficients for the examples quoted only increase by a factor of ca. 2 up to 1 atm⁺ total pressure.

$HO_2 + NO_2 + M$

Our measurements on the rate coefficient of the Reaction $HO_2 + NO_2 + M$ cover much of the gap between Howard's¹⁸ maximum pressure of 3 Torr, and the lowest pressures used by Sander and Peterson³ (40 Torr) and by Kurylo and Ouellette⁴ (25 Torr). The value for k_3 found here for M = He is lower than the values of $(10.0 \pm 2.5) \times 10^{-32}$ cm⁶ molec⁻² s⁻¹ obtained by Howard¹⁸ or the extrapolated low-pressure limit of $(12 \pm 3) \times 10^{32}$ cm⁶ molec⁻² s⁻¹

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the pressure range 100-700 Torr. However, even at 10 Torr total pressure there is a slight fall-off of the third-order rate coefficient. If we allow for this effect using Troe's equation²² with a broadening factor of the fall-off curve $F_c = 0.6$ and a high-pressure limiting rate coefficient $k_{\infty} = 4.7 \times 10^{-12} \text{ cm}^3$ molec⁻¹ s⁻¹ at 300 K,^{4,17} the fall-off corresponds to 8% of the measured rate coefficient at the highest pressure used. On this basis our data correspond to a limiting low-pressure rate coefficient of $(6.5 \pm 1.5) \times 10^{-32}$ cm⁶ molec⁻² s⁻¹ at 297 K for M = He. Applying a corresponding factor to these data for M = Ar gives a limiting low-pressure rate coefficient of $(1.37 \pm 0.35) \times 10^{-31} (T/300)^{-2.37 \pm 0.16}$ cm⁶ molec⁻² s⁻¹. There are no other data for M = Ar with which to compare our measurement, but the value obtained and its temperature coefficient do not disagree with what might be expected on the basis of measurements with other third bodies.^{3,4,17} Howard¹⁸ has reported a rate coefficient $(6.6 \pm 3.0) \times 10^{-31}$ cm⁶ molec⁻² s⁻¹ for M = NO₂, in adequate agreement with our upper limit of $k_3 < 8 \times 10^{-31}$ cm⁶ $\operatorname{molec}^{-\widetilde{2}} \operatorname{s}^{-1}$ for $M = \operatorname{NO}_2$.

This work shows that mid-infrared LMR spectroscopy can be used to determine precise rate coefficients for elementary reactions of free radicals. This technique has the advantage that it can readily be used at total pressures exceeding 10 Torr, as can tunable diode laser spectroscopy. Both techniques exhibit high sensitivity because their inherent spectral widths are much less than the Doppler width of the vibration-rotation lines being observed. Although LMR shows a further gain in sensitivity being an intracavity technique, this is partly compensated by the real difficulty of achieving high laser stability, particularly of an isotopic CO₂ laser under the conditions of near critical gain which are needed to maximise sensitivity. The extra complexity of the apparatus needed and the fact that a strong Zeeman effect is exhibited by only a few transient species (mainly linear molecules in Π or Δ states, or small bent polyatomic molecules which correlate with Π or Δ states in a linear configuration) make mid-infrared LMR spectroscopy a less attractive option for kinetic studies than the use of tunable diode laser spectroscopy of the corresponding transitions.

We thank Dr T. M. F. Salmon who was much involved in the early development and testing of this equipment. We also thank NERC for a Research Grant and a Studentship for A.A.J-A.

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^{† 1} atm $\approx 1.01 \times 10^5$ Pa.

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Paper 0/01256D; Received 22nd March, 1990