J. Chem. Soc., Faraday Trans. 2, 1989, 85(6), 709-725

# Laboratory Studies of the Reactions of the Nitrate Radical with Chloroform, Methanol, Hydrogen Chloride and Hydrogen Bromide

**Carlos E. Canosa-Mas, Stuart J. Smith, Sidney Toby**<sup>†</sup> and Richard P. Wayne<sup>\*</sup> Physical Chemistry Laboratory, Oxford University, South Parks Road, Oxford, OX1 3QZ

> Arrhenius parameters have been measured over the temperature range 298-523 K for the hydrogen abstraction reactions of NO<sub>3</sub> with CH<sub>3</sub>OH, CHCl<sub>3</sub> and HCl. A rate constant was determined at room temperature for the reaction of NO<sub>3</sub> with HBr. Kinetic data were obtained by the discharge-flow technique operating at total pressures between 1.8 and 5.2 mmHg. The rate expressions derived for the interactions with CH<sub>3</sub>OH, CHCl<sub>3</sub> and HCl are  $1.2 \times 10^{-12} \exp(-2560/T)$ ,  $8.6 \times 10^{-13} \exp(-2815/T)$ , and  $4.0 \times 10^{-12} \exp(-3330/T) \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>. For the reaction of NO<sub>3</sub> with HBr, the rate constant is  $1.3 \times 10^{-16} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> at 298 K. The hydrogenabstraction reactions of NO<sub>3</sub> are compared with those of O(<sup>3</sup>P) and OH.

The nitrate radical, NO<sub>3</sub>, is now recognized as an important intermediate species in the chemistry of our atmosphere. At night, especially in the troposphere, NO<sub>3</sub> can act as a powerful oxidizing and nitrating agent with a variety of organic compounds, producing noxious species such as PAN and free radicals (*e.g.* HO<sub>2</sub>). The night-time chemistry of NO<sub>3</sub> can contribute significantly to acid generation in the polluted and, to a lesser extent, unpolluted troposphere. The nitrate radical reacts with NO<sub>2</sub> to produce N<sub>2</sub>O<sub>5</sub> which can further react with water, probably heterogeneously, to give HNO<sub>3</sub>. Another possible pathway leading to the formation of nitric acid is the abstraction of an H atom by NO<sub>3</sub>.

We have already characterized,<sup>1,2</sup> along with other workers,<sup>3</sup> the addition of NO<sub>3</sub> to multiple carbon-carbon bonds. As a complement to those studies, we report here the rate constants and temperature dependences of some reactions involving H-abstraction from organic and inorganic substrates by NO<sub>3</sub>. Previous studies of such abstraction processes, at room temperature only, have been carried out by Atkinson *et al.*,<sup>4</sup> Wallington *et al.*<sup>5</sup> and Cantrell *et al.*<sup>6</sup> We discuss the importance of the reactions of NO<sub>3</sub> with HCl and HBr as sources for the active species Cl and Br.

### **Experimental**

The discharge-flow system and the multipath absorption cell for the measurement of  $[NO_3]$  at  $\lambda = 662$  nm have already been described.<sup>1,2</sup> The nitrate radical was generated by the reaction

$$F + HNO_3 \rightarrow NO_3 + HF$$
 (1)

and the discharge-flow technique used provides time resolution and hence absolute rate constants. The flow tube was heated by an electric oven regulated electronically that provided temperatures between room temperature and 523 K. The injection ports (referred to as ports 1, 2, 3 and 4) are situated at 19.5, 44.0, 70.1 and 95.1 cm from the centre of the observation region, giving contact times in the region 60-320 ms. Experiments were conducted at total pressures of 1.8-5.2 mmHg.‡

† Permanent Address: Department of Chemistry, Rutgers University, New Brunswick, NJ 08903, U.S.A. ‡ 1 mmHg ≈ 133.322 Pa.

## 710 Reactions of NO<sub>3</sub> Radical with CHCl<sub>3</sub>, CH<sub>3</sub>OH, HCl and HBr

All reactants were the commercially available materials and were purified by successive trap-to-trap distillations.

## **Results and Discussion**

#### Analysis of Kinetic Data

For each of the compounds investigated, we obtained first a preliminary value of the rate constant by estimating the initial rate of reaction. Concentrations of added reactants were always much larger than those of  $NO_3$ , so that pseudo first-order kinetics obtain. In most cases, the preliminary rate constants were refined by fitting the time-dependent loss of  $[NO_3]$  over the complete range of contact times to values of  $[NO_3]$  calculated by numerical integration of the appropriate kinetic equations for the reaction scheme believed to apply.

#### Methanol

The rate constant for the reaction of NO<sub>3</sub> with methanol was determined as a function of temperature between 295 and 473 K under pseudo first-order conditions ( $[CH_3OH] \gg [NO_3]$ ). We suggest that the reaction proceeds *via* the channel

$$NO_3 + CH_3OH \rightarrow CH_2OH + HNO_3$$
(2)

which is exothermic by 24.7 kJ mol<sup>-1</sup>, and not via the alternative path

$$NO_3 + CH_3OH \rightarrow CH_3O + HNO_3$$
 (3)

which is endothermic by 15.8 kJ mol<sup>-1</sup>; thermochemical data are obtained from ref. (7), (8) and (9).

The experimental conditions, calculated rate constants and Arrhenius parameters are shown in table 1. Kinetic data from four typical experimental runs at different temperatures are shown in fig. 1. For all the reactions of NO<sub>3</sub> reported in this paper, the plots of  $\ln \{[NO_3]_0/[NO_3]_i\}$  vs. *l* are curved, indicating an increase in reaction rate with increasing contact time. Thus, for the preliminary calculation of the rate constants measured at room temperature, we take only the data from the two ports closest to the detection cell, between which changes in [NO<sub>3</sub>] are measurable (usually ports 1 and 2). At higher temperatures, however, port 1 was around 20 K below the flow-tube temperature. The two closest usable ports in this case become 2 and 3. The calculated rate constants for T > 298 K may thus be upper limits, a matter to be discussed shortly.

The reactions of NO<sub>3</sub> with CH<sub>3</sub>OH, and also with CHCl<sub>3</sub>, are rather slow at room temperature. The vapour pressure of the reactants limits the concentrations that can be admitted to the flow tube, and it was not possible to measure the pseudo first-order rate constant as a function of partial pressure of the reactant. Furthermore, in order to observe changes in optical absorption above the noise level, only the ports at either end of the flow tube (ports 1 and 4) were used to obtain time-resolved data. The  $NO_3$  and added reactants are in contact for times differing by ca. 0.27 s between these ports, so that secondary reactions may be important. The uncertainty of the data is reflected in the large error limits taken. We find the rate constant of reaction (2),  $k_2$ , to be  $(2.1 \pm 1.1) \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 294 K, on the assumption of 1:1 stoicheiometry between loss of NO<sub>3</sub> and CH<sub>3</sub>OH. We shall demonstrate shortly that the assumption appears to be valid, but we note that occurrence of secondary reactions would mean that the true value of  $k_2$  would have to be smaller than that quoted here. Wallington et al.<sup>5</sup> quote an upper limit of  $6 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, a value perfectly consistent with our determination. In order to estimate the influence of secondary reactions on our rate measurements, we carried out numerical integration of the differential equations

ri i
3:1
3
1
14
3
<u>10</u>
2
E.
No.
sit
Ver
Ξ.
5
en
ast
the
5
Ę.
Ę.
led
oac
Ē
Ň
<u> </u>
8
19
<u>y</u>
JUI
Jaı
0
R
ğ
she
bli
Pal

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			I AUIC	ι. Απιτιστιτίας ματαπιστ	ers, experimental conc	Innons and rate con	0,111,110	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	reactant	T/K	P(total) /mmHg	/10 <sup>13</sup> molecule cm <sup>-3</sup>	[X] <sub>0</sub> /10 <sup>13</sup> molecule cm <sup>-3</sup>	$k/10^{-16} \text{ cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup>	ln $(A/10^{-16} \text{ cm}^3)$ molecule <sup>-1</sup> s <sup>-1</sup> )	$E_{\rm a}/{ m kJ}$ mol <sup>-1</sup>
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	CH <sub>3</sub> OH"	294	2.0-5.2	2.8-3.8	1.6-1.8	2.1±1.1		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		323	5.1	2.9–3.4	1.5-1.7	$4.61 \pm 0.92$		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		348	2.0-5.1	3.3-4.3	1.3-1.5	$6.8 \pm 2.7$		
$ \begin{array}{lcccccccccccccccccccccccccccccccccccc$		373	2.0-5.0	2.3-3.4	1.1-1.4	12.9±4.9	$9.43 \pm 0.66^{h}$	$21.3 \pm 2^{b}$
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		423	2.0	2.9-4.1	1.0-1.1	$31.1 \pm 8.4$		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		428	5.0	3.6-3.8	0.9-1.0	$25.1 \pm 4.5$		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		473	2.0-5.0	1.6-3.5	0.8-1.0	63.2±13.5 J		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	CHCI, <sup>4</sup>	323	4.2	2.9	1.6	2.6		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	'n	373	4.1	3.1-3.2	0.9-1.3	$4.3 \pm 1.2$		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		423	4.1	2.9	0.9-1.0	$12.0 \pm 0.14$	$9.05 \pm 0.56^{b}$	$23.4 \pm 2^{b}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		473	4.1	2.6	0.8-0.9	$21.7 \pm 4.8$		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		523	4.1	3.9-4.2	0.5-1.2	$38.8 \pm 7.3$		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	HCI	333	1.99	2.03	3.24	1.3 <sup>d</sup>		
353       194       2.17       2.66       2.5         373       199       1.85       2.48       100         373       199       1.85       2.48       100         373       199       1.74       100       100         373       199       1.74       100       100         373       199       1.74       100       100         373       199       1.74       100       100         373       200       1.36       1.35       6.0       100         373       200       1.36       1.12       200       100         423       1.99       1.36       1.12       200       100         433       193       1.43       0.40       200       100         473       193       1.43       0.40       200       100         473       193       1.43       0.40       200       250       250         473       193       1.43       0.40       200       250       250       250       250       250       250       250       250       250       250       250       250       250       250       250		333	1.97	2.96	4.21	1.0		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		353	1.94	2.17	2.66	2.5		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		353	1.93	2.38	3.34	2.5		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		373	1.99	1.85	2.48	10.0		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		373	1.98	1.74	1.14	10.0		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		373	1.99	1.74	0.70	10.0		
373       2.03       1.98       1.52       6.0 $10.6\pm 1.7^{n}$ 277±57^{n}         423       1.99       1.39       0.54       2.00 $1.32$ 0.05       277±57^{n}       277±57^{n}         423       1.99       1.39       0.54       2.00 $1.112$ 200 $1.7^{n}$ 277±57^{n}         423       1.99       1.39       0.49       10.0 $0.49$ $10.0$ $1.23$ $20.0$ $1.12$ $20.0$ $1.12$ $277\pm57^{n}$ $277\pm57^{n}$ $277\pm57^{n}$ $277\pm57^{n}$ $277\pm57^{n}$ $277\pm57^{n}$ $275$ $200$ $200$ $200$ $210$ $210$ $277\pm57^{n}$ $277\pm57^{n}$ $277\pm57^{n}$ $275$ $210$ $210$ $217\pm57^{n}$ $277\pm57^{n}$ $275\pm57^{n}$ $272\pm57^{n}$ $272\pm57^{n}$ $272\pm57^{n}$ $272\pm57^{n}$ $272\pm57^{n}$ $272\pm57^{n}$ $272\pm57^{n}$ $272\pm57^{n}$ $272\pm57^{n}$ $27\pm57^{n}$ $27\pm57^{n}$ $220^{n}$		373	2.01	2.04	1.59	4.0		•
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		373	2.03	1.98	1.52	6.0	$10.6 \pm 1.7^{b}$	$27.7 \pm 5.7^{h}$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		423	1.99	1.39	0.54	20.0		
423       1.95       2.14       0.49       100         473       1.93       1.43       0.40       200         473       1.92       1.49       1.23       200         473       1.92       1.49       1.23       200         473       1.92       1.49       1.23       25.0         473       1.92       1.82       0.34       35.0         473       1.92       1.82       0.34       35.0         473       1.92       1.82       0.24       35.0         28       2.01       7.11       0.41       0.90         298       2.01       6.24       0.28       1.65         298       2.30       6.44       0.13       1.66         298       2.04       6.46       0.26       1.10         298       2.04       6.46       0.24       2.20         298       2.04       6.46       0.24       2.20         298       2.04       6.46       0.24       2.20         298       2.04       6.46       0.24       2.20         1.10       1.10       1.40       1.10       1.40		423	2.00	1.36	1.12	20.0		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		423	1.95	2.14	0.49	10.0		
473       1.92       1.49       1.23       20.0         473       1.94       1.42       0.45       25.0         473       1.93       1.67       0.34       35.0         473       1.92       1.82       0.24       35.0         473       1.92       1.82       0.24       35.0         298       2.01       7.11       0.41       0.90         298       2.01       7.11       0.41       0.90         298       2.01       7.11       0.28       1.65         298       2.30       6.44       0.13       1.40         298       2.04       6.46       0.26       1.10         298       2.04       6.46       0.24       2.20         298       2.04       6.46       0.24       1.10		423	1.93	1.43	0.40	20.0		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		473	1.92	1.49	1.23	20.0		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		473	1.94	1.42	0.45	25.0		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		473	1.93	1.67	0.34	35.0		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		473	1.92	1.82	0.24	35.0 J		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	HBr	298	2.02	6.27	0.82	0.75 <sup>d</sup>		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		298	2.01	7.11	0.41	06.0		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		298	2.01	6.24	0.28	1.65		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		298	2.30	6.44	0.13	1.40		
298 2.04 6.46 0.24 2.20 $k_{ave} = 1.3(\pm 1.1)^{b}$		298	1.82	7.80	0.26	1.10		
$k_{ave} = 1.3(\pm 1.1)^{h}$		298	2.04	6.46	0.24	2.20		
	$k_{ave}$					$1.3(\pm 1.1)^{h}$		

C. E. Canosa-Mas, S. J. Smith, S. Toby and R. P. Wayne

711

<sup>a</sup> Values of k are averaged for all runs at each temperature; <sup>b</sup> error limits are  $\pm 2\sigma$ ; <sup>c</sup> individual runs; <sup>d</sup> fitted rate constants.



**Fig. 1.** Plot of  $\ln \{[NO_3]_0/[NO_3]_i\}$  against distance for the reaction of NO<sub>3</sub> with CH<sub>3</sub>OH at 5 mmHg total pressure and at the flow velocity, v, given below for each temperature. The solid line indicates the slope used in the calculation of  $k_2$ .  $\bigcirc$ : T = 348 K,  $[CH_3OH]_0 = 1.5 \times 10^{15}$  molecule cm<sup>-3</sup>, v = 3.4 ms<sup>-1</sup>,  $k = 5.1 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.  $\bigoplus$ : T = 373 K,  $[CH_3OH]_0 = 1.4 \times 10^{15}$  molecule cm<sup>-3</sup>, v = 3.3 ms<sup>-1</sup>,  $k = 7.6 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.  $\bigoplus$ : T = 428 K,  $[CH_3OH]_0 = 9.1 \times 10^{14}$  molecule cm<sup>-3</sup>, v = 3.8 ms<sup>-1</sup>,  $k = 2.7 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.  $\bigoplus$ : T = 473 K,  $[CH_3OH]_0 = 7.5 \times 10^{14}$  molecule cm<sup>-3</sup>, v = 4.1 ms<sup>-1</sup>,  $k = 6.0 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

corresponding to a plausible mechanism. The mechanism of the reaction between O and CH<sub>3</sub>OH was used to produce a comparative scheme for the reaction of NO<sub>3</sub> with CH<sub>3</sub>OH. For O+CH<sub>3</sub>OH, Grotheer and Just<sup>10</sup> used a model including the reactions

$$O(^{3}P) + CH_{3}OH \rightarrow CH_{2}OH + OH$$

$$k_{4} = 5.7 \times 10^{-11} \exp \left[-2750/T\right] \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1} \text{ ref. (10)}$$
(4)

$$CH_2OH + CH_2OH \rightarrow \text{ products}$$

$$k_5 = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ ref. (11)}$$
(5)

$$CH_2OH + O(^{3}P) \rightarrow CH_2O + OH$$

$$k_6 = 2.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ ref. (10).}$$
(6)

By analogy, a possible mechanism for the  $NO_3 + CH_3OH$  system might be supposed to include the reactions

$$NO_3 + CH_3OH \rightarrow HNO_3 + CH_2OH$$
(2)

$$CH_2OH + CH_2OH \rightarrow \text{ products}$$
 (5)

$$CH_2OH + NO_3 \rightarrow CH_2O + HNO_3 \tag{7}$$

$$CH_2O + NO_3 \rightarrow HCO + HNO_3$$
 (8)

$$k_8 = 6.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ ref. (3)}.$$

Although NO<sub>3</sub> may react further with the formyl radical produced in reaction (8), we shall show shortly that the reaction is unimportant in our experiments. We measure the rate of reaction for the shortest contact times, as described above, to give an experimental rate constant that we use as a first approximation to  $k_2$ . As the temperature dependences of reactions (5) and (8) are not known, the fitting procedure was carried out at a temperature of 323 K (the temperature closest to room temperature at which reliable kinetic data could be obtained for each inlet port). The experimental data were fitted with the rate constants for reactions (5) and (8) fixed at the values quoted (vide supra). A good fit was obtained with  $k_2 = 4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_7 = 5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The ratio  $k_7/k_2$  is thus 1250. According to Grotheer and Just, the value of  $k_6/k_4$  is ca. 175 at 323 K. Reactions of O(<sup>3</sup>P) atoms with non-radicals are usually of the order 10-1000 times faster than the corresponding  $NO_3$  reactions  $(k_4/k_2 = 275)$ .<sup>1</sup> Furthermore, rates of reaction of NO<sub>3</sub> with other radicals (e.g. HO<sub>2</sub>, ClO)<sup>12-14</sup> can be up to a factor of 20 times slower than the rates of analogous reactions of O(<sup>3</sup>P) so that our derived ratio  $k_6/k_7 = 4$  appears reasonable. It follows that the modelled rate constants are thus of the correct relative and absolute magnitudes. The fitted value of  $k_2$  is, in fact, almost identical to the preliminary value obtained by the 'initial rate' method. A sensitivity analysis showed that even if  $k_7$  were to be as fast as  $k_6$ , then the effect on the derived rate constant,  $k_2$ , would be to lower it only to a value of  $3 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. More important, however, is that there is no kinetic or mechanistic justification for adopting a larger value of  $k_7$  and thus a correspondingly lower value for  $k_2$ . Abstraction of the hydroxyl H from CH<sub>3</sub>OH by CH<sub>2</sub>OH at room temperature can be ruled out as the process is endothermic. As noted already, it was only possible to observe a loss of NO<sub>3</sub> between neighbouring injection points at elevated flow-tube temperatures. It was assumed that reaction (5) had no temperature dependence and that the rate constant for reaction (8) at 323 K could be calculated by estimating an activation energy of 28 kJ mol<sup>-1</sup> for the process from the relationship between enthalpy of reaction and activation energy to be presented later in our discussion. Calculation by this method yielded a rate constant for reaction (8) at 323 K only twice its value at room temperature and inclusion of this value had no effect on the modelled rate constant for the primary process,  $k_2$ . This finding also provides the justification for the exclusion from the reaction scheme of further reactions of the HCO radical formed in reaction (8) with  $NO_3$ . We conclude that there is no evidence for secondary reactions having a major influence on the rate coefficients determined from the initial rates of decay of NO<sub>3</sub> so that the coefficients can be taken as the real values for  $k_2$  at least at 323 K.

The Arrhenius plot made using all the directly determined rate constants is a good straight line, as seen in fig. 2. Thus, if secondary reactions do occur, there can be no appreciable change in the overall stoicheiometry of the reaction with temperature. Since we have established that the occurrence of secondary reactions appears not to invalidate our measurements at 323 K, it thus follows that the rate coefficients at the higher temperatures also refer to rate constants for reaction (2). Two further considerations are relevant to the question of secondary reaction at temperatures higher than 323 K. First, the contact times for the same injection ports are reduced at elevated temperatures (the flow velocities are almost proportional to the absolute temperatures). Secondly, radical-radical reactions, such as reactions (5) and (7), are likely to increase in rate with increasing temperature much less than the primary interaction, reaction (2). The Arrhenius parameters are given in table 1. We have previously discussed<sup>1,2</sup> the use of



Fig. 2. Arrhenius plot for the reaction of NO<sub>3</sub> with CH<sub>3</sub>OH. The vertical lines represent error limits of  $\pm 2\sigma$ . The line is the least-squares fit to the experimental points.

 $O_2$  added to the reaction mixture as an aid to investigating the effects of secondary reactions involving radical species. In the case of reaction with CH<sub>3</sub>OH, such a procedure would be fruitless since the product of reaction (2) is CH<sub>2</sub>OH, which reacts with O<sub>2</sub> to produce HO<sub>2</sub>, itself highly reactive towards NO<sub>3</sub>.<sup>12,13,15</sup>

### Chloroform

The reaction

$$NO_3 + CHCl_3 \rightarrow CCl_3 + HNO_3 \tag{9}$$

is exothermic by 17.6 kJ mol<sup>-1</sup> at 300 K.<sup>7-9</sup> The abstraction of the Cl atom with subsequent formation of ClONO<sub>2</sub> is endothermic by 163 kJ mol<sup>-1</sup>. Fig. 3 shows the decay of ln [NO<sub>3</sub>] as a function of distance for typical experimental conditions at four different temperatures. At room temperature the reaction is too slow to be measured in our apparatus. At 323 K, a loss of NO<sub>3</sub> can be measured but only between the two ports at either end of the flow tube. For the relatively long contact times involved, secondary reactions may be important, so that the value of  $k_9 = 2.6 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> obtained at 323 K can only be quoted with certainty as an upper limit. We give the values of the rate constant determined at 373, 423, 473 and 523 K in table 1 and the corresponding Arrhenius plot in fig. 4.





**Fig. 3.** Plot of  $\ln \{[NO_3]_0/[NO_3]_i\}$  against distance, l, for the reaction of NO<sub>3</sub> with CHCl<sub>3</sub>. The solid line indicates the slope used in the calculation of  $k_9$ . Total pressure is 4.1 mmHg and at the flow velocity, v.  $\bigcirc$ : T = 373 K,  $[CHCl_3]_0 = 9.3 \times 10^{14}$  molecule cm<sup>-3</sup>, v = 3.6 ms<sup>-1</sup>,  $k = 4.8 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.  $\bigoplus$ : T = 423 K,  $[CHCl_3]_0 = 9.8 \times 10^{14}$  molecule cm<sup>-3</sup>, v = 4.1 ms<sup>-1</sup>,  $k = 1.2 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.  $\square$ : T = 473 K,  $[CHCl_3]_0 = 8.1 \times 10^{14}$  molecule cm<sup>-3</sup>, v = 4.5 ms<sup>-1</sup>,  $k = 2.2 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.  $\blacksquare$ : T = 523 K,  $[CHCl_3]_0 = 5.3 \times 10^{14}$  molecule cm<sup>-3</sup>, v = 5.0 ms<sup>-1</sup>,  $k = 4.3 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

The effects of secondary processes that might follow the primary step in the reaction of  $NO_3$  with  $CHCl_3$  are more difficult to estimate than in the case of the reaction with  $CH_3OH$ . The reaction

$$O(^{3}P) + CCl_{3} \rightarrow CCl_{2}O + Cl$$
(10)

has been studied<sup>16</sup> and a rate constant of  $(4.2 \pm 0.6) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> determined. If a process analogous to reaction (10) takes place in our system

$$NO_3 + CCl_3 \rightarrow CCl_2O + NO_2 + Cl \tag{11}$$

with a significant rate constant, then the Cl atom would react very fast with NO<sub>3</sub>, as we shall show in the next section.<sup>14,17</sup> The experimentally observed rate constant could then be larger than the true value of  $k_9$  by a factor of up to *ca*. three. Recombination of CCl<sub>3</sub> would be unimportant in this system as it would not be able to compete with reaction (11). Because of the high degree of uncertainty of the possible secondary processes we feel that kinetic modelling is not justified and prefer to quote the rate



Fig. 4. Arrhenius plot for the reaction of NO<sub>3</sub> with CHCl<sub>3</sub>. The vertical lines represent error limits of  $\pm 2\sigma$  and the filled circle is the experimental upper limit at 298 K.

constants as upper limits. As can be seen from fig. 4, the Arrhenius plot is apparently linear, so that, as for the reaction with  $CH_3OH$ , there is no evidence for a significant change in the stoicheiometry of the reaction with temperature. The value for the pre-exponential factor is thus an upper limit, yet the value for the activation energy is apparently representative of that for the primary step.

#### Hydrogen Chloride

The reaction of HCl with  $NO_3$  was studied in the temperature range 298–523 K. Of the two possible channels,

$$NO_3 + HCl \rightarrow HNO_3 + Cl \tag{12}$$

$$\rightarrow$$
 ClONO<sub>2</sub>+H (13)

we propose that reaction (12) is the major one as it is only slightly endothermic (by ca. 7.2 kJ mol<sup>-1</sup> at 300 K); reaction (13) is endothermic by 265 kJ mol<sup>-1</sup>.<sup>7-9</sup> We observed no reaction at room temperature. On the basis of the noise levels, we estimate the upper limit for the rate constant to be  $2.4 \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Experiments carried out at higher temperatures show that reaction does occur. However, plots of ln [NO<sub>3</sub>] against time (see fig. 5) show pronounced curvature, suggesting the involvement of secondary reactions. The chemistry of the Cl-ClO<sub>x</sub>-NO<sub>x</sub> system has been characterized by various workers, but most recently by Cox *et al.*<sup>14</sup> and Mellouki *et al.*<sup>17</sup> It was thus possible to undertake kinetic modelling to analyse the experimental data.

The reaction scheme used for the  $NO_3 + HCl$  system is given below. Rate constants (in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> unless otherwise stated) were adjusted for the temperature

## C. E. Canosa-Mas, S. J. Smith, S. Toby and R. P. Wayne



Fig. 5. Plot of  $\ln \{[NO_3]_0/[NO_3]_i\}$  against time for the reaction of NO<sub>3</sub> with HCl at 373 K. The open circles are the experimental points and the solid line illustrates the curvature, but is not derived from numerical modelling.

(variable) and pressure (ca. 2 mmHg) in the flow tube.

$$NO_3 + HCl \rightarrow Cl + HNO_3$$
;  $k_{12}$ : fitting parameter (12)

$$NO_3 + Cl \rightarrow ClO + NO_2; k_{14} = 5.5 \times 10^{-11} \text{ ref.} (14)$$
 (14)

NO<sub>3</sub>+ClO → ClOO+NO<sub>2</sub>; 
$$k_{15} = 1.6 \times 10^{-12} \exp \left[-(420 \pm 200)/T\right]$$
 ref. (14) (15)

$$ClOO + Cl \rightarrow Cl_2 + O_2; k_{16} = 1.4 \times 10^{-10} \text{ ref.} (14)$$
 (16)

$$ClOO + M \rightarrow Cl + O_2 + M; k_{17} = 1.5 \times 10^{-8} \exp(-3217/T)[M] \text{ ref.} (14)$$
 (17)

$$HNO_3 + Cl \rightarrow HCl + NO_3$$
;  $k_{18}$ : up to  $5.3 \times 10^{-14}$  ref. (18): see text (18)

$$NO_2 + Cl + M \rightarrow ClONO + M; k_{19}$$
: calculated from data in ref. (8) (19)

$$NO_2 + CIO + M \rightarrow CIONO_2 + M; k_{20}$$
: calculated from data in ref. (8) (20)

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M; k_{21} = 5.9 \times 10^{-14} \text{ ref.} (19)$$
 (21)

$$N_2O_5 + M \rightarrow NO_3 + NO_2 + M \tag{22}$$

 $k_{22}$ : calculated from  $k_{21}$  and the equilibrium constant  $(2.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1})$  ref. (8).

717



Fig. 6. Plot of  $[NO_3]$  against time for the reaction of NO<sub>3</sub> with HCl at 473 K.  $\bigcirc$ , Individual experimental points; —, model fit.

The sole fitting parameter for the modelling was the rate constant for reaction (12). The results derived are presented in table 1. A sensitivity analysis of the mechanism to deviations from the quoted rate constants was carried out. We took the rate constant calculated directly from the decay of NO<sub>3</sub> to be a good first approximation for  $k_{12}$  and varied its value to obtain the best fit to the data. The fits were successful in reproducing the shape of the  $[NO_3]$  vs. time profiles, as shown in fig. 6. As we do not know the temperature profile between the constant-temperature section of the flow tube and the detection point, it is an assumption in the calculations of  $[NO_3]$  and the contact time that the temperature falls sharply at the first injection port, from the flow tube temperature to room temperature. The calculation of [NO<sub>3</sub>], and the uncertainties in some of the rate constants used, are estimated to lead to errors in the region of  $\pm 20\%$ . The final fitted value for  $k_{12}$  was always at least two times smaller than the value initially chosen and often up to three and a half times less, depending upon the relative and absolute concentrations of NO<sub>3</sub> and HCl. The reaction of Cl atoms with the wall is not included in the model because the rate constant of such a process would have to exceed  $750 \text{ s}^{-1}$ in order to compete with reaction (14), whereas Judeikis and Wun<sup>20</sup> show the value of  $k_{wall}$  to be less than 30 s<sup>-1</sup>, for a quartz flow cell of 0.45 cm internal diameter. The self-reactions of ClO are unimportant, (in contrast to the situation with BrO, as is discussed later), as were the reactions of  $HNO_3$  with<sup>21</sup> ClO and<sup>18,22</sup> Cl [the reverse of reaction (12)] under our experimental conditions. Taking the values for  $k_{12}$  from table 1, we present the data in the form of an Arrhenius plot in fig. 7. Using the activation energy and A factor calculated from the figure, and quoted in table 2, the value of  $k_{12}$ is  $5 \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K. However, because of the large uncertainty associated with the A factor, the limits for  $k_{12}$  are  $1 \times 10^{-16}$  and  $2 \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The lower end of the range is thus consistent with our directly determined upper limit of  $k_{12} \le 2.4(\pm 0.9) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at room temperature. We note that Cantrell et al.<sup>6</sup> have published a smaller upper limit of





Fig. 7. Arrhenius plot for the reaction of NO<sub>3</sub> with HCl. Fitted rate constants derived from the kinetic model  $(\bigcirc)$  and the least-squares fit to the points (-----).

 $7 \times 10^{-18}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> which is below out nominal lowest value, although not by much.

It is possible to compare our value for the activation energy with the activation energies obtained for the reverse reaction

$$Cl + HNO_3 \rightarrow NO_3 + HCl$$
 (18)

of  $36 \pm 7 \text{ kJ mol}^{-1}$  by Poulet *et al.*<sup>22</sup> at 439 < T/K < 633, and of  $14.1 \pm 1.2 \text{ kJ mol}^{-1}$  by Kurylo *et al.*<sup>18</sup> between 240 and 300 K. Our activation energy for the forward reaction, combined with the exothermicity of reaction (12) at 298 K (13.7 kJ mol<sup>-1</sup>) yields a value for  $E_a(18)$  of  $34 \pm 7 \text{ kJ mol}^{-1}$ . This value agrees well with the experimental determination of Poulet *et al.*<sup>22</sup>

The reaction of NO<sub>3</sub> with HCl has been suggested by Austin *et al.*<sup>23</sup> as a possible minor contributor to the nitric acid present in the atmosphere. However, in their calculations these workers used  $k_{12} = 2 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at room temperature, as had been proposed by Davidson *et al.*<sup>24</sup> With a value of  $k_{12}$  of *ca.*  $10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> derived from our new Arrhenius parameters for stratospheric temperatures of *ca.* 260 K, it is clear that any contribution of reaction (12) to the total amount of nitric acid in the atmosphere must be ruled out. This conclusion can also, of course, be drawn from the upper limit for  $k_{12}$  published by the NCAR group.<sup>6</sup>

		ref.	5	-	و	١	see later).
· · · · · · · · · · · · · · · · · · ·		E <sub>act</sub> /kJ mol	21.3 <sup>4</sup>	23.4 <sup>4</sup>	27.7" 	15.7 <sup>c</sup>	ationship (s
	ON	k /cm³ molecule <sup>-1</sup> s <sup>-1</sup>	$\leq 2.1 \times 10^{-16}$ $\leq 6 \times 10^{-16}$	≤1×10 <sup>-17</sup> "	$\left\{ \begin{array}{l} \leqslant 2.4 \times 10^{-17}  ^{\circ} \\ (5 \pm 4) \times 10^{-17}  ^{\circ} \\ \leqslant 7 \times 10^{-18} \end{array} \right.$	$1.3 \times 10^{-16}$ "	ed on Evans-Polanyi rel
		ref.	10 34	1	œ	8	ata; <sup>c</sup> bas
	(	$E_{ m act}$ /kJ mol	22.9 21	I	27.4	12.9	nperature d
and HBr	O( <sup>3</sup> P	k /cm³ molecule <sup>1</sup> s <sup>-1</sup>	$6 \times 10^{-15}$ $5.8 \times 10^{-15}$	ł	1.4×10 <sup>-16</sup>	$3.7 \times 10^{-14}$	rapolated from higher ter
		ref.	32 33	8	œ	œ	value exti
		$E_{ m act} = -1$	6.6 4.0	8.6	2.9	0	<sup>h</sup> this work,
	но	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$\begin{cases} 7.7 \times 10^{-13} \\ 8.6 \times 10^{-13} \end{cases}$	$1 \times 10^{-13}$	8 × 10 <sup>-13</sup>	$1.1 \times 10^{-11}$	, direct determination;
		reactant	СН <sub>3</sub> ОН	CHCl <sub>3</sub>	НСІ	HBr	<sup>a</sup> This work,

Reactions of NO<sub>3</sub> Radical with CHCl<sub>3</sub>, CH<sub>3</sub>OH, HCl and HBr



Published on 01 January 1989. Downloaded by Northeastern University on 25/10/2014 14:03:12.

720



**Fig. 8.** Plot of ln {[NO<sub>3</sub>]<sub>0</sub>/[NO<sub>3</sub>},} against time for the reaction of NO<sub>3</sub> with HBr at 298 K and 2 mmHg total pressure. O, experimental points; —, illustrates curvature, but is not derived from numerical modelling.

#### Hydrogen Bromide

We also studied the reaction

$$NO_3 + HBr \rightarrow HNO_3 + Br$$
 (23)

 $\Delta_r H_{298}^{\oplus}(23) = -51.4$  kJ mol<sup>-1</sup>,<sup>7-9</sup> at room temperature only. The plots of ln [NO<sub>3</sub>] against time are strongly curved (see fig. 8) indicating that the rate of loss of the nitrate radical increases with increasing contact time and therefore is not solely determined by the primary process, reaction (23). The rate constant calculated using the initial slope of a plot such as that shown in fig. 8 will represent an upper limit for the rate constant,  $k_{23}$ . Our data treated in this simple way yield values for  $k_{23}$  in the range (0.3-2.0) × 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Thus the reaction of NO<sub>3</sub> with HBr proceeds, even at room temperature, at a rate in excess of that of the analogous reaction with HCl.

The rate constant for the primary process,  $k_{23}$ , was extracted from the data by numerical integration of the rate equations for the following reaction scheme

$$NO_3 + HBr \rightarrow HNO_3 + Br; k_{23}$$
: fitting parameter (23)

$$NO_3 + Br \rightarrow BrO + NO_2; k_{24} = 1.2 \times 10^{-11} \text{ ref.} (25)$$
 (24)

$$NO_3 + BrO \rightarrow BrOO + NO_2; k_{25}$$
: see discussion (25)

$$BrO + BrO \rightarrow 2Br + O_2; k_{26} = 2.3 \times 10^{-12} \text{ ref.} (8, 26)$$
 (26)

$$BrO + BrO \rightarrow Br_2 + O_2; k_{27} = 4.4 \times 10^{-13} \text{ ref.} (8, 26)$$
 (27)

## Reactions of NO<sub>3</sub> Radical with CHCl<sub>3</sub>, CH<sub>3</sub>OH, HCl and HBr

BrOO+M 
$$\rightarrow$$
 Br+O<sub>2</sub>+M;  $k_{28} > 2.0 \times 10^4 \,\mathrm{s}^{-1}$  ref. (26) (28)

BrOO+Br 
$$\rightarrow$$
 BrO+BrO;  $k_{29} > 5 \times 10^{-12}$  ref. (26, 27) (29)

Br+O<sub>2</sub>+M  $\rightarrow$  BrOO+M;  $k_{30} = 2 \times 10^{-33} (T/300)^{-1.4}$ [M]: see text (30)

$$NO_2 + BrO + M \rightarrow BrONO_2 + M; k_{31} = 3.2 \times 10^{-14} \text{ ref.} (8)$$
 (31)

together with reactions (21) and (22). Rate constants (given in units of  $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup>, unless otherwise stated) are adjusted for a temperature of 298 K and pressures of *ca*. 2 mmHg. The ranges of concentrations used in these experiments were, for NO<sub>3</sub>, between 1.6 and  $7.0 \times 10^{13}$  molecule  $cm^{-3}$  and, for HBr, between 0.2 and  $4.3 \times 10^{15}$  molecule  $cm^{-3}$ .

Rate constants for all but four of the reactions are available in the published literature. Those four are  $k_{23}$ ,  $k_{25}$ ,  $k_{29}$  and  $k_{30}$ . Reaction (30) is of little importance as a sink for bromine atoms, since it cannot compete with reaction (28), BrOO decomposition. The rate constant for reaction (29) is taken to be the same as that for the analogous chlorine reaction,<sup>26</sup> but it is of little importance in the scheme as it, also, is not fast enough to compete with reaction (28). A direct determination of the  $k_{29}$  was reported by Butakov-skaya *et al.*,<sup>27</sup> who obtained a value of *ca*.  $5.0 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Le Bras and co-workers<sup>25</sup> have measured the rate constant of reaction (24) to be  $1.2 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. No direct measurement exists of the rate constant for the reaction of BrO with NO<sub>3</sub> [reaction (25)]. However, Poulet *et al.*<sup>28</sup> found that a value for  $k_{25} = (7\pm3) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was needed to fit the data obtained in their study of the reaction of atomic bromine with NO<sub>3</sub>.

Good fits to the data were obtained using the model, as illustrated by fig. 9. The sensitivity of the model to all the rate constants used was determined, with particular attention being paid to the effect of alterations in  $k_{25}$ . The data are fitted well by the model for values of  $k_{25}$  between  $4 \times 10^{-12}$  and  $10 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, the range quoted by Poulet.<sup>28</sup> The fits for  $k_{25}$  within this range are apparently equally good. An increase in the value used for  $k_{25}$  leads to a decrease in the value derived for  $k_{23}$ , and we may employ this result to fix a lower limit for  $k_{25}$ . A value of  $k_{25}$  of  $4 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> yields an average  $k_{23} = (1.9 \pm 0.8) \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This is above the upper limit for  $k_{23}$  of  $<1 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, reported by Poulet *et al.*<sup>25</sup> For our results to be compatible with the data of Poulet *et al.*,  $k_{25}$  must be  $>4 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Model calculations using values of  $7 \times 10^{-12}$ ,  $1 \times 10^{-11}$  and even  $1 \times 10^{-9}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for  $k_{25}$  yield average  $k_{23}$  values of  $(1.3 \pm 0.5) \times 10^{-16}$ ,  $(1.1 \pm 0.5) \times 10^{-16}$  and  $(6.5 \pm 0.9) \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. We thus find that the decrease in the fitted rate constant is small within two standard deviations of the mean values, even for  $k_{25}$  as high as the gas-kinetic limit. We propose that  $k_{25}$  be taken as *ca.*  $7 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, and that  $k_{23}$  be taken as  $(1.3 \pm 1.1) \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, a value consistent, within experimental error, with the upper limit of Poulet *et al.*<sup>25</sup>

The production of Br atoms in the primary step introduces a sequence of secondary loss processes for NO<sub>3</sub>. Bromine atoms reacting with NO<sub>3</sub> in reaction (24) are quickly regenerated via reactions (26), (25) and (28), leading to a catalytic destruction of NO<sub>3</sub>. In the HCl+NO<sub>3</sub> system, the chains are shorter than in the HBr+NO<sub>3</sub> case, largely because of the different products of the XOO+X interactions (16) and (29) (where X = Cl or Br) and because of the different rates and products of the XO+XO interactions. The ClO+ClO reaction is too slow to be of importance in our system, while the BrO+BrO interaction, reactions (26) and (27), are fast and the dominant channel, reaction (26), regenerates atomic bromine. As a result, formation of ClOO is partly a terminating



Fig. 9. Plot of NO<sub>3</sub> against time in the reaction with HBr.  $\bullet$ , experimental points; ----, model fit with  $k_{23} = 9.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The bars represent errors in [NO<sub>3</sub>] due to the noise alone.

process, in competition with reaction (17), which regenerates Cl. Formation of BrOO, on the other hand, results in the regeneration of Br either in the direct thermal decomposition of BrOO or via reaction (29) followed by (26). For these reasons, far more secondary conversion of NO<sub>3</sub> occurs in its reaction with HBr than in its reaction with HCl. Consequently, we were unable to study the temperature dependence of reaction (23), because the loss of NO<sub>3</sub> became too great to measure at the contact times obtainable in the apparatus.

## **Evans-Polanyi Relationship**

An assumed linear relationship between activation energy and enthalpy of reaction (the 'Evans-Polanyi plot'<sup>29</sup>) can be used to compare our results with those for the H-abstraction reactions by O(<sup>3</sup>P) and OH determined by other workers. In fig. 10,  $E_a$  is plotted against  $-\Delta_r H_{298}^{\ominus}$  for a series of similar reactions of the form

$$X + RH \rightarrow XH + R \tag{33}$$

where  $X = NO_3$ ,  $O({}^{3}P)$  or OH and  $R = CH_3O$ ,  $CCl_3$ , Cl, Br,  $CH_3$  or  $C_2H_5$ . All the points corresponding to exothermic reactions in the figure are well represented by the line

$$E_{\rm a}/\rm kJ\ mol^{-1} = 27 + 0.22\Delta_{\rm r}H_{298}^{\odot}/\rm kJ\ mol^{-1}$$
.

Even the slightly endothermic reactions of HCl with NO<sub>3</sub> and O(<sup>3</sup>P) fit well onto the line. This treatment of the correlation shows that our data fit very well into the pattern of reactivity for the H-abstraction reactions by atoms and radicals. In table 2, we present data to permit the comparison between the H-abstraction reactions of NO<sub>3</sub>, O(<sup>3</sup>P) and OH. The increase in reactivity from NO<sub>3</sub> through O(<sup>3</sup>P) to OH clearly follows that already reported for the addition reactions of these species.<sup>1,2</sup> Concentration profiles of HBr in the atmosphere are not known. However, it seems unlikely that reaction (23) could play an important role either in producing HNO<sub>3</sub> or releasing active Br in the atmosphere.



**Fig. 10.** The Evans-Polanyi relationship for H atom abstraction.  $\bigcirc$ : Reaction of NO<sub>3</sub> with (a) CH<sub>3</sub>OH (this work), (b) CHCl<sub>3</sub> (this work) and (c) HCl (this work).  $\triangle$ : Reaction of O(<sup>3</sup>P) with (d) C<sub>2</sub>H<sub>4</sub> (ref. 30), (e) CH<sub>3</sub>OH (ref. 10 and 34), (f) HBr (ref. 8), (g) HCl (ref. 8) and (h) CH<sub>4</sub> (ref. 31).  $\Box$ : Reaction of OH with (i) CH<sub>4</sub> (ref. 30), (j) HCl (ref. 8), (k) C<sub>2</sub>H<sub>6</sub> (ref. 31), (l) CHCl<sub>3</sub> (ref. 8), (m) CH<sub>3</sub>OH (ref. 32 and 33), (n) HBr (ref. 8).

S.J.S. thanks the N.E.R.C. for a studentship during the tenure of which this work was performed. We gratefully acknowledge the financial support given by the N.E.R.C. under grants GST/020/131 and GR3/5472, and by the C.E.C. under contract number EV4V-0093-C(AM), at various stages during this work, for the support of C.E.C.M. and for the purchase of equipment.

## References

- 1 C. E. Canosa-Mas, S. J. Smith, S. Toby and R. P. Wayne, J. Chem. Soc., Faraday Trans. 2, 1988, 84, 247.
- 2 C. E. Canosa-Mas, S. J. Smith, S. Toby and R. P. Wayne, J. Chem. Soc., Faraday Trans. 2, 1988, 84, 263.
- 3 B. J. Finlayson-Pitts and J. N. Pitts Jr., Atmospheric Chemistry (J. Wiley & Sons, New York, 1986).
- 4 R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer and J. N. Pitts Jr, J. Phys. Chem., 1984, 88, 2361.
- 5 T. J. Wallington, R. Atkinson, A. M. Winer and J. N. Pitts Jr, Int. J. Chem. Kinet., 1987, 19, 243.
- 6 C. A. Cantrell, J. A. Davidson, R. E. Shetter, B. A. Anderson and J. G. Calvert, J. Phys. Chem., 1987, 91, 6017.
- 7 S. W. Benson, Thermochemical Kinetics (J. Wiley & Sons, New York, 2nd edn 1976).
- 8 NASA Panel for data evaluation, Chemical Kinetics and Photochemical Data for use in Stratospheric Modeling. Evaluation No. 8 (JPL publication 87-41, Jet Propulsion Laboratory, Pasadena, California, 1987).
- 9 A. H. Daniel, J. A. Davidson, C. A. Cantrell and R. E. Shetter, J. Phys. Chem. 1988, 92, 4172.
- 10 H. H. Grotheer and Th. Just, Chem. Phys. Lett., 1981, 78, 71.
- 11 H. H. Grotheer, G. Riekert, U. Meier and Th. Just, Ber. Bunsenges. Phys. Chem., 1985, 89, 187.
- 12 I. W. Hall, R. P. Wayne, R. A. Cox, M. E. Jenkin and G. D. Hayman, J. Phys. Chem., 1988, 92, 5049.
- 13 A. Mellouki, G. Le Bras and G. Poulet, J. Phys. Chem., 1988, 92, 2229.
- 14 R. A. Cox, M. Fowles, D. Moulton and R. P. Wayne, J. Phys. Chem., 1987, 91, 3361.
- 15 A. Mellouki, A. M. Gumery, G. Le Bras and G. Poulet (XIIIth International Conference on Photochemistry, Budapest, Hungary, August, 1987).
- 16 K. R. Ryan and I. C. Plumb, Int. J. Chem. Kinet., 1984, 16, 591.
- 17 A. Mellouki, G. Le Bras and G. Poulet, J. Phys. Chem., 1987, 91, 5760.
- 18 M. J. Kurylo, J. L. Murphy and G. L. Knable, Chem. Phys. Lett., 1983, 94, 281.
- 19 C. A. Smith, A. R. Ravishankara, and P. H. Wine, J. Phys. Chem., 1985, 89, 1423.

- 20 H. S. Judeikis and M. Wun, J. Chem. Phys., 1978, 68, 4123.
- 21 R. Mohlenbrock, M. Preidel and R. Zellner, 9th International Symposium on Gas Kinetics, Bordeaux, France, July 1986.
- 22 G. Poulet, G. Le Bras and J. Combourieu, J. Chem. Phys., 1978, 69, 767.
- 23 J. Austin, R. R. Garcia, J. M. Russell III and S. Solomon, J. Geophys. Res., 1986, 91, 5477.
- 24 J. A. Davidson, C. A. Cantrell, R. E. Shetter and J. G. Calvert, 189th National Meeting of the American Chemical Society, Miami, Florida, April 1985.
- 25 G. Poulet, A. Mellouki and G. Le Bras, COST611- Working Party 2; Chemical Transformations, 6th Meeting at Risø National Laboratory, Roskilde, Denmark, 17th-18th September 1987. Air Pollution Report 9, CEC, Brussels, Report EVR 11440, 1988, pp. 90-95.
- 26 S. P. Sander and R. T. Watson, J. Phys. Chem., 1981, 85, 4000.
- 27 N. I. Butakovskaya, I. I. Morozov, V. L. Tal'Rose and E. S. Vasiliev, Chem. Phys., 1983, 79, 21.
- 28 G. Poulet, personal communication, 1988.
- 29 M. G. Evans and M. Polanyi, Trans. Faraday Soc., 1938, 34, 11.
- 30 J. T. Herron and R. E. Huie, J. Phys. Chem. Ref. Data, 1973, 2, 467.
- 31 R. Atkinson, Chem. Rev., 1986, 86, 69.
- 32 V. Meier, H. H. Grotheer and Th. Just, Chem. Phys. Lett., 1984, 106, 97.
- 33 T. J. Wallington and M. J. Kurylo, Int. J. Chem. Kinet, 1987, 19, 1015.
- 34 G. D. Keil, T. Tanzawa, E. G. Skolrik, R. B. Klemm and J. V. Michael, J. Chem. Phys., 1981, 75, 2693.

Paper 8/04574G; Received 16th November, 1988