

## THE PHOTOLYSIS OF NITROUS ACID IN THE PRESENCE OF CARBON MONOXIDE AND SULPHUR DIOXIDE

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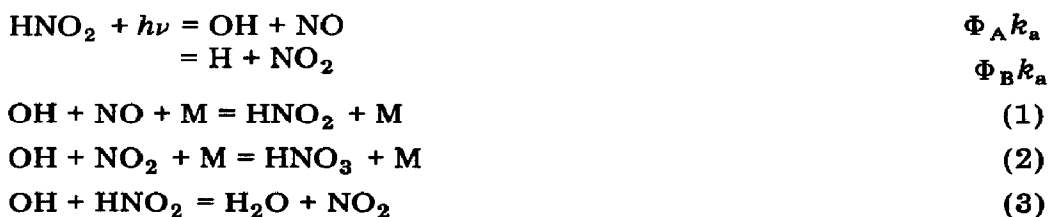
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### Summary

The effect of CO and of SO<sub>2</sub> on the rate of photolysis of part per million concentrations of gaseous nitrous acid in N<sub>2</sub>-O<sub>2</sub> mixtures has been studied. The photolyses were conducted at atmospheric pressure and room temperature (294 ± 2 K) in a flow system. The results give information on several competing reactions of the hydroxyl radical which is produced by photodissociation of HNO<sub>2</sub>. Rate constants for the reactions: OH + NO + M = HNO<sub>2</sub> + M (1) (M = N<sub>2</sub> + O<sub>2</sub> at 1 atm); OH + HNO<sub>2</sub> = H<sub>2</sub>O + NO<sub>2</sub> (3) and OH + SO<sub>2</sub> + M = HSO<sub>3</sub> + M (7) relative to the rate constant for OH + CO = CO<sub>2</sub> + H (6) have been determined. Based on a literature value of  $k_6 = 1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  the values obtained are  $k_1[M] = 6.1 \pm 1.1 \times 10^{-12}$ ,  $k_3 = 2.2 \pm 0.2 \times 10^{-12}$  and  $k_7[M] = 6.0 \pm 0.8 \times 10^{-13}$  in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  units with [M] = 1 atm. N<sub>2</sub> + O<sub>2</sub>. Comparison of the data for reactions (1) and (7) with those obtained at low pressures shows that both reactions are in the pressure dependent region below 1 atm. Some implications of these results on the chemistry of SO<sub>2</sub> and HNO<sub>2</sub> in the lower atmosphere are briefly discussed.

### 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 measured formation rates of nitric oxide and nitrogen dioxide, at low conversion of HNO<sub>2</sub> the following mechanism was proposed for the photolysis:





The overall quantum yield for dissociation was close to unity with  $\Phi_B \simeq 0.1$   $\Phi_A$ ,  $k_3/k_1[\text{M}] = 0.37 \pm 0.06$  and  $k_1[\text{M}] \simeq k_2[\text{M}]$  at 1 atm. pressure and 300 K. Since the primary dissociation process A predominates, the photolysis provides a useful source of hydroxyl radicals for kinetic studies. However, only relative rate parameters for the processes involving OH could be determined for this system. The first objective of the present study was to obtain estimates of the absolute rate constants by a kinetic competition technique using a well known reaction of OH, *i.e.*



The effect of added carbon monoxide on the rates of formation of NO and NO<sub>2</sub> in the photolysis of HNO<sub>2</sub> was therefore examined.

The second objective of this study was to obtain information regarding the reaction of hydroxyl radicals with sulphur dioxide. The occurrence of a reaction of OH with SO<sub>2</sub> has been suggested by Wheeler *et al.* [2] as a result of a study of the effect of SO<sub>2</sub> on radical recombination rates in propane-air flames. Recently Payne *et al.* [3] have reported a value of  $k_7[\text{M}] = 1.9 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the reaction:



with M = N<sub>2</sub> + H<sub>2</sub>O (18 and 20 Torr respectively), from a study of the photolysis of H<sub>2</sub>O-SO<sub>2</sub>-CO-N<sub>2</sub>-O<sub>2</sub> mixtures at 300 K. Davis and Schiff [4] made preliminary measurements of reaction (7) in the third order region which gave  $k_7 = 2 \times 10^{-32}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> (M = helium). In a very recent study Harris and Wayne [5] obtained a value of  $k_7 = 4.5 \pm 1.5 \times 10^{-31}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> using Ar as chaperone gas; with M = N<sub>2</sub>,  $k_7$  was a factor of ~ 2 greater. These results show that the association of OH with SO<sub>2</sub> is a moderately fast reaction at 300 K.

In view of the possible importance of reaction (7) in the oxidation of SO<sub>2</sub> in the atmosphere, a knowledge of  $k_7[\text{M}]$  for M = air at 1 atm. pressure, and also the subsequent rate of the HSO<sub>3</sub> free radical under these conditions is desirable. In an attempt to obtain this information, the effect of SO<sub>2</sub> on the photolysis of HNO<sub>2</sub> has been examined.

## Experimental

The flow apparatus used to study the photolysis of HNO<sub>2</sub>-CO and HNO<sub>2</sub>-SO<sub>2</sub> mixtures was identical to that used in the previous study of the photolysis of HNO<sub>2</sub> [1]. The gas mixtures were made up in a 250 l bag fabricated of Tedlar film which provided a reservoir at atmospheric pressure. The gases were withdrawn at a controlled flow rate through a 27 cm<sup>3</sup> cylindrical cell which was irradiated with u.v. light (330 - 380 nm) from a filtered high pressure mercury arc. The photon flux was approximately  $5 \times 10^{16}$  quanta/s. The light transmitted through the cell was monitored on a blue

sensitive photodiode (Mullard 90CV). The intensity was constant to within 3% during a given series of experiments but day-to-day variations in the u.v. lamp output of up to 20% were observed. The photolysis rates were not corrected for these variations in light intensity.

The concentrations of  $\text{HNO}_2$ ,  $\text{NO}$  and  $\text{NO}_2$  were measured either in the reservoir or in the outlet stream from the photolysis cell, using a commercial " $\text{NO}_x$ " analyser (Thermoelectron Corporation Model 12A) in the manner described previously [1]. The instrument was calibrated using a source of  $\text{NO}$  ( $110 \pm 5$  ppm) in pure nitrogen, which was standardized by titration against a constant ozone source calibrated by  $\text{I}_2$  liberation from neutral potassium iodide.

The rates of formation of  $\text{NO}$  and  $\text{NO}_2$  ( $R_{\text{NO}}$  and  $R_{\text{NO}_2}$ ) were measured from the change in concentration of these components when the gas mixture passed through the irradiated cell. At the flow rate ( $8 \text{ cm}^3/\text{s}$ ) and light intensity employed, approximately 4.5% of the  $\text{HNO}_2$  was photolyzed. The measured changes in the concentrations of  $\text{NO}$  and  $\text{NO}_2$  were corrected for the small conversion of  $\text{NO}_2$  to  $\text{NO}$  resulting from photolysis of the  $\text{NO}_2$  present in the mixtures. The estimated errors on a single determination of  $R_{\text{NO}}$  and  $R_{\text{NO}_2}$  were  $\pm 5\%$  and  $\pm 7\%$  respectively. In the presence of added  $\text{CO}$  and  $\text{SO}_2$ , the percentage error in  $R_{\text{NO}}$  and  $R_{\text{NO}_2}$  increased owing to the inhibiting effect of these gases, resulting in smaller concentration changes on irradiation.  $\text{CO}$  and  $\text{SO}_2$  gave no observable interference with the chemiluminescence analysis at the concentrations employed.

The gas mixtures contained part per million concentrations of  $\text{HNO}_2$ ,  $\text{CO}$  and  $\text{SO}_2$  (1 part per million =  $2.41 \times 10^{13}$  molecules/ $\text{cm}^3$  at the temperature and pressure of these experiments, *i.e.*  $294 (\pm 2)$  K and 1 atm.), diluted in a 2:1 mixture of  $\text{N}_2 + \text{NO}_2$ ) in the mixtures was  $\text{HNO}_2$ , the balance vapour (approximately  $6 \times 10^3$  ppm), which resulted from the procedure used to introduce  $\text{HNO}_2$  to the reservoir.  $\text{HNO}_2$  was generated from acidified sodium nitrite solution as described previously [1]. Between 87 and 94% of the total  $\text{NO}_x$  ( $\text{HNO}_2 + \text{NO} + \text{NO}_2$  in the mixtures was  $\text{HNO}_2$ , the balance being  $\text{NO}$  and  $\text{NO}_2$  in the proportion 1:0.75 approximately. Aliquots of pure  $\text{CO}$  (B.D.H. Ltd C.P. grade 99.5%  $\text{CO}$ ,  $\text{N}_2 = 0.3\%$ ,  $\text{O}_2 = 0.1\%$ ) and  $\text{SO}_2$  (Air Products Ltd, Research grade, 99.95%  $\text{SO}_2$ ) were added to the reservoir by injection from a graduated gas syringe into a stream of nitrogen.

To determine the effect of  $\text{CO}$  or  $\text{SO}_2$  on the photolysis of  $\text{HNO}_2$ , the mixture composition and the rates of formation  $R_{\text{NO}}$  and  $R_{\text{NO}_2}$  were first measured in the absence of additive. An aliquot of  $\text{CO}$  (or  $\text{SO}_2$ ) was then injected and the mixture allowed to mix for 10 - 15 min. The new mixture composition and photolysis rates were then measured. A further aliquot of additive was then injected and the procedure repeated.

In order to determine the concentration of  $\text{CO}$  or  $\text{SO}_2$  after each addition, an accurate knowledge of the total volume of the reservoir was required. This was achieved by carefully metering the gas volumes introduced to and pumped out from the Tedlar bag during a series of determinations. For  $\text{SO}_2$ , the concentration after each addition was measured independently by

trapping the  $\text{SO}_2$  from a known volume of the mixture in 20 ml 0.3% hydrogen peroxide solution. The resulting sulphate ion was determined by colorimetric analysis using the Thoranol method [6]. Duplicate analyses were well reproducible and the  $\text{SO}_2$  concentration in the mixture could be determined to within  $\pm 3\%$ . The concentrations determined in this way agreed to within 10% of the concentrations calculated on the basis of the volume of  $\text{SO}_2$  injected and the total volume of the reservoir. A suitable technique for the accurate determination of CO concentration was not available, and it was assumed that the concentrations determined from the respective volumes were accurate to within 10%, as for  $\text{SO}_2$ .

## Results and Discussion

### *Photolysis of $\text{HNO}_2$ in the presence of CO*

Two series of experiments were carried out in which increasing amounts of CO were added to mixtures containing initially 3.96 ppm and 6.24 ppm  $\text{HNO}_2$ . The  $\text{HNO}_2$  constituted 91 and 87% respectively of the total  $\text{NO}_x$  in these mixtures. For each mixture at least two determinations of  $R_{\text{NO}}$  and  $R_{\text{NO}_2}$  were carried out.

Figure 1 shows the effect of increasing CO concentration on the formation rates  $R_{\text{NO}}$ ,  $R_{\text{NO}_2}$  and  $R_{\text{NO}+\text{NO}_2}$  in the two series of experiments. The error bars indicate the spread of the individual measured rates for each mixture, which was often less than indicated by the size of the symbols. The data are expressed relative to the average concentration of  $\text{HNO}_2$  in each experiment. It will be seen that  $R_{\text{NO}}$  and  $R_{\text{NO}+\text{NO}_2}$  decreased and  $R_{\text{NO}_2}$  increased with increasing CO concentration. The relative rates in the series using the higher concentration of  $\text{HNO}_2$  were slightly lower due to the higher proportion of NO and  $\text{NO}_2$  in this mixture. As will be shown below, the dissociation rate of  $\text{HNO}_2$ , calculated from  $R_{\text{NO}}$  and  $R_{\text{NO}_2}$  in the absence of CO, was almost equal in the two series. The rate data are presented in detail in Table 1 where the concentrations given are mean values of the concentrations at the inlet and outlet of the photolysis cell during irradiation.

The observed inhibiting effect of CO on the rate of formation of NO can readily be explained in terms of reaction (6) followed by reactions (4) and (5). However, this mechanism requires the total rate of formation of NO and  $\text{NO}_2$  ( $R_{\text{NO}} + R_{\text{NO}_2}$ ) to be constant since there is no loss of OH following reaction (6) (OH is regenerated in reaction 5). The observed decline in  $R_{\text{NO}} + R_{\text{NO}_2}$  with added CO indicates that a new process leading to loss of radicals occurs. Possible reactions are:



For reactions (8) - (10) to compete with reaction (5) for removal of  $\text{HO}_2$  the quantities  $k_8[\text{HO}_2]$ ,  $k_9[\text{OH}]$  and  $k_{10}[\text{NO}_2]$  must be of comparable magni-

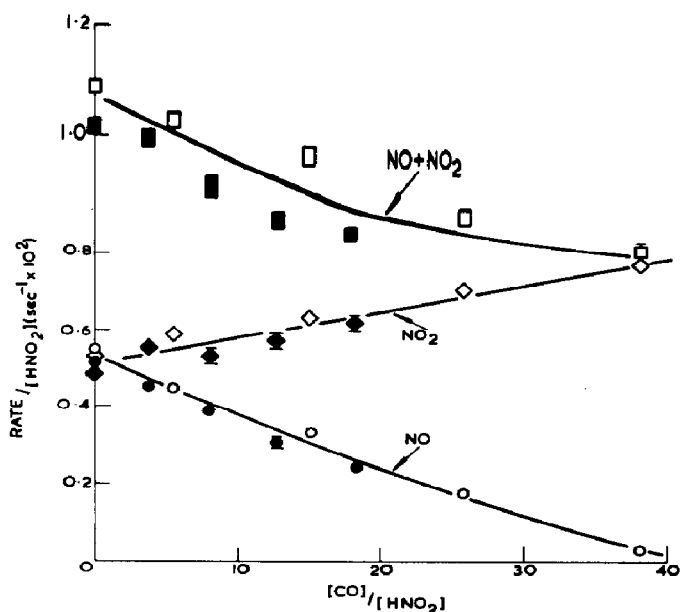


Fig. 1. Effect of added CO on the rates of formation of NO and NO<sub>2</sub> in the photolysis of HNO<sub>2</sub>. Solid symbols: [HNO<sub>2</sub>]<sub>Av</sub> = 5.6 ppm; open symbols: [HNO<sub>2</sub>]<sub>Av</sub> = 3.5 ppm. Temperature = 293 ± 1 K.

tude to  $k_5[\text{NO}]$ . The rate constant  $k_5$  is not known accurately but a recent estimate by Payne *et al.* [3] of  $k_5 = 3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  ( $\pm$  a factor of 3) is in accord with other estimates. Thus for an NO concentration of 0.25 ppm (experiment CO 1.3),  $k_5[\text{NO}] \approx 1.8 \text{ s}^{-1}$ . For the same representative experiment, the maximum steady-state OH and HO<sub>2</sub> concentrations, estimated on the basis of reactions (1) - (6) (*i.e.* assuming no additional radical loss process) are approximately  $2.5 \times 10^9$  and  $2.5 \times 10^{11}$  molecules/cm<sup>3</sup> respectively.

There is some uncertainty in the absolute values of  $k_8$  and  $k_9$ . The preferred literature values are  $k_8 = 3.3 \times 10^{-12} [7-9] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_9 \approx 3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [9, 10] giving  $k_8[\text{HO}_2] \lesssim 0.83 \text{ s}^{-1}$  and  $k_9[\text{OH}] \lesssim 0.008 \text{ s}^{-1}$ . Thus the rate of reaction (8) is of comparable magnitude to reaction (5) and could account for the observed radical loss in the present system. Reaction (9) would appear to be unimportant.

In all the experiments the relative concentrations of NO and NO<sub>2</sub> were similar and therefore for reaction (10) to be important,  $k_{10} \approx k_5$ . There appears to be no experimental results relating to  $k_{10}$  but an estimate of  $k_{10} \approx 3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , based on thermochemical considerations and data for other H abstraction reactions of NO<sub>2</sub>, has been given [10]. Thus, it would appear that reaction (10) is also too slow to be an important radical loss process.

#### Photolysis of HNO<sub>2</sub> in the presence of SO<sub>2</sub>

The effect of SO<sub>2</sub> on the photolysis was studied in a similar manner to the effect of CO. Experiments were carried out in which increasing amounts of SO<sub>2</sub> (up to 90 ppm) were added to three different mixtures containing

TABLE 1

Rates of formation of NO and NO<sub>2</sub> in the photolysis of HNO<sub>2</sub> in the presence of CO and SO<sub>2</sub>

Experiment number	[HNO <sub>2</sub> ] (ppm)	[NO] (ppm)	[NO <sub>2</sub> ] (ppm)	[CO] or [SO <sub>2</sub> ] (ppm)	$R_{NO}^* \times 10^2$ (ppm/s)	$R_{NO_2}^* \times 10^2$ (ppm/s)	
CO	1.1	3.86	0.28	0.20	0	2.13	2.07
	1.2	3.63	0.27	0.20	20.2	1.62	2.13
	1.3	3.45	0.25	0.21	48.8	1.15	2.18
	1.4	3.17	0.24	0.22	78.1	0.546	2.22
	1.5	3.03	0.24	0.25	116.5	0.078	2.33
	2.1	6.14	0.60	0.46	0	3.16	3.02
	2.2	5.83	0.58	0.47	21.9	2.60	3.23
	2.3	5.51	0.57	0.46	44.6	2.00	2.82
	2.4	5.35	0.56	0.45	68.5	1.55	2.92
	2.5	5.12	0.54	0.45	94.1	1.17	3.00
SO <sub>2</sub>	1.1	3.37	0.22	0.19	0	2.30	1.85
	1.2	3.26	0.21	0.18	3.6	1.96	1.69
	1.3	3.06	0.20	0.17	12.4	1.42	1.88
	1.4	2.85	0.20	0.17	20.2	0.791	1.88
	1.5	2.68	0.19	0.17	36.2	0.186	1.96
	1.6	2.44	0.18	0.17	89.9	0.859	1.82
	2.1	4.94	0.44	0.33	0	3.32	3.06
	2.2	4.75	0.42	0.31	5.7	2.74	2.80
	2.3	4.61	0.40	0.29	11.8	2.29	2.70
	2.4	4.25	0.39	0.32	15.3	1.87	2.51
	2.5	3.97	0.38	0.31	26.9	1.27	2.35
	2.6	3.72	0.37	0.30	41.1	0.594	2.33
	3.1	4.22	0.38	0.27	0	2.91	2.68
	3.2	4.11	0.36	0.26	5.6	2.32	2.55
3.3	4.06	0.35	0.25	15.1	1.69	2.48	
3.4	3.90	0.33	0.25	26.7	0.999	2.59	

\*Average values corrected for NO formation from NO<sub>2</sub> photolysis.

initially 3.43, 4.28 and 5.02 ppm HNO<sub>2</sub> which constituted 94, 89 and 88% of the total NO<sub>x</sub> respectively. The data for the average concentrations during photolysis and the formation rates  $R_{NO}$  and  $R_{NO_2}$  are given in Table 1 and the latter rates, expressed relative to the HNO<sub>2</sub> concentration, are plotted against the ratio  $[SO_2]/[HNO_2]$  in Fig. 2. It will be seen that the effect of SO<sub>2</sub> on the formation rates was similar to that of CO. Of the two gases, SO<sub>2</sub> is the more effective inhibitor for NO formation since the amount of CO necessary to give a 50% reduction in  $R_{NO}$  was roughly a factor of 3 greater than the amount of SO<sub>2</sub> required for the same effect. It will be noted that  $R_{NO}$  was negative at the highest concentration of SO<sub>2</sub>, indicating that reactions involving SO<sub>2</sub> could remove NO at a rate faster than it was produced by photolysis of HNO<sub>2</sub>. The total rate  $R_{NO} + R_{NO_2}$  also decreased with added SO<sub>2</sub>, showing the occurrence of an additional radical loss process in the presence of SO<sub>2</sub>.

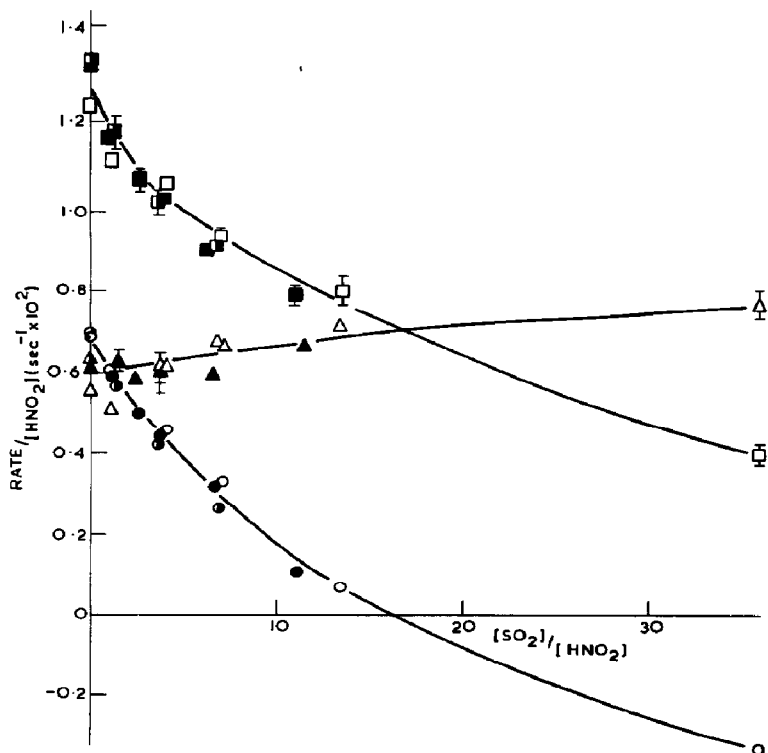
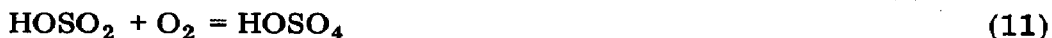


Fig. 2. Effect of added  $\text{SO}_2$  on the rates of formation of NO and  $\text{NO}_2$  in the photolysis of  $\text{HNO}_2$ .  $\circ = R_{\text{NO}}/[\text{HNO}_2]$ ;  $\triangle = R_{\text{NO}_2}/[\text{HNO}_2]$ ;  $\square = R_{\text{NO}} + R_{\text{NO}_2}/[\text{HNO}_2]$ . Solid symbols:  $[\text{HNO}_2]_{\text{Av}} = 4.4$  ppm; half-filled symbols:  $[\text{HNO}_2]_{\text{Av}} = 4.1$  ppm; open symbols:  $[\text{HNO}_2]_{\text{Av}} = 3.0$  ppm. Temperature =  $294 \pm 2$  K.

The results suggest that subsequent reactions of the  $\text{HSO}_3$  radical produced in reaction (7) lead to the oxidation of NO to  $\text{NO}_2$ . In view of the concentration advantage of  $\text{O}_2$  in the mixtures employed, the most likely reaction of  $\text{HSO}_3$  is:



The peroxy radical may then either react directly with NO or decompose to give  $\text{HO}_2$ , which can react with NO in reaction (5):



In the latter case the effect of  $\text{SO}_2$  would be similar to that of CO, in that reactions (7), (11), (13), and (5) do not lead to loss of radicals. The decline in  $R_{\text{NO}} + R_{\text{NO}_2}$  could then be ascribed to reaction (8). If reaction (12) occurs the radical loss mechanism would depend on the fate of the  $\text{HOSO}_3$  free radical, which is unknown. In a study of the steady-state photolysis of  $\text{SO}_2$ - $\text{HNO}_2$ -air mixtures using radioactive  $^{35}\text{SO}_2$  as a tracer [11], it was found that a large proportion of the  $\text{SO}_2$  oxidized was converted to a sulphur-containing aerosol, indicating that either  $\text{SO}_3$  or  $\text{H}_2\text{SO}_4$  are the ultimate reaction products.

The reaction of  $\text{SO}_2$  with hydroperoxyl radicals could also occur in the present system, *i.e.*



However, the rate constant for this reaction ( $k_{14} = 9 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K) is roughly a factor of 300 less than  $k_5$  [3]. Therefore, at all but the highest concentrations of  $\text{SO}_2$  employed, reactions (5) and (8) were the predominant loss mechanisms for  $\text{HO}_2$ .

*Rate constants for the reactions of OH with  $\text{HNO}_2$  and NO*

For a kinetic analysis of the data for the photolysis of the CO- $\text{HNO}_2$  mixtures it will be assumed that reaction (8) is the only important radical loss process and that in the absence of CO,  $k_5[\text{NO}] \gg k_8[\text{HO}_2]$  i.e. reaction (8) can be neglected. Application of the steady-state approximation to the concentrations of OH and  $\text{HO}_2$  radicals gives the following expressions:

$$k_5[\text{NO}][\text{HO}_2] + k_8[\text{HO}_2]^2 = \Phi_B k_a[\text{HNO}_2] + k_6[\text{CO}][\text{OH}] \quad (i)$$

$$[\text{OH}] = \frac{(\Phi_A + \Phi_B)k_a[\text{HNO}_2] - k_8[\text{HO}_2]^2}{k_x[\text{NO}_x]} \quad (ii)$$

where  $k_x[\text{NO}_x] = k_1[\text{M}][\text{NO}] + k_2[\text{M}][\text{NO}_2] + k_3[\text{HNO}_2]$  and  $k_x$  is the effective rate constant for the removal of OH by reactions (1) - (3) in mixtures of constant total pressure (1 atm.) containing  $\text{HNO}_2$ , NO and  $\text{NO}_2$  in constant proportion. These latter conditions apply since in all experiments the amounts of NO and  $\text{NO}_2$  present were relatively small and in an approximately constant ratio to the total  $\text{NO}_x$ . It will be noted that eqn. (ii) contains no term involving [CO]; the OH concentration is only influenced by CO inasmuch as the rate of eqn. (8) increases with [CO].

The rate of formation of NO is given by:

$$R_{\text{NO}} = \Phi_A k_a[\text{HNO}_2] - k_5[\text{NO}][\text{HO}_2] - k_1[\text{NO}][\text{OH}][\text{M}]$$

By substituting eqns. (i) and (ii), the following expression may be derived for the difference between the rates of formation of NO in the absence and in the presence of CO:

$$\Delta_{\text{NO}} = \left( \frac{R_{\text{NO}}}{[\text{HNO}_2]} \right)_0 - \left( \frac{R_{\text{NO}}}{[\text{HNO}_2]} \right)_{\text{CO}} = (\Phi_A + \Phi_B)k_a \cdot \frac{k_6[\text{CO}]}{k_x[\text{NO}_x]} - \frac{k_8[\text{HO}_2]^2}{[\text{HNO}_2]_{\text{CO}}} \cdot \left( 1 + \frac{k_6[\text{CO}]}{k_x[\text{NO}_x]} \right) \quad (iii)$$

In deriving eqn. (iii) it was assumed that, since the relative amount of NO present was small, the terms involving  $k_1[\text{M}][\text{NO}]([\text{OH}]_0 - [\text{OH}]_{\text{CO}})$  could be neglected, to a first approximation.

By a similar analysis it can be shown that the difference between the rates of formation of NO +  $\text{NO}_2$  ( $R_{\text{NO}_x}$ ) in the absence and presence of CO is given by:

$$\Delta_{\text{NO}_x} = \left( \frac{R_{\text{NO}_x}}{[\text{HNO}_2]} \right)_0 - \left( \frac{R_{\text{NO}_x}}{[\text{HNO}_2]} \right)_{\text{CO}} = \frac{k_8[\text{HO}_2]^2}{[\text{HNO}_2]_{\text{CO}}} \quad (iv)$$



Thus, as expected, the decrease in  $R_{NO_x}$  gives a measure of the radical loss rate.

Combining eqns. (iii) and (iv) and re-arranging, the following expression is obtained:

$$\frac{\Delta_{NO} + \Delta_{NO_x}}{(\Phi_A + \Phi_B)k_a - \Delta_{NO_x}} = \frac{k_6[CO]}{k_x[NO_x]} \quad (v)$$

In order to test the data against eqn. (v), a knowledge of the total dissociation rate of  $HNO_2$ ,  $(\Phi_A + \Phi_B)k_a$ , is necessary. This may be calculated from the  $R_{NO}$  and  $R_{NO_2}$  values in the absence of CO (or  $SO_2$ ), using the following equations which were derived in the previous work on  $HNO_2$  [1]:

$$\frac{R_{NO}}{[HNO_2]} = \Phi_A k_a (1 - X) - \Phi_B k_a (1 + X)$$

$$\frac{R_{NO_2}}{[HNO_2]} = \Phi_A k_a \cdot Y + \Phi_B k_a (2 + Y)$$

where

$$X = \frac{[NO]}{[NO] + [NO_2] + 0.37 [HNO_2]}$$

and

$$Y = \frac{0.37 [HNO_2] - [NO_2]}{[NO] + [NO_2] + 0.37 [HNO_2]}$$

The X and Y expressions were derived on the assumption that  $k_1[M] \simeq k_2[M]$  and using the experimentally determined ratio  $k_3/k_1[M] = 0.37$  at 1 atm. and 300 K.

TABLE 2

Primary dissociation rates ( $s^{-1} \times 10^2$ ) in the photolysis of  $HNO_2$

Experiment number		$\Phi_A k_a$	$\Phi_B k_a$	$(\Phi_A + \Phi_B) k_a$	$\Phi_B/\Phi_A$
CO	1.1	0.695	0.035	0.730	0.051
	2.1	0.691	0.042	0.733	0.064
$SO_2$	1.1	0.810	0.020	0.830	0.025
	2.1	0.897	0.048	0.945	0.054
	3.1	0.893	0.045	0.938	0.050

Table 2 shows the calculated dissociation rates for each series of experiments. The lower values of  $(\Phi_A + \Phi_B)k_a$  in the CO series are attributed to the slightly lower light flux in these experiments. The ratio  $\Phi_B/\Phi_A$  is lower than the average value of approximately 0.12 found in the previous study; no explanation for this is offered.

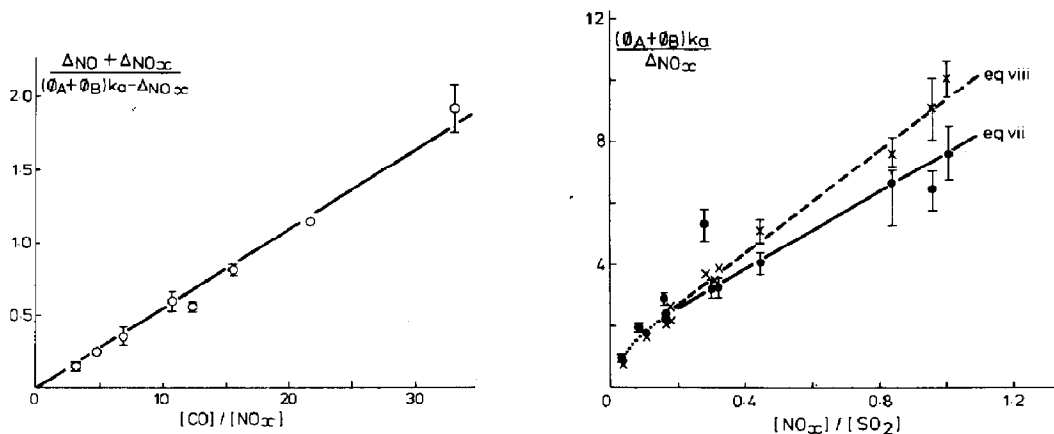


Fig. 3. Plot of the quantity  $(\Delta\text{NO} + \Delta\text{NO}_x) / [(\Phi_A + \Phi_B)k_a - \Delta\text{NO}_x]$  against the ratio  $[\text{CO}] / [\text{NO}_x]$  for the photolysis of  $\text{HNO}_2$ - $\text{CO}$  mixtures.  $\Delta\text{NO}$  and  $\Delta\text{NO}_x$  refer to the difference in the quantities  $R_{\text{NO}}/[\text{HNO}_2]$  and  $(R_{\text{NO}} + R_{\text{NO}_2})/[\text{HNO}_2]$  respectively in the absence and in the presence of  $\text{CO}$ .  $\text{NO}_x = \text{HNO}_2 + \text{NO} + \text{NO}_2$ . Error bars show maximum spread of values from individual rate measurements in the presence of  $\text{CO}$ .

Fig. 4. Plots of the quantities  $(\Phi_A + \Phi_B)k_a / \Delta\text{NO}_x$  (eqn. vii) and  $(\Phi_A + \Phi_B)k_a / \Delta\text{NO}$  (eqn. viii) against the ratio  $[\text{NO}_x] / [\text{SO}_2]$  for the photolysis of  $\text{HNO}_2$ - $\text{SO}_2$  mixtures.  $\Delta\text{NO}$  and  $\Delta\text{NO}_x$  refer to the difference in the quantities  $R_{\text{NO}}/[\text{HNO}_2]$  and  $R_{\text{NO}+\text{NO}_2}/[\text{HNO}_2]$  respectively in the absence and presence of  $\text{SO}_2$ .  $\text{NO}_x = \text{HNO}_2 + \text{NO} + \text{NO}_2$ . Error bars show maximum spread from individual rate measurements in the presence of  $\text{SO}_2$ .

The data for different amounts of added  $\text{CO}$  are plotted according to eqn. (v) in Fig. 3. A reasonable fit to the expected functional relationship was obtained and least squares analysis gave a slope of  $5.5 \times 10^{-2}$ . The error on the slope was estimated graphically to be approximately  $\pm 10\%$ . Thus, the ratio  $k_6/k_x \approx 5.5 \pm 0.6 \times 10^{-2}$ .

The rate constant for the reaction of  $\text{OH}$  with  $\text{CO}$  at 300 K is now well established. Drysdale and Lloyd [12] in their 1970 evaluation give  $k_6 = 1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and several recent determinations lie to within 20% of this figure [13]. The corresponding value of the effective rate constant  $k_x$  is  $2.73 \pm 0.28 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Assuming that  $k_2[\text{M}] = k_1[\text{M}] = 2.7 k_3$ , it can be readily shown that, for the mixtures used, in which on average 87% of the total  $\text{NO}_x$  was  $\text{HNO}_2$ ,  $k_3 \approx 0.82 k_x$ . Therefore,  $k_3 = 2.2 \pm 0.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This confirms the previous conclusion [1] that reaction (3) is considerably faster than the analogous reaction of  $\text{OH}$  with  $\text{HNO}_3$  ( $k = 1.3 \pm 0.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K [14]).

From the relationship  $k_3 = 0.37 \pm 0.06 k_1[\text{M}]$ , a value of  $k_1[\text{M}] = 6.1 \pm 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is derived for the reaction of  $\text{OH}$  with  $\text{NO}$  with  $\text{M} = \text{N}_2 + \text{O}_2$  at 1 atm. This value is intermediate between the limiting high pressure rate constant for the bimolecular reaction  $\text{OH} + \text{NO} = \text{HNO}_2$  of  $1.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , estimated by Morley and Smith [14] from their low pressure data, and the experimental values of  $k_1[\text{M}]$  at low pressure. The third order rate constant  $k_1$  has been measured for several different  $\text{M}$  gases by a number of investigators [5, 14 - 16]. Harris and Wayne

[5] have recently determined a value of  $k_1 = 1.5 \pm 0.5 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for  $M = \text{N}_2$  which gives  $k_1[M] = 3.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $[M] = 1 \text{ atm}$ . It would appear, therefore, that reaction (1) is in the pressure dependent region at atmospheric pressure.

In view of the assumptions made previously regarding the relative rates of reactions (1) and (2), it is of interest to compare the value of  $k_1[M]$  derived above with available estimates of  $k_2[M]$  at 300 K and 1 atm. Simoniatis and Heicklen [17] have determined the rate constant ratio  $k_2[M]/k_6$  at 300 K for total pressures of up to 1.4 atm. The value for  $k_2[M]$  at 1 atm. was  $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Extrapolation of the data of Morley and Smith [14] for reaction (2) with  $M = \text{He}$  and pressures up to 0.4 atm. would suggest a value closer to their estimated limiting high pressure value of  $1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , for  $\text{N}_2 + \text{O}_2$  at 1 atm. In either case, the present result for  $k_1[M]$  would suggest that the assumption of approximately equal rates for reactions (1) and (2) at 1 atm. is fully justified.

#### Rate constant for the reaction of OH with $\text{SO}_2$

For the  $\text{SO}_2\text{-HNO}_2$  data kinetic analysis is more difficult since the radical loss mechanism is unknown. If the  $\text{HO}_2$  radical is formed (*i.e.* reaction (13) occurs) the data should be described by an equation analogous to equation (v):

$$\frac{\Delta_{\text{NO}} + \Delta_{\text{NO}_x}}{(\Phi_A + \Phi_B)k_a - \Delta_{\text{NO}_x}} = \frac{k_7[M][\text{SO}_2]}{k_x[\text{NO}_x]} \quad (\text{vi})$$

where  $\Delta$  refers to the difference in the quantities  $R_{\text{NO}}/[\text{HNO}_2]$ ,  $R_{\text{NO}+\text{NO}_2}/[\text{HNO}_2]$  in the absence and presence of  $\text{SO}_2$ .

Alternatively if reaction (12) occurs and radicals are lost by reactions of  $\text{HSO}_5$  and/or  $\text{HSO}_4$  (but not involving NO and  $\text{NO}_2$ ), the difference  $\Delta_{\text{NO}_x}$  should be described by the equation:

$$\frac{\Phi_A + \Phi_B}{\Delta_{\text{NO}_x}} k_a = \frac{k_x[\text{NO}_x]}{k_3[\text{HNO}_2]} \left( 1 + \frac{k_x[\text{NO}_x]}{k_7[M][\text{SO}_2]} \right) \quad (\text{vii})$$

In the special case when only  $\text{HSO}_4$  is lost (*i.e.* each  $\text{HSO}_5$  radical reacts with NO) the following equation can be derived in addition to equation (vii):

$$\frac{\Phi_A + \Phi_B}{\Delta_{\text{NO}}} k_a = 1 + \frac{k_x[\text{NO}_x]}{k_7[M][\text{SO}_2]} \quad (\text{viii})$$

The data are plotted according to eqns. (vii) and (viii) in Fig. 4. The scatter in the points on Fig. 4 does not allow a definite conclusion regarding the functional dependence of the data but there is an indication of curvature at low  $[\text{NO}_x]/[\text{SO}_2]$  for both plots. Furthermore, the value for the ratio  $k_x/k_7[M]$  determined from the least squares parameters of the "best" straight lines for the plots of eqns. (vii) and (viii) differ significantly as will be seen from Table 3. Evidently the special conditions for eqn. (viii) are not fulfilled, *i.e.* there is an additional loss or radicals which oxidise NO to  $\text{NO}_2$ .

TABLE 3

Least squares parameters for plots of rate data for the photolysis of SO<sub>2</sub>-HNO<sub>2</sub> mixtures

Equation Number	Slope	Intercept	$k_x/k_7[M]^*$
vi (Fig. 5)	$0.220 \pm 0.014$	$0.09 \pm 0.08$	$4.55 \pm 0.29$
vii (Fig. 4)	$5.83 \pm 0.66$	$1.56 \pm 0.33$	$3.74 \pm 0.85$
viii (Fig. 4)	$8.62 \pm 0.27$	$0.84 \pm 0.13$	$8.62 \pm 0.27$

\*The uncertainty limits determined by least squares are considered unrealistically low in view of the experimental error. The error on  $k_x/k_7[M]$  from eqn. (vi) was estimated graphically to be approximately  $\pm 10\%$ .

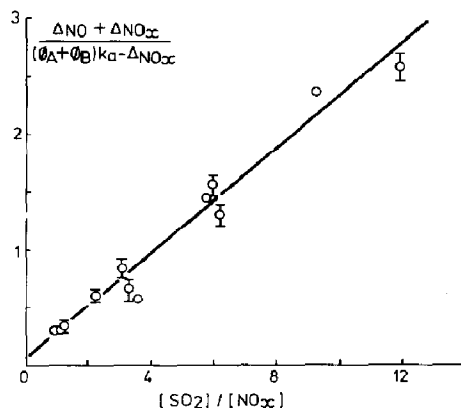


Fig. 5. Plot of the quantity  $(\Delta_{NO} + \Delta_{NO_x})/[(\Phi_A + \Phi_B)k_a - \Delta_{NO_x}]$  against the ratio  $[SO_2]/[NO_x]$ . Quantities as for Fig. 4.

Figure 5 shows a plot of the data according to eqn. (vi). A reasonable fit was obtained, with the exception of the data for the highest  $[SO_2]/[NO_x]$  ratio (not shown in Fig. 4). The value of the ratio  $k_x/k_7[M] = 4.5 \pm 0.5$  derived from the slope of this plot (see Table 3) is similar to that obtained from the data plotted according to eqn. (vii). This equality is almost certainly fortuitous, however, since it is not expected on the basis of the mechanisms considered. Therefore, the nature of the reactions following the addition of OH to SO<sub>2</sub> in this system remain unclear. Nevertheless, a consideration of the possible mechanisms in this system shows that the ratio  $k_x/k_7[M]$  is unlikely to be less than the value derived from eqn. (vi) and this is considered the best estimate on the basis of the present data. Since the relative amounts of HNO<sub>2</sub>, NO and NO<sub>2</sub> in the experiments with SO<sub>2</sub> were similar to those with CO, the value of  $k_x$  from the latter may be used to determine  $k_7[M]$  for M = N<sub>2</sub> + O<sub>2</sub> at 1 atm. The value obtained is  $k_7[M] = 6.0 \pm 0.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . On the basis of observations for similar 3-body reactions, e.g. OH + NO<sub>2</sub> + M = HNO<sub>3</sub> + M [14], reaction (7) would be expected to be in the pressure dependent region at pressures below 1 atm. In accord with this the present value of  $k_7[M]$  is a factor of approximately 3 greater than

the value reported by Payne *et al.* [3] for  $M = N_2 + H_2O$  (0.05 atm.). However, extrapolation of the low pressure data of Harris and Wayne [5] for  $k_7$  would suggest a value for  $k_7[M]$  at 1 atm. rather higher than the present value.

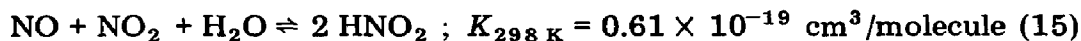
### Atmospheric photochemistry

The results obtained in the present study provide some useful information regarding the chemistry of  $SO_2$  and  $HNO_2$  in the lower atmosphere. Recent models [18, 19] for the photochemical processes governing the life cycles of the trace gases  $CH_4$ ,  $CO$  and  $H_2$  in the natural troposphere predict an average hydroxyl radical concentration of  $\sim 2 \times 10^6$  molecules/cm<sup>3</sup> with summer daytime concentrations of  $OH$  of  $1 \times 10^{-7}$  molecules/cm<sup>3</sup>. Using the present value of  $k_7[M] = 6.0 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, the predicted average lifetime for  $SO_2$  in the lower atmosphere on the basis of reaction with  $OH$  is approximately 10 days. This is rather longer than the expected lifetime due to precipitation scavenging processes and diffusion to the earth's surface, *i.e.* 4 - 6 days [20] and the latter are, therefore, more important in determining the overall lifetime of atmospheric  $SO_2$ .

The concentration of nitrous acid in the atmosphere will be governed primarily by the photodissociation rate and reactions (1) and (3), *i.e.*

$$[HNO_2] = \frac{k_1[NO][OH]}{k_3[OH] + (\Phi_A + \Phi_B)k_a}$$

The photodissociation rate of  $HNO_2$  is approximately one-third of that of  $NO_2$  in the 330 - 380 nm region [1]. At average sunlight intensities the dissociation rate of  $NO_2$  resulting from absorption in the 290 - 380 nm region is approximately  $6 \times 10^{-3}$  s<sup>-1</sup> [21] and therefore  $(\Phi_A + \Phi_B)k_a = 2 \times 10^{-3}$  s<sup>-1</sup>. With  $[OH] = 1 \times 10^7$  molecules/cm<sup>3</sup>,  $(\Phi_A + \Phi_B)k_a \approx 100 k_3$  and the average concentration of gaseous  $HNO_2$  is given by  $[HNO_2] \approx 0.03 [NO]$ . The concentration of  $NO$  in the natural troposphere is of the order of  $2.5 \times 10^{10}$  molecules/cm<sup>3</sup> [22] and therefore the daytime concentration of nitrous acid will be very small indeed ( $\sim 10^9$  molecules/cm<sup>3</sup>). It is of interest to compare this value with the equilibrium concentration of  $HNO_2$  calculated from the equilibrium constant [23] for the reaction:



For representative concentrations of  $NO$ ,  $NO_2$  and  $H_2O$  in the lower atmosphere ( $2.5 \times 10^{10}$ ,  $5 \times 10^{10}$  and  $5 \times 10^{17}$  molecules/cm<sup>3</sup> respectively), the concentration of  $HNO_2$  at equilibrium is  $6.2 \times 10^9$  molecules/cm<sup>3</sup>. Since this is greater than the above photostationary concentration, the formation of  $HNO_2$  from reaction (11) could provide a source of hydroxyl radicals in the atmosphere. Current evidence [24] seems to indicate that the homogeneous reaction of  $NO$ ,  $NO_2$  and  $H_2O$  is too slow to be significant, but a heterogeneous reaction may occur on the surface of atmospheric particles.

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### *Note added in proof (August 26, 1974)*

Very recently Simonaitis and Heicklen, *J. Phys. Chem.*, 78 (1974) 653, have reported a value of  $7 \pm 1$  for the rate constant ratio  $k_5/k_{10}$ . Thus reaction (10) could have been responsible for part of the HO<sub>2</sub> removal in the CO/HNO<sub>2</sub> photolyses !