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# The Reactions of NO<sub>3</sub> with OH and H

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Rate constants for the reaction

 $NO_3 + OH \rightarrow products$  (1)

have been measured in a flow system.  $NO_3$  radicals were generated from the reaction of F with HNO<sub>3</sub>, and OH radicals were generated by the reaction of H with  $NO_2$ . Concentrations of  $NO_3$  were determined by multipass optical absorption in the visible region, while [OH] was measured by resonance fluorescence. Numerical modelling allowed a rate coefficient to be derived for the reaction at room temperature of

 $k_1 = (2.0 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$ 

The modelling shows that secondary reactions are of only minor importance. We describe a hitherto-unknown reaction between H and NO<sub>3</sub>

$$NO_3 + H \rightarrow OH + NO_2.$$
 (2)

Production of OH was demonstrated explicitly from the resonance fluorescence measurements. The reaction is fast, with a room-temperature rate constant given by

$$k_2 = (1.1 \pm 0.6) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Reaction (1) follows the formation of OH in reaction (2), so that the time-dependence of [OH] can be used to give further information about  $k_1$ . The rate constants so obtained were entirely consistent with those obtained in the direct study.

The possible influence of steric effects and orbital degeneracy on the relative rates of the H and OH interactions with  $NO_3$  are pointed out. Atmospheric involvement of the reactions, in either troposphere or stratosphere, is shown to be improbable, although the new data illustrate that  $NO_3$  can be highly reactive towards suitable partners.

The kinetics of the reactions of simple free radicals provide valuable insights into the mechanisms of chemical interactions. Such reactions are also of great importance in the chemistry of the atmosphere, and the need to understand atmospheric transformations has provided an additional stimulus to laboratory study of radical reactions. The chemistry of the radicals OH,  $HO_2$  and ClO has been the subject of intensive study. Until recently, however, the nitrate radical,  $NO_3$ , has been relatively poorly investigated. The radical is now recognized as a possible key species, especially in tropospheric chemistry. It is a powerful oxidant, and can promote oxidation processes at night when other radicals such as OH are absent. It can abstract hydrogen to yield nitric acid and thus contribute to the acidification of rainwater. It can also react with organic species to form toxic and noxious compounds, including nitrates.

The reasons for the comparative neglect of the  $NO_3$  radical are partly experimental. It is more difficult to measure low concentrations of  $NO_3$  than it is for many other radical species. The sources of  $NO_3$  also present certain difficulties, because the agents of production of  $NO_3$  are frequently also the agents of its destruction. Furthermore, it



Fig. 1. Discharge-flow tube and detection system.

had been thought that the radical is rather unreactive. It has become apparent, however, that  $NO_3$  enters into several types of reaction, some of which are rapid. In our own laboratory, we have studied addition reactions (with some unsaturated hydrocarbons)<sup>1,2</sup> and hydrogen-abstraction reactions with several compounds.<sup>3</sup> We have also studied the reactions of  $NO_3$  with other free radicals, including Cl, ClO and  $HO_2$ .<sup>4,5</sup> Radical-radical reactions often proceed *via* an energized collision complex that is formed from the reactants with virtually no (electronic) energy barrier. They thus form an interesting class of process for theoretical interpretation at a number of levels of sophistication. The rates of these reactions may sometimes approach the gas-kinetic collision rates, so that radical-radical interactions can be fast, even at low temperatures.

A general picture of the reactivity of  $NO_3$  has begun to emerge from the recent studies. The pattern shown is one in which  $NO_3$  reacts more slowly than OH, Cl, O and so on, with closed-shell molecules, but in which the interactions with other radicals are rapid. In this paper, we describe further experiments on reactions of  $NO_3$  with other radicals, in an attempt to broaden the canvas on which the patterns can be recognized. The reactions are oxygen-atom transfers from  $NO_3$  to OH and to H:

$$OH + NO_3 \rightarrow HO_2 + NO_2 \tag{1}$$

$$H + NO_3 \rightarrow OH + NO_2.$$
 (2)

A discharge-flow technique was used, with resonance fluorescence being used to detect OH. Rate constants were measured at room temperature, and the values obtained confirm the high reactivity of  $NO_3$  towards other radicals. As far as we know, ours is the first investigation of reaction (2), both with regard to the kinetics of the process and the identification of the products of the interaction. Another study of reaction (1) was performed<sup>6,7</sup> concurrently with ours, using e.p.r. to detect the radicals. The kinetic results fully confirm the rate constant obtained in the present work.

### Experimental

### **Apparatus and Procedure**

Fig. 1 gives an outline of the apparatus used for the discharge-flow experiments. Hydrogen atoms were generated by passing a microwave discharge through a flow of

hydrogen in helium, while OH radicals were prepared by titrating H atoms with NO<sub>2</sub> under carefully controlled conditions. Nitrate radicals were formed by the reaction between anhydrous HNO<sub>3</sub> and atomic F (generated by a microwave discharge passed through  $F_2$ /He mixtures). A detailed account of the use of this method for producing known concentrations of NO<sub>3</sub> has appeared recently.<sup>8</sup> A sliding injector arrangement was used to mix the reactant gases, with the NO<sub>3</sub> in a carrier gas being admitted through the moving injector equipped with a spray nozzle. Hydroxyl radicals or atomic hydrogen were present, diluted with the helium carrier gas, in the main flow. Typical flow velocities were 14 m s<sup>-1</sup>, and total pressures were in the range 1.2-5.0 mmHg.<sup>†</sup>

Hydroxyl radical concentrations were determined by resonance fluorescence in the  $A^{2}\Sigma \rightarrow X^{2}\Pi$  transition. Optical absorption at  $\lambda = 662$  nm was used to monitor [NO<sub>3</sub>], the absorption cell being of the multipass White type, and giving an optical path of 156 cm. The cell was situated 25 cm downstream from the OH resonance cell, so that the [NO<sub>3</sub>] concentrations reported here refer to longer contact times than those for [OH], typical values being 1-30 ms for OH and 20-50 ms for  $NO_3$ . More significant is the difficulty in knowing the precise contact time to employ, since the White cell is 13 cm long. We use a weighted average for the residence period, but recognize that there could be an uncertainty of up to  $\pm 5$  ms. Fortunately, most of the kinetic information in our experiments is carried by the [OH] measurements, NO<sub>3</sub> decays being relatively small since this species is chosen to be in excess to provide nominally pseudo-first-order kinetics. Absolute sensitivities for [OH] and for [NO<sub>3</sub>] are ca.  $10^{10}$  and  $10^{11}$  molecule  $cm^{-3}$  for a signal-to-noise ratio of unity and a 10 s integration time. Calibrations for NO<sub>3</sub> were based on an absorption cross-section,<sup>8</sup> corrected for the filter function, of  $1.9 \times 10^{-17}$  cm<sup>2</sup> at  $\lambda = 662$  nm. However, in situ calibrations were also performed by titrating NO<sub>3</sub> with NO according to the procedure described earlier by us.<sup>8</sup> Absolute hydroxyl radical concentrations were determined by generating the radicals using an excess of H over  $NO_2$  that was sufficient, according to model calculations, to ensure essentially complete and rapid conversion of the NO<sub>2</sub> to OH. Separate measurements of the rate of loss of OH on the flow tube walls (see next paragraph) then enabled [OH] in the detection region to be determined. We note that simple titration of H by  $NO_2$ to the endpoint is not a satisfactory method of determining [H] at low concentrations  $(<10^{11} \text{ molecule cm}^{-3})$ , because conversion is not complete by the time the reactant gases reach the detection region.

All reaction system walls in contact with OH or  $NO_3$  radicals are coated with halogenocarbon wax (Halocarbon Corp., series 15-00). Rates of loss of OH on the walls were generally obtained by measuring the difference in observed resonance fluorescence intensity for addition of  $NO_2$  at the two fixed injectors marked  $J_1$  and  $J_2$  in fig. 1. Checks were made to ensure that the wall-loss efficiency remained virtually the same throughout the flow tube by adding  $NO_2$  through the sliding injector instead, and measuring the loss rates in the downstream part of the tube. The wall efficiency in the final metal part of the system may differ, but losses here must be small because the residence time of the gases is short (<4 ms) between the end of the glass section and the OH-fluorescence region. The effect of the injector itself on the loss of OH is small.

### Materials

Helium (B.O.C., commercial grade) was passed through a cartridge to remove traces of oxygen (Oxisorb, Messer-Griesheim), over red-hot copper turnings, through molecular sieve and  $P_2O_5$  drying towers and finally through cold traps (77 K) on both high- and low-pressure sides of the main needle valve. Hydrogen (B.O.C., commercial grade) was passed through a catalytic converter (DeOxo, Engelhard Industries) to reduce oxygen

 $<sup>\</sup>dagger 1 \text{ mmHg} = 101 \ 325/760 \text{ Pa}.$ 

impurities, and then through a  $P_2O_5$  drying tower. NO<sub>2</sub> (B.D.H., purity >99.5%) was degassed by repeated freeze-pump-thaw cycles. NO (B.O.C., purity >99.8%) was purified by trap-to-trap distillation to remove NO<sub>2</sub>. Anhydrous gaseous HNO<sub>3</sub> in an He carrier was made by bubbling He through a 2:1 mixture of H<sub>2</sub>SO<sub>4</sub> (Fisons, 98%) and HNO<sub>3</sub> (B.D.H., AristaR, *ca.* 70%).

### **Results and Discussion**

# (i) Reaction of NO<sub>3</sub> with OH Radicals

For these experiments, excess of NO<sub>2</sub> over H was used to ensure removal of H atoms from the main carrier flow. When NO<sub>3</sub> radicals were injected into this flow, [OH] decreased to an extent dependent on the time that the two gas streams were in contact. No destruction of OH was observed when the mixture of  $F_2$ , HNO<sub>3</sub> and He was added to the OH-containing carrier gas in the absence of F atoms. Excess [HNO<sub>3</sub>] over [F] was used, and [OH] did not depend on [HNO<sub>3</sub>] so long as the excess was maintained, so that the removal of OH may be ascribed with certainty to NO<sub>3</sub> itself, since there is no residual F that could react with OH. The concentration of NO<sub>3</sub>, in turn, was decreased by reaction with the OH-containing main gas flow. The depletion observed is a consequence of the reaction of NO<sub>3</sub> both with OH and with the NO product of the H+NO<sub>2</sub> reaction, as we shall discuss later.

Table 1 shows the data on which our kinetic measurements are based. Contact times and initial and final concentrations of [OH] and  $[NO_3]$  are displayed, together with the values of  $[NO]_0$  and  $[OH]_0$  calculated from the rate of wall loss to be present at the tip of the injector just before the reactant gas streams mix.

A first estimate of the rate constant for the reaction of OH with NO<sub>3</sub> may be obtained by assuming pseudo- first-order kinetics and by ignoring secondary reactions. Fig. 2 shows two typical plots of ln [OH] against contact time, and it is seen that the graphs are reasonably linear. Table 2 lists in the third column the second-order rate constants,  $ca. 2 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, derived in this way.

In order to examine the effects of secondary reactions, we have used numerical integration of the kinetic equations for the reactions that are likely to be important in our system:

$$NO_3 + OH \rightarrow HO_2 + NO_2$$
 (1)

 $k_1$  adjustable (see text)

$$NO_3 + NO \rightarrow NO_2 + NO_2$$
 (3)  
 $k_3 = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [\text{ref. (9)}]$ 

$$NO_3 + HO_2 \rightarrow NO_2 + OH + O_2$$
 (4)

$$k_4 = 3.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [\text{ref. (6), (7)}]$$

$$NO_3 + HO_2 \rightarrow HNO_3 + O_2 \tag{5}$$

$$k_5 = 9.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [\text{ref. (6), (7)}]$$

$$NO+HO_2 \rightarrow NO_2+OH$$
 (6)

$$k_6 = 8.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [\text{ref. (9)}]$$

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

$$k_7 = 7.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [\text{ref. (9)}]$$

$$OH + HNO_3 \rightarrow NO_3 + H_2O$$

$$k_8 = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [\text{ref. (9)}]$$
(8)

	[OH] <sub>NO3=0</sub>	[OH] <sub>NO3</sub>	[OH]₀	[NO] <sub>0</sub>	[OH] <sub>corr</sub>	[NO <sub>3</sub> ] <sub>OH=0</sub>	[NO <sub>3</sub> ] <sub>он</sub>
run t/s		$/10^{12}$ molecule cm <sup>-3</sup>					
a							
0.0018	2.65	2.47	2.70	4.07	2.56	2.93	2.61
0.0018	2.83	2.57	2.88	4.34	2.50	2.98	2.19
0.0037	2.57	1.99	2.66	3.97	2.09	3.08	2.98
0.0081	2.52	1.68	2.73	3.89	1.72	3.11	3.00
0.0094	3.09	1.95	3.40	4.79	1.61	3.08	2.61
0.0126	2.57	1.19	2.91	3.97	1.15	3.13	3.03
0.0170	2.35	0.88	2.78	3.63	0.89	3.11	2.90
0.0215	2.30	0.71	2.84	3.55	0.70	3.11	2.87
0.0243	2.79	0.66	3.55	4.31	0.52	3.11	2.59
а			2.80	3.92		3.07	
ь							
0.0015	2.25	2.12	2.29	3.45	2.65	2.81	2.28
0.0026	2.43	2.07	2.50	3.74	2.38	2.71	2.28
0.0049	2.47	2.03	2.60	3.82	2.24	2.76	2.25
0.0091	2.57	1.63	2.81	3.97	1.67	2.76	2.18
0.0134	2.79	1.46	3.19	4.31	1.32	2.71	2.12
0.0175	2.79	1.33	3.32	4.31	1.15	2.76	—
0.0234	2.65	0.97	3.35	4.10	0.83	2.71	2.12
а			2.87	3.96		2.74	
с							
0.0015	2.74	2.61	2.78	4.18	2.82	2.39	2.02
0.0040	2.69	2.34	2.80	4.16	2.51	2.49	2.18
0.0092	2.39	1.73	2.62	3.68	1.98	2.49	2.04
0.0138	2.47	1.33	2.84	3.82	1.40	2.28	1.91
0.0175	2.69	1.24	3.21	4.16	1.16	2.12	1.64
0.0228	2.57	1.06	3.22	3.97	0.99	2.28	1.75
0.0281	2.43	0.75	3.22	3.77	0.70	2.18	1.64
0.0348	2.47	0.66	3.50	3.83	0.57	2.18	1.59
а			3.02	3.95		2.30	

Table 1. Experimental data for the reaction of OH with NO<sub>3</sub>

<sup>a</sup> Average values for the initial concentrations. The contact time for the decay of NO<sub>3</sub> is *ca.* 18 ms longer than that for OH. The measurements for each position of the sliding injector are of [OH] and [NO<sub>3</sub>] at the respective detectors. These quantities are referred to by the symbols  $[OH]_{NO_3}$ ,  $[OH]_{NO_3=0}$  for [OH] measurements, according to whether or not NO<sub>3</sub> is present as a reactant, and  $[NO_3]_{OH=0}$  and  $[NO_3]_{OH}$  for the  $[NO_3]$  measurements in the absence and presence of OH. For OH, which decays appreciably with time in the flow tube as a result of wall losses even when NO<sub>3</sub> is not present, it is necessary to extrapolate the value of  $[OH]_{NO_3=0}$  to the concentration at the tip of the sliding injector, a quantity represented by the symbol  $[OH]_{NO_3=0}$  to the extrapolation is performed using a value of  $k_9 = 10 \text{ s}^{-1}$ . For ease of comparison in the figures, the real values of  $[OH]_{NO_3}$  are scaled to the average  $[OH]_0$  throughout the run to give a quantity we refer to as  $[OH]_{corr}$ .

$$OH \rightarrow products$$
 (9)

$$k_9 = 10 \text{ s}^{-1}$$
 (measured wall rate constant).

The products of the  $NO_3 + OH$  interaction are assumed to be  $NO_2 + HO_2$  (although  $HNO_3 + O$  are just thermodynamically accessible).

The nature of the fitting of the numerically modelled curves to the experimental data is shown in fig. 3. The points are the experimental data from run c, while the solid



**Fig. 2.** Plot of the ln [OH] against contact time for the reaction of OH with NO<sub>3</sub>. The OH concentrations are normalized to the average initial concentration for display purposes (see footnote to table 1).  $\bullet$ ,  $[NO_3]_{OH=0} = 2.3 \times 10^{12}$  molecule cm<sup>-3</sup> (run c);  $\bigcirc$ ,  $[NO_3]_{OH=0} = 3.1 \times 10^{12}$  molecule cm<sup>-3</sup> (run a).

Table 2. Derived rate constants for the reaction of OH with NO<sub>3</sub>

		rate constant $/10^{-11}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>			
run	$[NO_3]_{OH=0} / 10^{12} \text{ molecule cm}^{-3}$	first-order treatment	fitted to model		
a	3.1	2.2	2.0 (±0.2)		
b	2.7	1.9	$1.8(\pm 0.2)$		
с	2.3	2.2	2.0 (±0.3)		

curve (a) is that generated with  $k_1 = 2.0 \times 10^{-11} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>, and with all other rate constants from the published literature ( $k_3$  to  $k_7$ ) or measured in our reaction system ( $k_9$ ). The two dashed curves were obtained with  $k_1 = 1.6 \times 10^{-11} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> (upper) and  $k_1 = 2.4 \times 10^{-11} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> (lower). The experimental points are clearly accommodated well within this range, so that

$$k_1 = (2.0 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

for this experimental run, as indicated by the entry in table 2. The table shows that the values of  $k_1$  obtained from the other runs were very similar.



Fig. 3. Hydroxyl radical concentrations as a function of contact time in the reaction of OH with NO<sub>3</sub>. Circles are the values from run c of [OH]<sub>corr</sub>, defined in the footnote to table 1; solid and dashed curves are from a numerical model as described in the text.  $[NO_3]_{OH=0} = 2.3 \times 10^{12}$  molecule  $cm^{-3}$ ;  $[OH]_0 = 3.02 \times 10^{11}$  molecule  $cm^{-3}$ .

Reaction (8) between OH and HNO<sub>3</sub> could potentially affect [OH], since NO<sub>3</sub> is generated with [HNO<sub>3</sub>] in excess of [F]. Calculations suggest that the process cannot contribute significantly to OH loss for the concentrations of HNO<sub>3</sub> actually used, and experiment confirms that [OH] was the same with and without the HNO<sub>3</sub> flow when the F-atom discharge is not excited. We propose to show shortly that reaction (2) between H and NO<sub>3</sub> is fast and that it forms OH. Reaction (8) would thus be followed by reaction (2) if H atoms are present, and there would be no net consumption of OH. An important additional part of the test for reaction (8) was therefore to establish, by adding further NO<sub>2</sub>, that there were no residual H atoms by the time the main flow had reached the tip of the injector.

Each experimental measurement corresponds to a different initial hydroxyl radical concentration,  $[OH]_0$ , since it is obtained with the injector tip in a different position. For display purposes, we scale each point to an  $[OH]_0$  corresponding to the average. This procedure is legitimate so long as the dependence of the fitted result is only weakly dependent on  $[OH]_0$  (as we shall shortly show it to be), and the scaling factor is near unity (which it is for the measured rate of loss of OH at the walls). In fact, the experimental scatter in the points shown in fig. 3 is slightly greater than the correction itself, so that the fitted curves to be presented are essentially unaffected by the correction. Furthermore, fitting to the individual points gives values for  $k_1$  identical to those obtained with the corrected curves.

# Influence of Calibration Factors

The values for  $k_1$  obtained from curve-fitting to the full reaction scheme are only slightly smaller than those obtained by the simple pseudo-first-order analysis (see table 2), thus indicating that secondary reactions are, in reality, of only very minor importance. Errors



**Fig. 4.** Effect of the calibration factor for [OH] on the calculated value of  $k_1$ . The points represent the corrected experimental OH concentrations for run c and the lines are the modelled curves with  $k_1 = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .  $\bigcirc$ , [OH]<sub>corr</sub> as given in table 1;  $\Box$ ,  $1.17 \times [OH]_{corr}$ ;  $\bullet$ ,  $0.83 \times [OH]_{corr}$ .

in calibration factors and assumed rate constants should thus be of importance only in relation to the primary step, a conclusion immediately borne out by altering the initial value of  $[NO_3]$  by a factor of up to  $\pm 50\%$  in the integrations. The fitted value of  $k_1$  is in direct proportion to the reciprocal initial concentration over this range. The absolute concentrations of OH might be of importance if loss of the radicals had a significant non-first-order component. We therefore re-examined the experimental data using calibration factors 17% higher and lower than the one used normally. Fig. 4 shows the results. The three sets of data points correspond to the measured [OH] values of table 1 being multiplied by factors of 0.83, 1.00 and 1.17, while the three modelled curves are all for  $k_1 = 2.0 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and the appropriate [OH]<sub>0</sub>. It can be seen that the change in absolute [OH] has no significant effect on the agreement between experimental points and the model.

### Wall Losses of OH

A potential problem related to the absolute OH concentrations concerns the rate constant for wall loss,  $k_9$ , since this value is used in determining the concentration,  $[OH]_0$ , of OH at the injector. We have therefore re-analysed both the experimental data and the numerical modelling for a value of  $k_9 = 20 \text{ s}^{-1}$ , double that obtained by measurement. The open circles in fig. 5 show five of the eight experimental points from run c in the same way as in fig. 3 and 4: *i.e.* with [OH] corrected in each case to a common averaged value for  $[OH]_0$ . The modelled curve is for  $k_1 = 2.0 \times 10^{-11} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>, and demonstrates that the change in  $k_9$  has no impact on the fit. With the increased range of  $[OH]_0$  implied by the larger  $k_9$ , it is now also possible to display the individual uncorrected experimental points and the modelled curves for the corresponding (nonaveraged) values of  $[OH]_0$ . The closed circles in fig. 5, and the dashed lines terminating



**Fig. 5.** Effect of varying the rate constant for wall loss of OH  $(k_9)$  on calculated  $k_1$ .  $\bigcirc$ , Experimental  $[OH]_{corr}$ . The solid line is the modelled curve for  $k_1 = 2.0 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $k_9 = 20$  s<sup>-1</sup>. •, Uncorrected experimental values  $[OH]_{NO_3}$ . The dashed lines are the modelled OH decays for each individual value  $[OH]_0$ . The values of  $[OH]_0$  are calculated from  $[OH]_{NO_3=0}$  using  $k_9 = 20$  s<sup>-1</sup>.

at them, are the experimental results and the modelled decays. The overall fit to the set of points remains good for the same rate parameters, thus confirming our earlier statement that the adjustment of initial concentrations is merely convenient for visual display and has no bearing on the derived value of the rate constant for reaction (1).

# Other Systematic Errors

Changes in the total rate constant  $k_4 + k_5$  for the secondary reactions between NO<sub>3</sub> and HO<sub>2</sub> by a factor of  $\pm 50\%$  again has a negligible effect on the derived value of  $k_1$ . The differences in predicted [OH] are greatest at the longest contact times (e.g.  $\pm 9\%$  at 40 ms), but these times also carry the largest experimental error because [OH] is small, and thus has the least weight in the fitting. At times around 14 ms, in the middle of the experimental range, the differences in [OH] predicted are  $<\pm 2\%$ . Similar results are obtained for changes in the rate constants for reactions (3) and (7). Furthermore, removal altogether of reaction (6), between NO and HO<sub>2</sub>, has no discernible effect, thus showing that virtually all reaction of NO is with NO<sub>3</sub> at the concentrations of the various species present in our experiments.

The most important contributor to systematic error has thus been established to be in the absolute concentrations of  $NO_3$  and a contribution of up to 15% has been allotted to this source. We estimate an additional total random and systematic error of not more

than 15%, so that we suggest a rate constant for reaction (1) of

 $k_1 = (2.0 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$ 

Consumption of NO<sub>3</sub>

Most of the loss of NO<sub>3</sub> can be shown to result from the primary reaction (1), taken together with the reaction of NO resulting from the  $H+NO_2$  reaction used to generate OH. Indeed,  $[NO]_0$  is substantially larger than  $[OH]_0$ , because OH is lost on the walls of the reaction system from the moment it is formed, whereas NO is not. Reaction with NO thus constitutes the major loss of NO<sub>3</sub>. Inspection of table 1 shows that the sum of  $[NO]_0$  and the loss of [OH] is indistinguishable, within experimental error, from the loss of  $[NO_3]$ , so that secondary reactions cannot play an important part. In particular, reaction (1) followed by reaction (4) does not constitute a chain decomposition cycle for NO<sub>3</sub>, nor does reaction (1) followed by reaction (6) provide a catalytic pathway for the decomposition of NO<sub>3</sub> by NO.

### (ii) Reaction of NO<sub>3</sub> with H Atoms

We have observed that when  $NO_3$  is injected into a stream of carrier gas containing atomic hydrogen, hydroxyl radicals are formed. We therefore conclude that the reaction

$$H + NO_3 \rightarrow OH + NO_2$$
 (2)

proceeds rapidly to form the radicals. Hydroxyl radicals are not formed if H is absent but all other components are present, nor do they appear if  $F_2$  and HNO<sub>3</sub>, but not F, are present in the injected gas stream, so that the radicals are not a consequence of the reaction of H with impurity NO<sub>2</sub> from the NO<sub>3</sub> source. The rate of formation of OH, to be discussed shortly, is also too great for the radicals to be due solely to a reaction between H and the small amount<sup>8</sup> of NO<sub>2</sub> generated in the NO<sub>3</sub> source reactions (especially in the reaction of F with NO<sub>3</sub>). According to our earlier calculations,<sup>8</sup> [NO<sub>2</sub>] from this source is certainly less than 0.2[NO<sub>3</sub>], and is probably closer to 0.05[NO<sub>3</sub>]; the rate constant measured recently by Mellouki *et al.*<sup>6,7,10</sup> for the reaction of F with HNO<sub>3</sub> would reduce these estimates even further.

We have performed kinetic experiments with varying contact times that show that [OH] initially builds up at short contact times and subsequently decays at longer times. This behaviour is exactly that expected with a source, such as reaction (2), where the reactant in lower concentration (in this case H) is consumed, while loss processes continue. Fig. 6 shows concentration-time profiles for two experimental runs (distinguished by a factor of *ca*. six in the initial H-atom concentration). The decay part of the curves can be treated by the approximate analytical method exemplified by fig. 2. Once again, the derived loss rate constant is *ca*.  $2 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, strongly suggesting that the loss processes consist of the same set of reactions (1)-(9) that operate in the OH + NO<sub>3</sub> system. To that scheme must be added reaction (2) and the two further reactions

$$H + NO_2 \rightarrow OH + NO$$
 (10)  
 $k_{10} = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [\text{ref. (11)}]$ 

$$H + HO_2 \rightarrow OH + OH$$
 (11)

 $k_{11} = 6.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [\text{ref. (9)}] (\text{only OH channel included}).$ 

Table 3 shows the values of  $[NO_3]_0$  for the runs on which our kinetic measurements are based.





**Fig. 6.** Hydroxyl radical concentrations as a function of contact time in the reaction of H with NO<sub>3</sub>. •, Run A:  $[NO_3]_0 = 3.5 \times 10^{12}$  molecule cm<sup>-3</sup>; curve (*a*) is the model calculation with  $k_2 = 1.0 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $[H]_0 = 2.6 \times 10^{11}$  molecule cm<sup>-3</sup>; curve (*b*) with  $k_2 = 1.5 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $[H]_0 = 2.5 \times 10^{11}$  molecule cm<sup>-3</sup>. •, Run B:  $[NO_3]_0 = 2.8 \times 10^{12}$  molecule cm<sup>-3</sup>; curve (*c*) was obtained with  $k_2 = 1.5 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $[H]_0 = 1.5 \times 10^{12}$  molecule cm<sup>-3</sup>.

# Analytical Treatment of Data

The simplest analytical method uses just the initial rise portion of the curve, but we thought it preferable to examine the data on the basis of formation and pseudo-first-order loss processes so that we could use all the experimental data in a given run. Thus we write the rate of formation of OH equal to  $k_f[H]$ , where  $k_f = k_2[NO_3]$ , and the rate of loss equal to  $k_L$ . We take  $k_L = (k_1[NO_3] + k_9 + k_x[X])$ , where  $k_x$  is the rate constant for any additional losses of OH for which the co-reactant X remains roughly constant. We assumed that  $[NO_3]$  remained essentially constant (*i.e.* 'pseudo-first-order conditions'; a small correction was applied to  $[NO_3]_0$  to obtain an effective mean concentration). The kinetic equations yield the integrated result

$$[OH] = \frac{k_{\rm f}}{k_{\rm L} - k_{\rm f}} [H]_0 [\exp(-k_{\rm f}t) - \exp(-k_{\rm L}t)].$$
(I)

This function can now be fitted to the experimental data using a non-linear least-squares (NLSQ) calculation in which  $k_{\rm L}$  is one of the fitting parameters. Because of the difficulties with assessing absolute [H] referred to in the Experimental section, the initial H concentration was also used as a fitting parameter. So long as reactions (1) and (9) dominate the loss of OH,  $k_{\rm L}$  can be calculated from the known values (*i.e.*  $k_{\rm X}$ [X] is taken to be zero). However, we use here  $k_{\rm L}$  as an additional fitting parameter; the values of  $k_{\rm L}$  so obtained can then be compared with  $k_{\rm L}$  and  $k_9$ .

For most experimental runs, where  $[NO_3]_0/[H]_0$  is large enough for  $[NO_3]$  to remain virtually constant, it is clear that reactions (1) and (9) dominate all other losses of OH, because the NLSQ fit gives a value of  $k_L$  close to that calculated from the sum of  $k_1$ 

	p	I FV	[NO <sub>3</sub> ] <sub>0</sub>	[H] <sub>0</sub>	[NO <sub>3</sub> ] <sub>f</sub>	[NO <sub>3</sub> ] <sub>L</sub>	- k	k
run	$n / mmHg / cm s^{-1}$		$/10^{12}$ molecule cm <sup>-3</sup>				$/s^{-1}$	$/s^{-1}$
Α	3.8	1418	3.52	0.26	3.50	3.40	$439 \pm 54$	$73 \pm 8$
В	3.8	1407	2.82	1.80	2.50	2.30	$363\pm54$	$75 \pm 12$
С	3.8	1412	6.52	0.22	6.50	6.40		
D	3.6	1430	1.58	1.00	1.45	1.38	$279 \pm 78$	$56 \pm 19$
Е	3.7	1430	6.20	0.74	5.80	5.40	$726 \pm 264$	
F	3.7	1453	4.00	0.52	3.88	3.76	$484 \pm 90$	$135 \pm 22$
G	3.7	1453	3.91	0.76	3.77	3.63	$611 \pm 64$	$114 \pm 10$
Н	3.7	1457	5.80	0.35	5.54	5.28	$881 \pm 192$	$118 \pm 19$
I	3.7	1457	1.71	0.25	1.63	1.55	$323\pm104$	$61 \pm 28$
S	3.7	1147	3.58	0.76	3.22	3.13	$499 \pm 38$	$103 \pm 7$
Т	3.7	1147	2.30	0.42	2.20	2.00	$374 \pm 76$	$41 \pm 14$
J	1.2	1146	3.54	0.37	3.28	3.00	$948 \pm 48$	$76 \pm 2$
K	1.2	1146	3.48	0.38	3.36	3.24	$959 \pm 138$	$114 \pm 10$
L	1.2	1159	1.58	0.25	1.45	1.32	$688 \pm 98$	$38 \pm 6$
Μ	1.2	1166	2.20	0.69	1.97	1.75	$838 \pm 180$	$68 \pm 12$
Ν	1.2	1166	2.02	0.35	1.94	1.86	$866 \pm 88$	$120 \pm 8$
Р	1.2	1149	1.68	0.40	1.62	1.56	$809 \pm 108$	$48 \pm 4$
Q	1.2	1138	3.69	0.42	3.40	3.10	$1176 \pm 170$	$85 \pm 3$
R	1.2	1138	1.21	0.21	1.12	1.03	$628 \pm 70$	$37 \pm 4$
U	2.0	1283	3.12	0.55	2.92	2.72	$590 \pm 74$	$80 \pm 9$
v	2.0	1283	3.94	0.64	3.74	3.54	$567 \pm 60$	$103 \pm 10$
Х	2.0	1270	3.49	0.62	3.23	2.97	$555 \pm 48$	$93 \pm 7$
Y	2.0	1270	2.09	0.23	1.94	1.81	$452\pm88$	$70 \pm 15$
Z	2.0	1270	4.24	0.40	3.97	3.70	$735 \pm 124$	$95 \pm 12$
W	5.0	1525	2.67	0.40	2.55	2.45	$336\pm150$	$69\pm38$

**Table 3.** Experimental conditions used to study the reaction of H with NO<sub>3</sub> and the derived values of  $[H]_0$ ,  $k_f$  and  $k_L$ 

Runs C and E were not completed (only 8 and 9 data points). Error limits on  $k_f$  and  $k_L$  are  $\pm 2\sigma$ . Small corrections to the initial concentration of NO<sub>3</sub>, [NO<sub>3</sub>]<sub>0</sub>, are needed in the calculation of  $k_f$  and  $k_L$ . The appropriate quantities are [NO<sub>3</sub>]<sub>f</sub> and [NO<sub>3</sub>]<sub>L</sub>, defined by (3[NO<sub>3</sub>]<sub>0</sub>/4+[NO<sub>3</sub>]<sub>H</sub>/4) and ([NO<sub>3</sub>]<sub>0</sub>/2+[NO<sub>3</sub>]<sub>H</sub>/2), respectively, where [NO<sub>3</sub>]<sub>H</sub> is the concentration measured when H is present.

and  $k_9$  as determined by the direct measurements described earlier. This situation does not apply in runs B and D, where  $[NO_3]_0/[H]_0$  is *ca.* 1.6. The experimental value of  $[NO_3]$  at any chosen time can be used to show that in these runs  $k_L$  is appreciably greater than  $k_1[NO_3] + k_9$ . For run B, it appears that the reaction of OH with HO<sub>2</sub>

$$OH + HO_2 \rightarrow O_2 + H_2O$$
 (7)  
 $k_7 = 7.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [\text{ref. (9)}]$ 

can account for the additional contribution to  $k_{\rm L}$ . For run D, yet another loss process seems to be required. In this run, [HNO<sub>3</sub>] was abnormally high (estimated as  $>1 \times 10^{13}$  molecule cm<sup>-3</sup> in the main flow tube), so that reaction of OH with HNO<sub>3</sub>

$$OH + HNO_3 \rightarrow NO_3 + H_2O$$

$$k_8 = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [\text{ref. (9)}]$$
(8)

suggests itself as the extra loss process. This hypothesis was tested directly by performing experiments in which abnormally high  $[HNO_3]$  (>2×10<sup>13</sup> molecule cm<sup>-3</sup>, run N) and 'normal'  $[HNO_3]$  [(0.5–1.0)×10<sup>13</sup> molecule cm<sup>-3</sup>, run M] were employed in runs where

other conditions were kept approximately constant. Table 3 shows that  $k_{\rm L}$  increases from ca. 70 s<sup>-1</sup> in run M to ca. 120 s<sup>-1</sup> in run N. Although it is apparent that excess HNO<sub>3</sub> increases the rate of OH loss, the required pseudo-first-order rate constant for loss of OH is 50 s<sup>-1</sup>, so that the reaction cannot be the simple homogeneous one. Heterogeneous reaction between OH and HNO<sub>3</sub> is well known,<sup>12</sup> and expected to occur in our experiments. It appears that NO<sub>3</sub> is regenerated in the reaction, because the consumption of NO<sub>3</sub> over 17.5 ms is  $11.4 \times 10^{11}$  molecule cm<sup>-3</sup> in run M, but only  $4.2 \times 10^{11}$  molecule cm<sup>-3</sup> in run N.

# Numerical Modelling of the Kinetic Scheme

We now discuss the fitting of the experimental data by the numerical modelling of the complete kinetic scheme. Initial [H] is adjusted to fit the peak concentration of [OH], while  $k_2$  is varied to obtain a good match with the rise portion of the curve. Fig. 6 illustrates the fitting procedure for runs A and B. For the closed circles (run A) in the figure, curve (a) gives a good fit with the experimental data; this curve was generated with  $k_2 = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  ([H]<sub>0</sub> = 2.6 × 10<sup>11</sup> molecule cm<sup>-3</sup>). Curve (b), with  $k_2 = 1.5 \times 10^{-10} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> ([H]<sub>0</sub> = 2.5 × 10<sup>11</sup> molecule cm<sup>-3</sup>), is a notably poorer fit in the rise portion. Curve (c) is chosen as a reasonable fit to the experimental data of the open circles (run B) in the figure; in this latter case,  $k_2 = 1.5 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $[H]_0 = 1.5 \times 10^{12}$  molecule cm<sup>-3</sup>. It is evident from table 3 that the values of  $[H]_0$  and  $k_2 (= k_f / [NO_3]_f$ , where  $[NO_3]_f$  is defined in the footnote to the table) obtained from the approximate NLSQ method are almost the same as those derived from the numerical integrations. The NLSQ procedure therefore provides a convenient way of examining the influence of potential errors in the experiments. We have been particularly concerned with the absolute calibrations for [OH], and the absolute value for  $[H]_0$  in these experiments. It turns out that, by using  $[H]_0$  as a fitting parameter (in both analytical and numerical calculations), the absolute calibration for [OH] is forced to have only a very small influence, since secondary losses of OH with H-containing radicals are of minor importance. Of course, the derived value of  $[H]_0$  itself depends on the [OH]-calibration factor, but  $k_2$  was found to be essentially unaffected by changes of  $\pm 50\%$  about the nominal calibration.

Fig. 7 shows the first-order rate constants obtained from the NLSQ procedure as a function of  $[NO_3]_f$ . The linear least-squares slope is  $(1.1\pm0.6)\times10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This line possesses a small intercept, although a line from the origin can be made to pass through all the points within their own limits of error. As described in the next paragraph, we feel that the non-zero intercept of the 'best' line may be a consequence of the technical limitations of our experiments, and that it better represents the data than the forced zero-intercept one. We conclude, on the basis of this evidence, that we may write

$$k_2 = (1.1 \pm 0.6) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

# Effect of Pressure

We have performed a few experiments to look for a possible effect of pressure on the rate constant  $k_2$ . Fig. 7 shows some results obtained at pressures of 2 and 5 mmHg. Within the limits of error, the data lie on the same line as the rate data for a pressure of *ca*. 3.7 mmHg, so that a real pressure effect seems improbable. However, results obtained at a pressure of 1.2 mmHg give values of  $k_2$  that are apparently both larger than those obtained at the higher pressures and dependent on [NO<sub>3</sub>]: that is, the analogue of fig. 7 shows a much more pronounced intercept at this lower pressure. As we shall



Fig. 7. First-order rate constant as a function of the mean concentration of NO<sub>3</sub> for the reaction of H with NO<sub>3</sub>.  $\bullet$ , P = 3.6-3.8 mmHg;  $\Box$ , P = 2.0 mmHg;  $\nabla$ , P = 5.0 mmHg. Error bars are  $\pm 2\sigma$ .

now explain, we believe that the results obtained at 1.2 mmHg are unreliable at short contact times and should be disregarded.

# Flow Characterization

Our apparatus was designed for the study of relatively slow reactions in which the contact times would be at least an order of magnitude longer than those which are applicable to the rise portion of the concentration-time profiles used here to extract  $k_2$ . The last part of the flow line that has to be employed consists of two sections of different diameter, and the sliding injector has to enter the first of these to obtain useful kinetic results. Although the flow velocities are calculated for each section individually, the assumption of plug flow, with instantaneous transition at each boundary, has to be made. Mixing at the short contact times used to obtain the rise portion of the profile appears to be satisfactory, but the accuracy of our value of  $k_2$  might be adversely affected if mixing were poor at the injection point. The results obtained for  $k_2$  at the lowest pressure used (1.2 mmHg) seem likely to have been invalidated as a result of poor mixing. Although the flow velocities are slower at low pressures than usual (see table 3), this effect alone cannot cause the abnormally high apparent rate constants, because measurements made at a pressure of *ca.* 3.7 mmHg, but with a flow velocity appropriate



Fig. 8. First-order rate constant as a function of the mean concentration of NO<sub>3</sub> for the loss of OH.  $\bullet$ , P = 3.6-3.8 mmHg;  $\Box$ , P = 2.0 mmHg;  $\bigtriangledown$ , P = 5.0 mmHg;  $\bigcirc$ , P = 1.2 mmHg.

to experiments at 1.2 mmHg, gave a pseudo-first-order rate constant falling, within experimental error, on the line of fig. 7 (runs S and T).

# Effects of Diffusion

The dimensions of the apparatus and the magnitudes of the rates and flow velocities suggest that axial and radial diffusion could begin to interfere with a simple interpretation of the results. Incorrectly assessed contact times could well account for the non-zero intercepts attributed to fig. 7, because increasingly short distances from injector tip to detector are used in the analysis as the value of  $[NO_3]_0$  is made higher. The effect must be relatively unimportant, because the intercept is small, and the second-order rate coefficients obtained at each individual  $[NO_3]_0$  are the same within experimental error, for all experimental runs made at pressures above ca. 2 mmHg. Difficulty with the use of a diffusion correction imposes a further reason for disregarding the data obtained at the lowest pressures (1.2 mmHg). Incomplete radial diffusion interferes less with the extraction of valid data than at the higher pressure, but axial diffusion requires a large correction that is impossible to calculate exactly in our apparatus. We therefore note the observations made at low pressure, while rejecting them for quantitative consideration. For the main body of the results, we can estimate the necessary corrections for diffusion, following the approach outlined by Keyser.<sup>13</sup> The corrections to the pseudofirst-order rate constants range from multiplying factors of 1.06 to 1.19 over the range  $[NO_3] = 1.6 \times 10^{12} - 5.8 \times 10^{12}$  molecule cm<sup>-3</sup>, and the value of  $k_1$  becomes  $1.3 \times 10^{12}$  $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

# Decay of OH

We turn now to a more detailed consideration of the further information that the decay portion of the experimental [OH]-time profiles provides. Kinetic behaviour in this region is dominated by the loss of OH, so that it can be used for comparison with the direct experiments performed to examine the reaction of OH with NO<sub>3</sub>. The NLSQ analysis gives a value for a total first-order rate constant for the decay of OH. Fig. 8 shows these values plotted as a function of  $[NO_3]_L$ , where  $[NO_3]_L$  refers to a mean concentration of NO<sub>3</sub> corrected for half the (small) measured decay in  $[NO_3]$  (see footnote to table 3). The weighted least-squares fit gives

$$k_1 = (2.3 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where the error limits are  $2\sigma$ . This value is in excellent accord with the value derived by kinetic modelling of direct experiments in the OH+NO<sub>2</sub> system [see section (i)]. The intercept in fig. 8 is  $13 \pm 10 \text{ s}^{-1}$ , a value that agrees well with the measured rate constant for wall loss,  $k_9$ , of ca.  $10 \text{ s}^{-1}$ . The relatively large error limits in both slope and intercept are a consequence of the inclusion of runs where additional processes that lead to loss of OH may be operating, as described earlier. However, we note that there is no evidence of abnormal behaviour for the data obtained at a pressure of 1.2 mmHg, thus indicating that mixing and flow behaviour are perfectly acceptable at this pressure at the longer contact times (>6 ms) used for analysing the decay of OH.

#### Conclusions

We present here a direct measurement of the rate constant for the reaction of  $OH + NO_3$ ,  $k_1 = (2.0 \pm 0.6) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Our work has been performed concurrently with experiments by Mellouki *et al*<sup>6,7</sup> using e.p.r. for the detection of radicals. These workers quote a value of  $k_1 = (2.6 \pm 0.9) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, in excellent agreement with ours within the quoted error limits. There is, however, a feature worth noting. The central value obtained is rather higher than ours. It was obtained using the reaction of F with H<sub>2</sub>O as the source of OH. With the H + NO<sub>2</sub> source we adopted, Mellouki *et al.* find  $k_1 = (1.5 \pm 0.9) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. We also wished to use the F + H<sub>2</sub>O source on the grounds that it does not bring with it NO that reacts with NO<sub>3</sub>, but we found that addition of excess HNO<sub>3</sub> for the generation of NO<sub>3</sub> led to greatly enhanced loss rates for OH in this system. Our interpretation of these observations is that the presence of both water and  $HNO_3$  in the system leads to rapid consumption of OH, probably on the walls of the flow system. We have already pointed out that the apparent rate of the reaction between OH and HNO<sub>3</sub> exceeds the accepted<sup>9</sup> rate constant for the homogeneous process even when water is absent, and it seems likely that interfering heterogeneous processes become yet faster when water is deliberately added to the system. Mellouki et al. use faster flows than us, so that wall processes are of less relative importance. Nevertheless, an increased but unnoticed wall-loss rate in the presence of H<sub>2</sub>O would lead to erroneously large values of  $k_1$ .

We also describe in this paper a hitherto unreported reaction between atomic hydrogen and  $NO_3$ , which is shown to have OH radicals as one of the products, and the rate constant is of the same order of magnitude as the gas-kinetic collision frequency factor for hard spheres; it is the largest rate constant yet reported for reactions of  $NO_3$ .

The rate constants measured for reactions (1) and (2) show that NO<sub>3</sub> is a highly reactive radical towards certain species. Both reactions are radical-radical interactions involving oxygen-atom transfer from NO<sub>3</sub> to the other radical. In both cases, the reactions can formally proceed *via* energized collision complexes corresponding to known molecules

$$HO+O-N \bigvee_{O}^{O} \rightarrow HO\cdots O-N \bigvee_{O}^{O} \rightarrow HO_{2}+NO_{2}$$
(12)

and

$$H+O-N \bigvee_{O}^{O} \rightarrow H\cdots O-N \bigvee_{O}^{O} \rightarrow HO+NO_{2}.$$
(13)

The rate constant that we have determined for reaction (2) [or (13)] is almost identical to that for O-atom exchange from  $NO_2$  to H

$$H + NO_2 \rightarrow OH + NO$$
(10)  
$$k_{10} = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [\text{ref. (11)}]$$

and from OH to D

$$D+OH \rightarrow OD+H$$
 (14)  
 $k_{14} = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [\text{ref. (14)}].$ 

Since reactants and products are in every case doublets, reactions (1), (2), (10) and (14) possess adiabatic pathways on both singlet and triplet surfaces. Reaction (14) may well proceed through the bound state of HDO, although the non-statistical disposal of energy in the products of reaction (14) suggests that it proceeds in a direct manner on the triplet surface.<sup>15</sup> In any event, if reactants pass over to products on a single surface, then the degeneracy of the radicals will influence the probability of reaction. Because of the orbital degeneracy of OH, reaction (1) might be expected to have a rate constant a factor of two slower than that for reactions, and in the case of reactions with NO<sub>3</sub>, the constraints imposed by the symmetric NO<sub>3</sub> itself must be small. However, it is tempting to see an additional steric factor in the reaction of OH with NO<sub>3</sub> being imposed by the orientational requirement implied by the sequence of reaction (12). The combination of electronic degeneracy and steric effects would then explain the relative reactivities of OH and H towards NO<sub>3</sub>.

### Reactions of other Atoms and Radicals with NO<sub>3</sub>

The rate constant<sup>4,10</sup> for the reaction

$$Cl + NO_3 \rightarrow ClO + NO_2$$
 (15)

is  $5.5 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, or *ca.* one-half of the value for the reaction with H: the electronic degeneracy of the radical pair is twice that for the H-atom interaction. The reaction with ClO

$$ClO + NO_3 \rightarrow Cl + NO_2 + O_2$$
 (16)

is much slower  $(k_{16} = 4.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ , suggesting that, if the reaction initially involves transfer of an oxygen atom, then the measured rate constant also includes the rate at which the energized ClOO decomposes to Cl and O<sub>2</sub>. For the radical HO<sub>2</sub>, the major reaction channel seems to yield OH radicals

$$NO_3 + HO_2 \rightarrow NO_2 + OH + O_2 \tag{4}$$

with<sup>6,7</sup> a rate constant  $(3.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ , a factor of almost ten greater than that for the ClO reaction, (16), but still a factor of nearly ten slower than the more simple oxygen-atom transfer in reaction (1).

# **Atmospheric Chemistry**

It seems unlikely that either reaction (1) or reaction (2) are of great importance in themselves in atmospheric chemistry. The  $NO_3$  radical is rapidly photolysed by visible radiation, so that reaction with any photochemically generated radical has to compete with this photochemical loss. For a typical daytime value of  $[OH] = 10^6$  molecule cm<sup>-</sup> in the troposphere, the first-order loss rate for NO<sub>3</sub> via reaction (1) will be  $2 \times 10^{-5} \text{ s}^{-1}$ . which is *ca*, four orders of magnitude slower than the photolysis rate. Peak stratospheric concentrations of [OH] could be an order of magnitude higher than those in the troposphere, but it is still clear that photolysis dominates the loss of  $NO_3$  during the daytime. The situation at night is more complex. Hydroxyl concentrations rapidly decay after sunset in the troposphere and lower stratosphere. Near the stratopause and in the mesosphere, OH can persist at night, and atomic hydrogen begins to be a significant component of the atmosphere. However, the main source of  $NO_3$  is at the lower altitudes, so that slow vertical transport to the higher regions would be accompanied by almost complete photolysis during daytime illumination. Probably the most important conclusion to be drawn for atmospheric chemistry from the present experiments is the confirmation that radical-radical reactions of NO<sub>3</sub> can be fast and that transformations involving other radicals that persist at night because of their otherwise low reactivity remain plausible contributors to night-time atmospheric chemistry.

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# References

- 1 C. E. Canosa-Mas, S. J. Smith, S. Toby and R. P. Wayne, J. Chem. Soc., Faraday Trans. 2, 247.
- 2 C. E. Canosa-Mas, S. J. Smith, S. Toby and R. P. Wayne, J. Chem. Soc., Faraday Trans. 2, 263.
- 3 C. E. Canosa-Mas, S. J. Smith, S. Toby and R. P. Wayne, in preparation.
- 4 R. A. Cox, M. Fowles, D. Moulton and R. P. Wayne, J. Phys. Chem., 1987, 91, 3361.
- 5 I. W. Hall, R. P. Wayne, R. A. Cox, M. E. Jenkin and G. D. Hayman, J. Phys. Chem., submitted for publication.
- 6 A. Mellouki, A-M. Gumery, G. Le Bras and G. Poulet, XIIIth International Conference on Photochemistry, Budapest, Hungary, August 1987.
- 7 A. Mellouki, G. Le Bras and G. Poulet, to be published.
- 8 C. E. Canosa-Mas, M. Fowles, P. J. Houghton and R. P. Wayne, J. Chem. Soc., Faraday Trans. 2, 1987, 83, 1465.
- 9 NASA Panel for data evaluation, Chemical Kinetics and Photochemical Data for use in Stratospheric Modeling. Evaluation No. 7, JPL publication 85-37 (Jet Propulsion Laboratory, Pasadena, CA, 1985).
- 10 A. Mellouki, G. Le Bras and G. Poulet, J. Phys. Chem., 1987, 91, 5760.
- 11 M. A. A. Clyne and P. B. Monkhouse, J. Chem. Soc., Faraday Trans. 2, 1977, 73, 298.
- 12 J. J. Margitan, F. Kaufman and J. G. Anderson, Int. J. Chem. Kinet., 1975, Suppl. 1, 281.
- 13 L. F. Keyser, J. Phys. Chem., 1984, 88, 4750.
- 14 J. J. Margitan, F. Kaufman and J. G. Anderson, Chem. Phys. Lett., 1975, 34, 485.
- 15 I. W. M. Smith, Kinetics and Dynamics of Elementary Gas Reactions (Butterworths, London, 1980).

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