KINETICS OF THE REACTION OF HO_2 WITH NITRIC OXIDE AND NITROGEN DIOXIDE

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Summary

The photolysis of low concentrations of nitrous acid in $CO + N_2 + O_2$ mixtures at 1 atm. has been used as a source of HO_2 radicals. The photolyses were carried out in a flow system in which the rates of formation or removal of the oxides of nitrogen, NO and NO_2, were measured at small conversion. From the effect of added NO and NO_2 on these rates, it is concluded that the following reactions of HO_2 radicals with the oxides of nitrogen occur:

$$HO_2 + NO \quad \rightarrow \quad NO_2 + OH \tag{5}$$

$$HO_2 + NO\ (+M) \rightarrow HONO_2\ (+M) \tag{10}$$

$$HO_2 + NO_2 \quad \rightarrow \quad HONO + O_2 \tag{7}$$

By computer simulation of the kinetic system using available literature rate constants for the reaction $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (8) and the OH-radical reactions which occur, all of the experimental results could be accurately predicted using the following rate constants for the $HO_2 + NO_x$ reactions at room temperature (296 ± 2 K): $k_5 = 1.2 \times 10^{-12}$; $k_{10} = 1.4 \times 10^{-13}$; $k_7 = 1.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The uncertainty on these rate constants is $\pm 25\%$. These values of k_5 and k_7 are consistent with previous experimental estimates, although k_5 has usually been assumed to be approximately a factor of five less than found in this work. The alternative path for $NO + HO_2$, reaction (10), does not appear to have been proposed previously on the basis of experimental observations.

Introduction

In a recent paper [1], an experimental study of the photolysis of gaseous nitrous acid, at low concentrations in nitrogen–oxygen mixtures has been reported. On the basis of the observed formation rates the following mechanism was proposed:

$$HNO_2 \xrightarrow{h\nu} OH + NO \qquad\qquad \Phi_A k_a$$

$$HNO_2 \xrightarrow{h\nu} H + NO_2 \qquad\qquad \Phi_B k_a$$

$$OH + NO + M \quad \rightarrow \quad HNO_2 + M \tag{1}$$

$$OH + NO_2 + M \quad \rightarrow \quad HNO_3 + M \tag{2}$$

$$OH + HNO_2 \quad \rightarrow \quad H_2O + NO_2 \tag{3}$$

$$H + O_2 + M \quad \rightarrow \quad HO_2 + M \tag{4}$$

$$HO_2 + NO \quad \rightarrow \quad NO_2 + OH \tag{5}$$

The dissociation process B was a minor pathway with $\Phi_B \lesssim 0.1 \ \Phi_A$. Further work on this system [2], using a kinetic competition technique involving carbon monoxide, allowed the estimation of the absolute rate constants for the hydroxyl radical reactions (1) - (3).

In the present study, a large excess of carbon monoxide is used to provide a source of HO_2 radicals for kinetic studies by means of reaction (6) followed rapidly by (4), which is the only significant reaction of H atoms under the experimental conditions used:

$$OH + CO \rightarrow H + CO_2 \tag{6}$$

The reactions of the HO_2 radicals with oxides of nitrogen were then studied with a view to obtaining an estimate of the rate constant for reaction (5). This reaction is a key process in atmospheric photochemistry but relatively few measurements of its rate constant have been made. Payne *et al.* [3] have reported k_5 as $(3 \pm 9) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. These authors also showed [3b] that the reaction of HO_2 with CO is extremely slow and therefore is unlikely to be of importance in our system. Simonaitis and Heicklen [4] have recently reported a determination of the relative rate constants of reactions (5) and (7):

$$NO_2 + HO_2 \rightarrow HNO_2 + O_2 \tag{7}$$
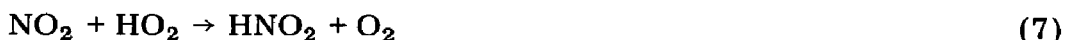
The ratio k_5/k_7 was found to be 7 ± 1 showing that the $NO_2 + HO_2$ reaction is several orders of magnitude faster than had previously been assumed. In view of the possible importance of the reaction (7) in atmospheric photochemistry, experiments were performed to assess the importance of this reaction in the photolysis of nitrous acid/carbon monoxide mixtures. This photolysis system provides a relatively clean and simple source of HO_2 radicals and the importance of the reactions of HO_2 with the oxides of nitrogen should be readily apparent.

Experimental

The photolysis of $HNO_2/CO/NO/NO_2$ mixtures was studied using the flow system described previously [1, 2]. The gas mixtures were made up in a 250 l bag fabricated of poly(vinyl fluoride) film (Tedlar, du Pont Ltd) and were withdrawn at a controlled flow rate through a 27 cm^3 cylindrical photolysis cell which was irradiated with u.v. light (330 - 380 nm) from a filtered high pressure mercury arc (Mazda type ME/D 250 W). The photon flux was approximately 4×10^{16} quanta s^{-1} which gave a conversion rate

of HNO_2 of the order 1% s^{-1}. The photolyses were carried out at atmospheric pressure and at room temperature, 296 ± 2 K.

The concentrations of HNO_2, NO and NO_2 were measured either in the reservoir or in the outlet stream from the photolysis cell, using a calibrated chemiluminescence "NO_x" analyzer (TECO Model 12A) in the manner described previously [1, 5]. Reaction rates were determined from the observed change in composition of the mixture when it passed through the irradiated photolysis cell at a known flow rate. The concentration–time relationships for the photolysis of mixtures containing excess CO, which were obtained by varying the residence time in the cell, were quite regular showing that the reaction rates determined from the concentration changes were well representative of the course of the photolysis. For most experiments a fixed photolysis time of 3.3 s was employed. The measured changes in the concentrations of NO and NO_2 were corrected for the conversion of NO_2 to NO resulting from the photolysis of the NO_2 present, which was measured independently for each mixture [1]. The correction was normally small ($\simeq$ 15% of the overall change in NO concentration) but at high NO_2 concentrations most of the observed change in NO concentration resulted from NO_2 photolysis. The percentage error on a single determination of the NO and NO_2 reaction rates depended on the magnitude of the observed concentration change. The reproducibility of a measured concentration was to within 1% and the error on the rate determinations was estimated to be on average approximately ± 6%. All concentration changes were measured in duplicate.

In a typical experiment to determine the influence of NO or NO_2 on the photolysis of HNO_2 (approximately 5 ppm; 1 ppm = 2.43 $\times$ 10^{13} molecules cm^{-3} at 296 K and 760 Torr) in a known volume of nitrogen + oxygen (2:1). HNO_2 was generated from acidified sodium nitrite solution [1] which also led to the presence of approximately 6 $\times$ 10^3 p.p.m. water vapour in the gas mixture. Approximately 90% of the total NO_x (HNO_2 + NO + NO_2) in these mixtures was HNO_2, the balance being NO and NO_2 in roughly equal proportions.

After allowing this mixture to mix well, its composition was determined and the rates of formation of NO and NO_2 on photolysis were measured. The photodissociation rates $\Phi_A k_a$ and $\Phi_B k_a$ (k_a = specific absorption rate of HNO_2 in the photolysis cell in s^{-1}), could then be determined on the basis of the previously measured rate parameters for the HNO_2 photolysis system [1]. In the present work Φ_B was always less than 5% of the total dissociation quantum yield, Φ_T (= Φ_A + Φ_B). Since the light intensity varied by less than 3% over a period of several hours it was assumed that the Φk_a values remained constant during a given series of experiments on a particular mixture.

A measured amount of pure carbon monoxide (BDH Ltd, CP grade; 99.5% CO, 0.3% N_2, 0.1% O_2) was then added to the reservoir from a gas syringe, to give a concentration of at least 500 p.p.m. CO in the mixture. After mixing, the photolysis rates for the new mixture were determined.

The concentration of nitric oxide or nitrogen dioxide in the mixture was then increased by the addition of aliquots of either gas and, after mixing, the composition and photolysis rates were measured following each addition. The aliquots of NO_2 were obtained from the addition of excess oxygen to known amounts of pure NO (Air Products Ltd, > 99%) measured from a vacuum system. The NO_2 was flushed into the reservoir with 2.5 l of pure N_2. Known amounts of NO were injected directly from a cylinder containing 118 ppm NO in nitrogen into a stream of pure nitrogen which passed to the reservoir. Unfortunately a fraction of the added nitric oxide was oxidized to NO_2 during the injection procedure, probably due to a poor quality cylinder regulator which was used, and it was therefore not possible to obtain data for increasing concentrations of NO without a small increase in the concentration of NO_2.

Results and Discussion

Photolysis of HNO_2/CO_2 mixtures with added NO

Two series of experiments were performed in which increasing amounts of nitric oxide were added to mixtures containing nitrous acid and a large excess of carbon monoxide. The details of the experiments together with the rate data are given in Table 1, and the rate data for experiment I are plotted as a function of the concentration ratio $[NO]/[NO_2]$ in Fig. 1.

At low nitric oxide and nitrogen dioxide concentrations, the rate of change of the nitric oxide concentration, divided by the HNO_2 concentration, R_{NO}, is negative, i.e. NO is consumed during photolysis. Addition of nitric oxide increases the rate of loss of nitric oxide, i.e. R_{NO} goes more negative (see Fig. 1). At the same time, the rate of production of nitrogen dioxide, divided by the HNO_2 concentration, R_{NO_2}, increased with increasing nitric oxide concentration.

The oxidation of nitric oxide to nitrogen dioxide can be readily explained by a short chain reaction involving reactions (5) and (6) + (4). The chain is not perfect since approximately 15% of the hydroxyl radicals are lost, i.e. do not regenerate an HO_2 radical, through reactions (1) to (3) which compete against the reaction (6).

Figure 1 shows that with increasing nitric oxide, R_{NO} appears to approach a limiting value. It is also apparent that $R_{NO_2} > -R_{NO}$, showing that the overall result of the photolysis of HNO_2 is net production of nitrogen dioxide. The quantity $R_{NO} + R_{NO_2}$ remained essentially constant with increasing nitric oxide. From a consideration of the rate constants for reactions (1) and (6), nitric oxide addition should only slightly decrease the proportion of OH radicals which regenerate HO_2 radicals by reactions (6) + (4).

Photolysis of HNO_2/CO mixtures with added NO_2

Two series of experiments were performed in which increasing amounts of nitrogen dioxide were added to mixtures containing nitrous

TABLE 1

Rates of formation of NO and NO_2 in the photolysis of HNO_2 in the presence of carbon monoxide and the oxides of nitrogen

Experiment		HNO_2 (ppm)	NO (ppm)	NO_2 (ppm)	CO (ppm)	$\Phi_T k_a$	$s^{-1} \times 100$		
							R_{NO}*	R_{NO_2}	$R_{NO} + R_{NO_2}$
I.	1	4.39	0.220	0.229	681	0.646	−0.479	0.969	0.490
	2	4.35	0.294	0.248	675		−0.630	1.122	0.492
	3	4.18	0.391	0.304	666		−0.766	1.278	0.512
	4	4.06	0.521	0.343	658		−0.932	1.424	0.492
	5	3.84	0.634	0.386	649		−1.043	1.563	0.520
	6	3.72	0.828	0.422	640		−1.182	1.701	0.519
	7	3.53	1.290	0.460	630		−1.373	1.861	0.488
II.	1	6.59	0.70	0.62	750	0.741	−0.638	1.220	0.582
	2	6.57	0.97	0.65	748		−0.765	1.290	0.525
	3	6.40	1.28	0.95	745		−0.835	1.380	0.545
	4	6.20	1.85	1.12	740		−0.857	1.330	0.473
	5	6.05	2.37	1.26	735		−0.915	1.385	0.470
III.	1	6.08	0.39	0.24	938	0.686	−0.646	1.183	0.537
	2	5.88	0.37	0.35	926		−0.592	1.121	0.529
	3	5.73	0.37	0.56	915		−0.459	0.945	0.486
	4	5.54	0.37	0.69	903		−0.410	0.865	0.456
	5	5.45	0.40	0.88	890		−0.371	0.793	0.422
	6	5.12	0.41	1.41	878		−0.191	0.610	0.419
	7	4.80	0.47	2.94	865		+ 0.044	0.325	0.369
IV.	1	5.05	0.46	0.39	524	0.713	−0.509	1.095	0.586
	2	4.95	0.43	0.99	517		−0.101	0.539	0.438
	3	4.72	0.45	1.71	510		+ 0.068	0.328	0.396
	4	4.08	0.46	2.51	502		+ 0.169	0.155	0.324
	5	3.74	0.47	3.24	494		+ 0.198	0.075	0.273

*Rates of formation divided by the initial HNO_2 concentration.

acid and a large excess of carbon monoxide. The details of these experiments are given in Table 1, and the results for experiment III are illustrated in Fig. 2.

With increasing amounts of nitrogen dioxide, R_{NO}, which is initially negative, increases towards zero and becomes positive. R_{NO_2} decreases towards zero and is always greater than $-R_{NO}$. $R_{NO} + R_{NO_2}$ shows a slight decrease but is always positive.

Nitrogen dioxide apparently has an inhibiting effect on the chain oxidation of nitric oxide and the decline in $R_{NO} + R_{NO_2}$ indicates that NO_2 removes free radicals from the system. Since the proportion of hydroxyl radicals which regenerate HO_2 radicals by reactions (6) + (4) is only slightly affected by these relatively small additions of nitrogen dioxide, its action is most probably accounted for by reaction (7). This process removes radicals from the chain system and is in direct competition with nitric oxide in reaction (5).

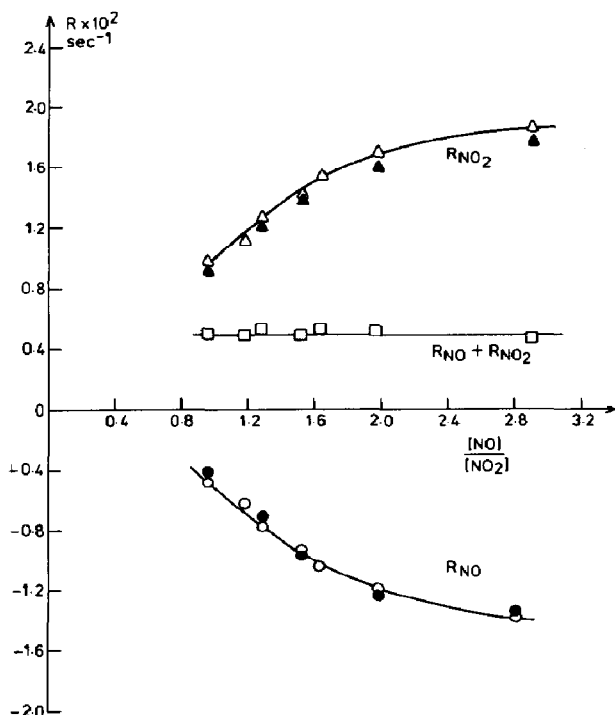In the presence of large nitrogen dioxide concentrations, the result of

Fig. 1. Variation of R_{NO}, R_{NO_2} and $R_{NO} + R_{NO_2}$ with the concentration ratio $[NO]/[NO_2]$ using the results from experiment I. R_{NO}, R_{NO_2} are respectively the rates of change of the concentrations of NO and NO_2 on photolysis, divided by the initial HNO_2 concentration. Open points: experimental results; filled points: computed results using rate constants detailed in Tables 2 and 3.

photolysis is net nitric oxide production since the hydroxyl radicals are removed by reactions (6) + (4) + (7) and also by reaction (2).

Kinetic analysis

In addition to reactions (1) - (7), the mechanism requires a removal process for HO_2 radicals in the absence of oxides of nitrogen. Following the previous studies, this is assumed to be HO_2 radical disproportionation according to:

$$HO_2 + HO_2 = H_2O_2 + O_2 \tag{8}$$

For reaction (9) to compete with (8), the following equality must be satisfied; $k_9[OH] \simeq 2k_8[HO_2]$.

$$HO_2 + OH = H_2O + O_2 \tag{9}$$

Using Lloyd's [7] evaluation of these rate constants, the equality simplifies to $[OH] \simeq 0.7[HO_2]$. Reaction (9) was neglected since the $[HO_2]/[OH]$ ratio in the present system, calculated on the basis of the rate constants given in Table 2 and the previous estimates [3, 4] of the reaction of HO_2 with NO and NO_2, is of the order of 100. By application of the steady state approximation to the HO_2, H and OH concentrations and neglecting
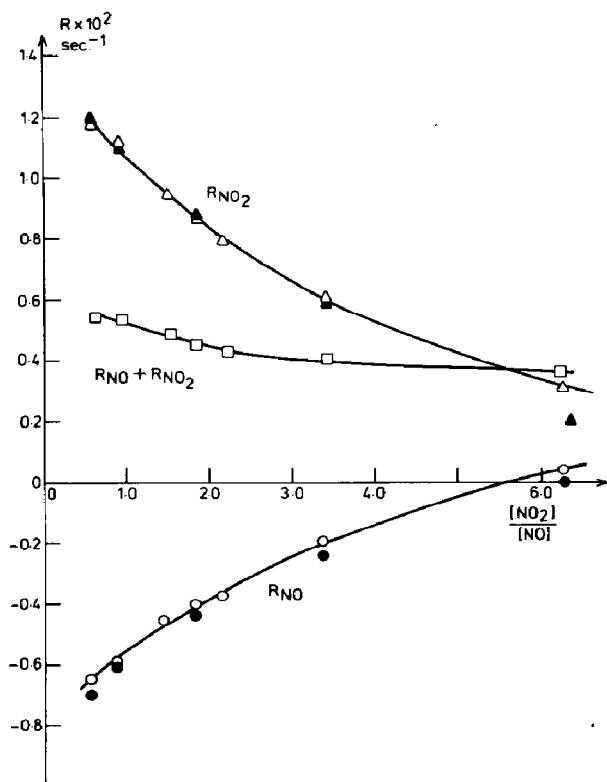
Fig. 2. Variation of R_{NO}, and R_{NO_2} and $R_{NO} + R_{NO_2}$ with the concentration ratio [NO]/[NO$_2$] using the results from experiment III. R_{NO}, R_{NO_2} are respectively the rates of change of the concentrations of NO and NO$_2$ on photolysis, divided by the initial HNO$_2$ concentration. Open points: experimental results; filled points: computed results using rate constants detailed in Tables 2 and 3.

TABLE 2

Rate constants used in the computer simulations of HNO$_2$/CO photolyses

Reaction			Rate constant*	Reference
OH + NO	$\rightarrow$	HNO$_2$	6×10^{-12}	2
OH + NO$_2$	$\rightarrow$	HNO$_3$	6×10^{-12}	2
OH + CO	$\rightarrow$	H + CO$_2$	1.5×10^{-13}	6
H + O$_2$ + M	$\rightarrow$	HO$_2$ + M	5.5×10^{-32} (M = N$_2$)	14
OH + HNO$_2$	$\rightarrow$	H$_2$O + NO$_2$	2×10^{-12}	2
HO$_2$ + HO$_2$	$\rightarrow$	H$_2$O$_2$ + O$_2$	3.3×10^{-12}	7

*Units are cm^3 molecule^{-1} s^{-1} or cm^6 molecule^{-2} s^{-1}

the minor photodissociation path B, the following expressions may be derived:

$$k_6[CO][OH] = \{k_5[NO] + k_7[NO_2] + 2k_8[HO_2]\}[HO_2] \qquad (i)$$

$$\Phi_A k_a[HNO_2] + k_5[NO][HO_2] = \{k_6[CO] + k_1[NO][M] + k_2[NO_2][M] + k_3[HNO_2]\}[OH] \qquad (ii)$$

By substituting

$$f = \frac{k_6[CO]}{k_6[CO] + k_1[NO][M] + k_2[NO_2][M] + k_3[HNO_2]} \quad \text{(iii)}$$

and adding eqns. (i) and (ii) together, the following expression for the HO_2 steady state concentration results:

$$f\Phi_A k_a[HNO_2] = \{k_7[NO_2] + (1-f)k_5[NO] + 2k_8[HO_2]\}[HO_2] \quad \text{(iv)}$$

where f is of the order of 0.85 for the present system. The rate of formation of nitric oxide is given by:

$$\frac{d}{dt}[NO] = \Phi_A k_a[HNO_2] - k_5[NO][HO_2] - k_1[OH][NO][M] \quad \text{(v)}$$

which, when neglecting the last term on the right-hand side, gives:

$$R_{NO} = \Phi_A k_a - \frac{k_5[NO][HO_2]}{[HNO_2]} \quad \text{(vi)}$$

Similarly:

$$R_{NO_2} = \left\{ \frac{k_5[NO]}{[HNO_2]} - \frac{k_7[NO_2]}{[HNO_2]} \right\} [HO_2] \quad \text{(vii)}$$

The form of eqns. (vi) + (iv) and (vii) + (iv) are illustrated using the extremes of conditions where $2k_8[HO_2]$ is negligible and dominant. Taking the condition of $k_7[NO_2] \gg 2k_8[HO_2]$, the following expressions are obtained:

$$R_{NO} (NO, NO_2 \text{ large}) = \Phi_A k_a \left\{ 1 - \frac{f k_5[NO]}{k_7[NO_2] + k_5[NO](1-f)} \right\} \quad \text{(viii)}$$

$$R_{NO_2} (NO, NO_2 \text{ large}) = f\Phi_A k_a \left\{ \frac{k_5[NO] - k_7[NO_2]}{k_7[NO_2] + (1-f)k_5[NO]} \right\} \quad \text{(ix)}$$

Taking the condition $2k_8[HO_2] \gg (k_7[NO_2] + (1-f)k_5[NO])$:

$$R_{NO} (NO, NO_2 \text{ small}) = \Phi_A k_a \left\{ \frac{-k_5[NO]f^{1/2}}{(2\Phi_A k_a k_8[HNO_2])^{1/2}} + 1 \right\} \quad \text{(x)}$$

$$R_{NO_2} (NO, NO_2 \text{ small}) = (k_5[NO] - k_7[NO_2]) \left(\frac{f\Phi_A k_a}{2k_8[HNO_2]} \right)^{1/2} \quad \text{(xi)}$$

$$R_{NO} + R_{NO_2} = (1 - f_1)\Phi_A k_a - \left(\frac{f\Phi_A k_a}{[HNO_2]} \right)^{1/2} \left(\frac{k_7[NO_2] - f_1 k_5[NO]}{(2k_8)^{1/2}} \right) \quad \text{(xii)}$$

where $f_1 = \dfrac{k_3[HNO_2]}{k_6[CO] + k_1[NO][M] + k_2[NO][M] + k_3[HNO_2]} \quad \text{(xiii)}$

From an examination of eqns. (viii) and (x) it will be seen that the mechanism predicts, both at low and high nitric oxide concentrations, a decrease in R_{NO}, *i.e.* R_{NO} becoming more negative, with added nitric oxide, in accord with experimental observations. From a consideration of the NO_2 dependence of eqns. (viii) and (ix) it is also apparent that the observed increase of R_{NO} and decrease of R_{NO_2} with added nitrogen dioxide is also predicted by the mechanism.

With a constant HNO_2 concentration and a low NO_2 concentration, $R_{NO} + R_{NO_2}$ should increase only very slightly with added nitric oxide through the $f_1 k_5 [NO]$ term in eqn. (xii). The magnitude of f_1 is estimated to be about 0.08 under these conditions. Experimentally the effect of added NO on $R_{NO} + R_{NO_2}$ is indeed small, but within the limits of experimental precision may be of opposite sign to that predicted by eqn. (xii).

Addition of nitrogen dioxide is predicted by eqn. (xii) to decrease $R_{NO} + R_{NO_2}$, and this is indeed observed. The mechanism also predicts a limiting value of R_{NO} at high nitric oxide concentrations which is large and negative. Thus, the model provides a qualitative explanation of the behaviour of the system, and it is of interest to examine the results in more detail in an attempt to estimate the rate parameters for reactions (5) and (7).

The nitrogen dioxide dependence of the rate of production of nitric oxide as required by eqn. (viii) was tested in Fig. 3. A plot of $\Phi_A k_a / (\Phi_A k_a - R_{NO})$ against $[NO_2]/[NO]$ is expected to be linear and of slope, $k_7/f k_5$, and intercept, $(1 - f)/f$. From a least-squares analysis of the data in Fig. 3, the slope and intercept were 0.16 ± 0.01 and 0.36 ± 0.02 respectively. The values of f in these experiments ranged from 0.74 to 0.90 with the majority of values > 0.80. Thus an intercept of < 0.25 would be expected on the basis of the kinetic analysis given above. The observed intercept is significantly higher than this, indicating that an additional loss process for HO_2 radicals may be present in the system.

However, straight line behaviour is both predicted and observed experimentally for the NO_2 dependence. The effect of nitrogen dioxide on the system would appear to be quite simple; radical removal by reaction (7). The slope of the plot provides an estimate of the relative rate constants for the reactions of NO and NO_2 with HO_2. For $f = 0.80$, this ratio is found to be 7.8 ± 0.5.

An estimate of the relative magnitudes of k_5 and k_7 can also be obtained from the value of the $[NO_2]/[NO]$ ratio for $R_{NO_2} = 0$ as defined by eqn. (ix). By extrapolation from the R_{NO_2} values obtained in experiments III and IV a value of $k_5/k_7 = 8 \pm 1$ is estimated. This value must be considered a lower limit since the OH-radical reaction [2] also contributes to the observed decrease in R_{NO_2} with increasing NO_2 concentration.

The limiting value of R_{NO} with increasing nitric oxide concentration required by eqn. (viii) is $\Phi_A k_a (1 - 2f)/(1 - f)$, *i.e.* $4.3 \Phi_A k_a$ for $f = 0.84$ (run I.7). The experimental estimate of this limiting rate, based on the data
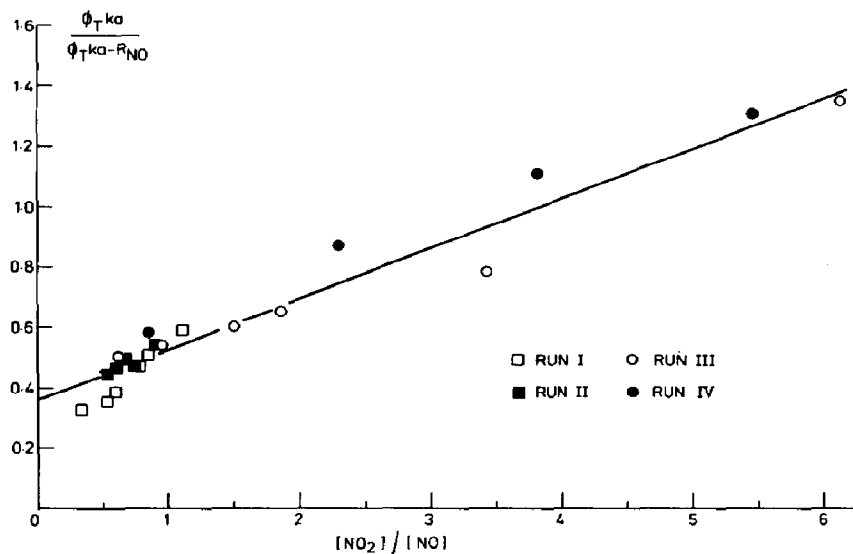
Fig. 3. The nitrogen dioxide dependence of the R_{NO} values according to eqn. (viii) (see text). $\square$, expt. I; $\blacksquare$, expt. II; $\bigcirc$, expt. III; $\bullet$, expt. IV.

plotted in Fig. 1, is approximately $-1.9\Phi_A k_a$. There is quite a large experimental error in this estimate since, with the relatively large additions of nitric oxide, not only did the OH radical reactions become non-negligible but also the nitrogen dioxide concentrations increased. Since nitrogen dioxide has an inhibiting effect, the limiting value of R_{NO} as NO $\to \infty$ is clearly underestimated. However, the experimental error is not considered to be large enough to explain the large discrepancy between the predicted and observed limiting value for R_{NO}. The occurrence of an additional loss process for HO_2 is indicated and this loss process appears to be more important with increasing nitric oxide concentration.

The reaction of NO with HO_2 has two exothermic routes available, reaction (5) and also reaction (10) as an alternative:

$$NO + HO_2 \ (+M) = HONO_2 \ (+M) \tag{10}$$

Combination of NO with HO_2 to give nitric acid does not appear to have been proposed previously on the basis of experimental results; it would, however, explain the additional radical loss which apparently occurs in the present system. If reaction (10) is included in the kinetic analysis the data plot shown in Fig. 3 is still expected to be linear but with a slope and intercept of $f^{-1} \times k_7/(k_5 + k_{10})$ and $(k_{10} + (1 - f)k_5)/f(k_5 + k_{10})$ respectively. From the observed intercept, an estimate of 9.1 ± 1.5 is obtained for the lower limit of the ratio $(k_5 + k_{10})/k_{10}$ using $f = 0.8$. The lower limit applies because other removal processes for HO_2 have been neglected and the data are extrapolated into a region where the inequality $k_7[NO_2] > 2k_8[HO_2]$ may no longer apply.

The limiting value of R_{NO} at high nitric oxide concentration, when reaction (10) is included is given by:

$$R_{NO} \text{ (limit NO} \to \infty) = \Phi k_a \left\{ 1 - \frac{1 + k_{10}/k_5}{(1-f) + k_{10}/k_5} \right\}$$

Using the lower limit for the ratio $(k_5 + k_{10})/k_{10}$ derived above the limiting value of R_{NO} is predicted to be $-(2.5 \pm 0.3) \Phi_A k_a$, in much better agreement with the experimental rate.

At low NO and NO_2 concentrations reaction (8) becomes relatively more important. An extrapolation of the data into this region is illustrated in Fig. 4, where the quantity $\Phi_A k_a - R_{NO}$ is plotted against the ratio $[NO]/[HNO_2]^{1/2}$, using the data for low nitric oxide concentrations. The basis of this plot is to be found in eqn. (x). The limiting slope allows an estimate of the ratio $(k_{10} + k_5)/k_8^{1/2}$ for which a value of 2.7 p.p.m.$^{1/2}$ is obtained. Using a literature value of $k_8 = 3.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (= 81 p.p.m.$^{-1}$ s^{-1} at 298 K) we estimate $(k_{10} + k_5) \geqslant 24$ p.p.m.$^{-1}$ s^{-1}.

An estimate of the ratio $(k_{10} + k_5)/k_8^{1/2}$ can also be made from the previously reported experiments with smaller amounts of added carbon monoxide [2]. In these experiments the decline in the total rate $R_{NO} + R_{NO_2}$ when CO is added gives an approximate measure of the rate of the radical loss processes for HO_2. If the small loss of NO and NO_2 by reaction with OH is neglected, it can be shown that, when sufficient CO has been added to make $R_{NO} = 0$ (see Fig. 1 in ref. 2), the following equation applies:

$$\frac{(R_{NO} + R_{NO_2})_0 - (R_{NO} + R_{NO_2})_{CO}}{\Phi_A k_a} = \frac{2k_8 \Phi_A k_a [HNO_2]}{(k_5 + k_{10})^2 [NO]^2} +$$

$$\frac{k_7}{(k_5 + k_{10})} \frac{[NO_2]}{[NO]} + \frac{k_{10}}{(k_5 + k_{10})}$$

Using $k_7/(k_5 + k_{10}) = 0.13$ and $0 < k_{10}/(k_5 + k_{10}) < 0.11$ as derived in the present work, the previous experimental data give $17 < (k_5 + k_{10}) < 24$ in p.p.m.$^{-1}$ s^{-1} units, which is consistent with the lower limit estimate from Fig. 4.

Clearly, however, it is not possible to obtain an analytical solution of the nitric oxide and nitrogen dioxide dependences over all the conditions used in the experiments. It is therefore difficult to obtain rate constants for conditions other than for the extremes dictated by the inequalities $k_7[NO_2] \gg 2k_8[HO_2]$ or $2k_8[HO_2] \gg k_7[NO_2]$. Under the first of these conditions OH radical reactions become important. The second of these conditions is difficult to reach experimentally.

Computer simulation

In an attempt to obtain values for the rate constants k_5, k_7 and k_{10} which give the best description of the observed kinetic behaviour over the whole range of experimental conditions, a computer simulation of the photolysis system was carried out. The reaction scheme embodied in steps (1) - (8) + (10) was simulated on the IBM System/370 computer using a
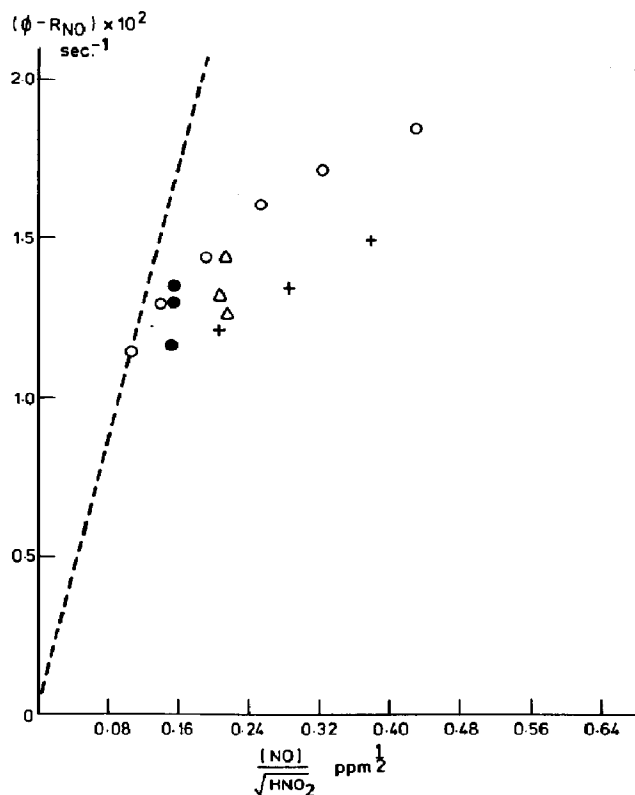
Fig. 4. The nitric oxide dependence of the R_{NO} values for low concentrations of nitric oxide according to eqn. (x). $\circ$, expt. I; +, expt. II; $\bullet$, expt. III; $\triangle$, expt. IV.

Harwell program CHEK [8]. This program integrates the differential equations representing the chemical reactions, taking typically 1.5 s to integrate over 3 s of photolysis. No steady state concentrations were implicitly used, but the integration record showed that all steady states were established within 20% of the photolysis period, about 0.5 s. The rates of change of concentration were determined from the initial concentrations and the computed concentrations after 3.3 s of photolysis, so that a direct comparison with the experimental data could be made.

Table 2 specifies the rate constants which were used in the simulation but not considered as variable parameters. Initial concentrations and photolysis rates were taken from Table 1. Under all conditions, the integrations were performed without instability in the concentration $vs.$ time plots being apparent.

The computer model predicted rates of reaction with comparable accuracy for the widely different experimental conditions detailed in Table 1. The rate constants k_5, k_7 and k_{10} were varied from simulation to simulation to obtain the best fit to the nitric oxide and nitrogen dioxide dependences of the rates of production of both nitric oxide and nitrogen dioxide. Figures 1 and 2 illustrate the computer fit to the experimental oxides of nitrogen dependences using the best estimates of k_5, k_7 and k_{10}

TABLE 3

Computer fit estimates of rate constants for reactions of HO_2

Reaction		Rate constant (cm^3 molecule^{-1} s^{-1})	Uncertainty
$NO + HO_2$	$\rightarrow NO_2 + OH$ (5)	1.2×10^{-12}	$\pm$ 25%
$NO + HO_2$	$\rightarrow HNO_3$ (10)	1.4×10^{-13}	$\pm$ 25%
$NO_2 + HO_2$	$\rightarrow HNO_2 + O_2$ (7)	1.2×10^{-13}	$\pm$ 25%

detailed in Table 3. The agreement between the computer fit and experimental results was typically better than $\pm$ 10% over the whole experimental range, including runs II and IV which are not shown on Figs. 1 and 2. The computer model slightly underestimated the R_{NO} values with the discrepancies in the R_{NO_2} values insignificant.

Discussion of the results

In the kinetic analysis given above, processes which affect the R_{NO} and R_{NO_2} values other than those involving the HO_2 radical have been neglected. Under the worst conditions OH radical reactions would contribute -0.06×10^{-2} s^{-1} to an experimental R_{NO_2} value of $+0.08 \times 10^{-2}$ s^{-1}. For most conditions the contribution of the OH reactions to the observed R_{NO_2} values is much less. These side reactions do, however, limit the accuracy of the rate constant data estimated using the simple kinetic analysis. It should be noted that the OH reactions with NO, NO_2 and HNO_2 were included in the computer analysis and any contributions from these processes were accounted for.

Table 4 contains details of the rate constants and rate constant ratios estimated from the kinetic analysis and the computer analysis. In view of the assumptions made in the kinetic analysis concerning the OH reactions and the relative importance of the HO_2 disproportionation reaction, the agreement is quite reasonable.

Some available measurements and assessments of the rate constant k_5 are given in Table 5. The present value of k_5 is about a factor of 5 higher than has been previously assumed but is not inconsistent with the few experimental determinations. It should be noted that the accuracy of k_5 obtained in the present study is limited by the uncertainty in the value of k_8.

The value of $k_7 = 1.2 \pm 0.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} obtained in the present work shows some measure of consistency with the results of Simonaitis and Heicklen [4]. Using $k_8 = 3.3 \times 10^{-12}$ their data give $k_7 > 2.9 \times 10^{-13}$ in cm^3 molecule^{-1} s^{-1} units. It should be noted that reaction (7) has been neglected in the majority of atmospheric photochemical models. Demerjian *et al.* [9] considered this reaction but concluded that its rate constant, which they estimated to be of the order of 10^{-17} cm^3 molecule^{-1} s^{-1}, was too low for it to be important. The present results, which confirm those of Simonaitis and Heicklen, indicate to the contrary;

TABLE 4

Comparison of rate constants and their ratios obtained from kinetic and computer analysis

Parameter	Kinetic model	Computer fit
$(k_5 + k_{10})/k_7$	$\geqslant 7.8$	11.5
$(k_5 + k_{10})/k_{10}$	$\geqslant 9$	9.8
k_5/k_7	$\geqslant 8$	10.3
$k_{10} + k_5$	$\geqslant 24$	34.5
(p.p.m.$^{-1}$ s^{-1})	$\geqslant 17; \leqslant 24$*	

*Estimated on basis of data from ref. [2].

TABLE 5

Rate constants for the reaction $NO + HO_2 \rightarrow NO_2 + OH$ at 298 K

Source	$k_5 \times 10^{13}$ (cm^3 molecule^{-1} s^{-1})	Notes
This work	12 ± 3	Experimental observations
Payne et al. [3]	3 ± 9	Experimental observations
Simonaitis and Heicklen [4]	$\geqslant 1.5$	Experimental observations
Simonaitis and Heicklen* [9]	$\geqslant 21.0$	Experimental observations
Demerjian et al. [10]	1.3	Kinetic model; estimate for k_5
Crutzen [11]	0.9	Kinetic model; estimate for k_5
McConnel and McElroy [12]	4.0	Kinetic model; estimate for k_5
Levy [13]	5.0	Kinetic model; estimate for k_5

*Calculated from lower limit for k_7 and their k_5/k_7 ratio.

whereas the reaction between nitric oxide and HO_2 is sufficiently rapid to be the dominant reaction path for HO_2 under most conditions, the reaction $NO_2 + HO_2$ will become quite important when the concentration of NO_2 greatly exceeds that of NO, e.g. in the later stages of photochemical smog formation.

Since nitrous acid produced in reaction (7) is readily photolyzed in a sunlit atmosphere [1], the overall result of the $NO_2 + HO_2$ reaction will be:

$$NO_2 + HO_2 \overset{h\nu}{\rightarrow} OH + NO + O_2$$
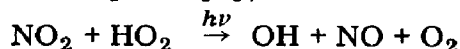
Thus for these conditions reaction (7) may play an important role in recycling HO_2 to OH radicals in the photochemical oxidation of hydrocarbons in the atmosphere.

Although the alternate pathway for the reaction of NO with HO_2, i.e. reaction (10) has not been observed previously, it has been included in a number of atmosphere models, and our results suggest that it may have minor significance in atmosphere photochemistry. If nitric acid is the final product, formed possibly via an energy rich HOONO intermediate, the

exothermicity of reaction (10) is 58.5 kcal/mol. By analogy with reaction (2) the effective bimolecular rate constant k_{10} would be expected to be in the pressure dependent region near 1 atm. pressure and may also decrease with increasing temperature. Under the experimental conditions of the present study reaction (10) is only a minor pathway compared with reaction (5) and in previous experimental investigations of the HO_2 + NO reaction (7) may have been even less important, and therefore even less easily observed.

Acknowledgements

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