# THE PHOTOLYSIS OF GASEOUS NITROUS ACID

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Summary

The photolysis at 330 - 380 nm of mixtures containing parts per million concentrations of gaseous nitrous acid in pure nitrogen and oxygen has been studied in a flow system. The rates of formation of the products NO and NO_2, have been measured at low conversion of HNO_2. From these data it has been shown that the predominant process following absorption by HNO_2 in this wavelength region is the dissociation
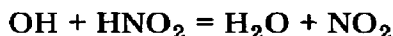
$$HNO_2 \xrightarrow{h\nu} OH + NO$$
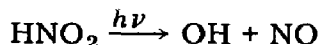
There is some evidence for the occurrence of the alternative process:

$$HNO_2 \xrightarrow{h\nu(\lambda < 366 \text{ nm})} H + NO_2$$
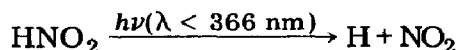
which may account for ~ 10% of the overall photodissociation.
An estimate of the rate constant for the reaction

$$OH + HNO_2 = H_2O + NO_2$$

has also been obtained. The value, $k_3 = 1.8 \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1} (based on a literature value for the rate constant for the reaction of OH with NO_2), is about one order of magnitude higher than for the analogous reaction of OH with HNO_3.
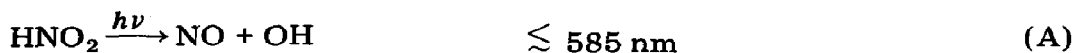
Introduction

Nitrous acid has been postulated as an intermediate in many gas-phase reactions involving the oxides of nitrogen and hydrogen containing compounds. However, there is very little experimental information regarding the chemical and photochemical behaviour of gaseous nitrous acid. This results mainly from the practical difficulty in obtaining reasonable concentrations of gaseous HNO_2 because of the rapid establishment of the equilibrium (I) at pressures of a few Torr [1]:

$$2HNO_2 \rightleftharpoons NO + NO_2 + H_2O \tag{I}$$

We have recently reported a method for the preparation and quantitative analysis of mixtures containing low concentrations of gaseous nitrous acid in air at 1 atm. ($\equiv 101.33$ kN/m^2) pressure [2]. Although both NO and NO$_2$ were unavoidably present, stable concentrations of HNO$_2$ greatly in excess of those predicted by the equilibrium (I) could be obtained. This has facilitated, for the first time, systematic studies of the photolysis of gaseous nitrous acid. The results of a preliminary investigation on this system have already been reported [3]. It was found that the products of the steady-state photolysis of HNO$_2$ at λ = 365 nm are NO, NO$_2$ and probably HNO$_3$. The kinetics of the reactions following photolysis were complex and could not be adequately described by the following simple mechanism which was based on available spectroscopic, thermodynamic and kinetic information:

$$HNO_2 \xrightarrow{h\nu} NO + OH \qquad\qquad \lesssim 585\ nm \tag{A}$$

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

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

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

In particular, the yield of NO was much less than expected and it was suggested that this may be due to the occurrence of the alternative dissociation process:

$$HNO_2 \xrightarrow{h\nu} H + NO_2 \qquad\qquad \lambda \lesssim 366\ nm \tag{B}$$
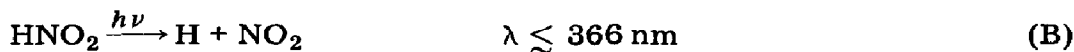
There are, however, other possible explanations of the observed behaviour, and it seemed desirable to establish with more certainty the nature of the primary photodissociation process(es) in the photolysis of HNO$_2$.

The present paper describes a study of the photolysis (at 330 - 380 nm) of dilute mixtures containing predominantly nitrous acid in pure nitrogen and oxygen, in a flow system, using short irradiation periods. The rates of formation of the products NO and NO$_2$ have been determined at HNO$_2$ conversions of approximately 3%. From these data it has been shown that the predominant ($\sim$ 90%) primary dissociation process yields hydroxyl radicals and nitric oxide with a possible small contribution from process (B). Estimates of the quantum yield for dissociation and of the rate constant for the reaction of OH with HNO$_2$ have also been made.

Experimental

The photolyses were carried out in a 27 cm^3 cylindrical Pyrex cell, 7 cm in length and 2.2 cm diameter, with planar quartz end windows cemented on with Araldite. The cell was mounted in an optical system comprising a

high pressure mercury arc lamp (Mazda type ME/D, 250 W), two quartz lenses (f = 5 cm), glass filters (4 mm Pyrex + Chance OX1) and an adjustable stop. The system was arranged to give a slightly convergent beam through the cell. The waveband isolated by the filters was 330 - 380 nm and approximately 50% of the radiation entering the cell was at 365 ± 5 nm. The wavelength region utilized corresponds to the principal absorbing region for gaseous nitrous acid in its first absorption band [4].
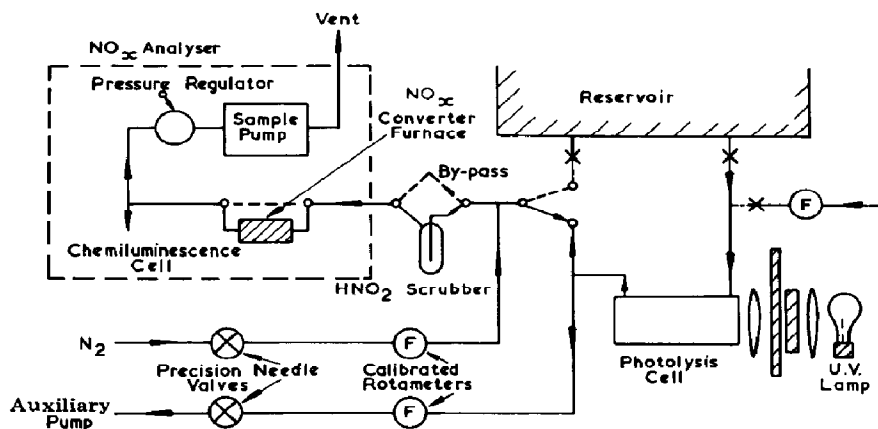

Fig. 1. Diagram of flow apparatus.

A diagram of the flow system used for the photolysis measurements is shown in Fig. 1. Entry and exit tubes to the cell were positioned close to the front and rear windows. Gas mixtures were drawn through the cell from a 250 l bag constructed of Tedlar film (du Pont Ltd). The flexible bag, which was shielded from room light provided a convenient, constant pressure (1 atm.) reservoir for the gas mixtures. The gas flow was provided by a combination of the analyzer sample pump and an auxiliary diaphragm pump (Charles Austin, Capex Mk II). The analyzer drew a constant flow of 10 cm^3/s at 1 atm. When a faster flow was required, additional gas was metered through the system by means of the auxiliary pump. If the gas flow to the analyzer exceeded the required flow through the cell, pure nitrogen was metered into the gas stream, downstream from the cell. The total flow through the reaction vessel could be measured directly at the cell inlet prior to taking measurements. It was assumed that the flow rates used (1 - 20 cm^3/s) gave sufficient turbulence for the gases to be completely mixed within the cell. The photolyses were carried out at atmospheric pressure and at room temperature (300 ± 2 K). All gas lines were of 1/8 in. (1 in. = 25.4 mm). Teflon tubing to minimize adsorption loss of the oxides and oxyacids of nitrogen.

Analysis of the nitrogen gases was carried out with a commercial chemiluminescence "NO$_x$" analyzer (Thermo-Electron Corp. Model 12A) using the same techniques as described previously [2]. The instrument can measure directly both NO and "total NO$_x$" $i.e.$ NO + NO$_2$ + HNO$_2$, in a gaseous sample.

Gaseous HNO_2 can be quantitatively removed from the sample gas by absorption in aqueous 0.1 N NaOH contained in a miniature scrubber. Thus the concentrations of all three components can be determined after allowance for the small but constant fraction (12.5 ± 0.5%) of the NO_2 which is also absorbed in the alkali. Samples to the analyzer could be taken either directly from the reservoir or downstream of the photolysis cell.

In order to prepare mixtures of gaseous nitrous acid the reservoir was first flushed with N_2 and pumped out with a high volume rotary blower. 90 l O_2 were then admitted to the bag. Dilute HNO_2 was added by passing N_2 at 167 cm^3/s through a 100 ml flask containing ~ 35 ml 0.02 M sodium nitrite acidified to pH = 0 with H_2SO_4. The gases passed into the reservoir through a short length of PTFE tubing. The glass surfaces of the flask were coated with PTFE and the glassware was oven dried before use. With this procedure approximately 85% of the "nitrous fumes" swept into the reservoir was gaseous HNO_2, the balance being NO and NO_2 in roughly equal proportions. After sufficient HNO_2 had been added, the reservoir was filled to 250 l with N_2. Mixtures containing up to 20 ppm HNO_2 (1 ppm = 2.46 × 10^{13} molecules/cm^3 at 300 K and 1 atm. pressure) were prepared in this way and were found to undergo little change in composition on standing for several hours in the reservoir.

The rate of photolysis of HNO_2 was measured from the change of composition of the gas mixture when it was passed through the photolysis cell at a given flow rate. First, it was necessary to examine any changes in composition resulting from passage of the mixture through the unirradiated cell. An extensive series of tests showed that there was no detectable change in the concentrations of NO and NO_2 when HNO_2–NO–NO_2 mixtures were passed through the cell (without irradiation). There was a small loss in HNO_2 which was more pronounced at the lower HNO_2 concentrations and at the slower flow rates used. The maximum loss for the conditions employed for rate measurements was 4% and it was normally less than 1%.

Since the concentrations of NO and NO_2 were unaffected by passage through the unirradiated cell, the rate of formation, R_f, of these components during photolysis could be determined from the change in concentration of NO and NO_2 in the cell effluent resulting from irradiation of the mixture, $i.e.$

$$R_f = \frac{F}{V} \times \Delta C$$

where F = volumetric flow rate (cm^3/s), V = volume of the cell (27 cm^3) and ΔC = change in concentration. In a typical experiment the following procedure was adopted: the concentrations of HNO_2, NO and NO_2 in the reservoir were measured and the gas mixture was drawn through the photolysis cell at the required flow rate until a constant "total NO_x" reading was obtained in the effluent. A series of measurements of the effluent NO and "NO + NO_2" ($i.e.$ sampling through the scrubber) were taken with and without irradiation and the average differences ΔC_{NO} and ΔC_{NO+NO_2} determined. Finally a check

on "total NO_x" was made and any change noted.

A complicating feature in the irradiation of these mixtures arises from the photolysis of NO_2. NO_2 absorbs throughout the wavelength region employed and, at low [NO_2], produces NO by the reactions:

$$NO_2 \xrightarrow{h\nu} O + NO$$

$$O + O_2 + M \rightarrow O_3 + M$$

$$NO + O_3 \rightarrow NO_2 + O_2$$
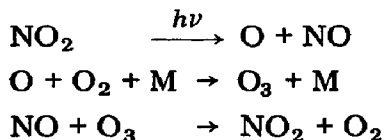
At the light intensity and the photolysis times used the net change in NO and NO_2 concentration from these reactions was not negligible. Therefore, in order to determine the rates of formation of NO and NO_2 (R_{NO_2}) in the photolysis of HNO_2 it was necessary to correct the observed ΔC values for the changes produced by the photolysis of NO_2. This was achieved by independent measurements taken when mixtures containing NO and NO_2 but no HNO_2 where photolyzed. The HNO_2 was removed by passage of the gas mixture through the alkali scrubber prior to entering the photolysis cell. The NO and NO_2 concentrations were then close to those present in the original mixture and the ΔC_{NO} values, determined at the appropriate flow rate were used to correct the observed changes in NO and "NO + NO_2" for the HNO_2–NO–NO_2 mixture,* i.e.

$$R_{NO} = \frac{F}{V} [\Delta C_{NO} - (\Delta C_{NO})_{NO_2}]$$

$$R_{NO_2} = \frac{F}{V} \Delta C_{NO+NO_2} - R_{NO}$$

For mixtures containing predominantly HNO_2, the correction $(\Delta C_{NO})_{NO_2}$ was between 5 and 37% of the total ΔC_{NO}. Thus the photolysis of NO_2 contributed a sizeable fraction of the total NO production and hence reduced the accuracy with which R_{NO} and R_{NO_2} could be determined. In a typical experiment ΔC_{NO} and ΔC_{NO+NO_2} were approximately 15 and 20% of the initial NO and NO+NO_2 concentrations respectively. The reproducibility of a measured concentration was to within 1% and therefore the ΔC values had an estimated error of ± 3%. After correction for $(\Delta C_{NO})_{NO_2}$ (which typically had an error of ± 10%), the estimated errors in single determinations of R_{NO} and R_{NO_2} were ± 6 and ± 7.5% respectively. The errors were proportionally larger at higher relative NO and NO_2 concentrations but the uncertainty could be reduced by repeated measurements on a given mixture.

In order to check that the concentration changes produced by photolysis were representative of the initial rates of product formation, a series of tests were carried out in which the ΔC values were determined at different

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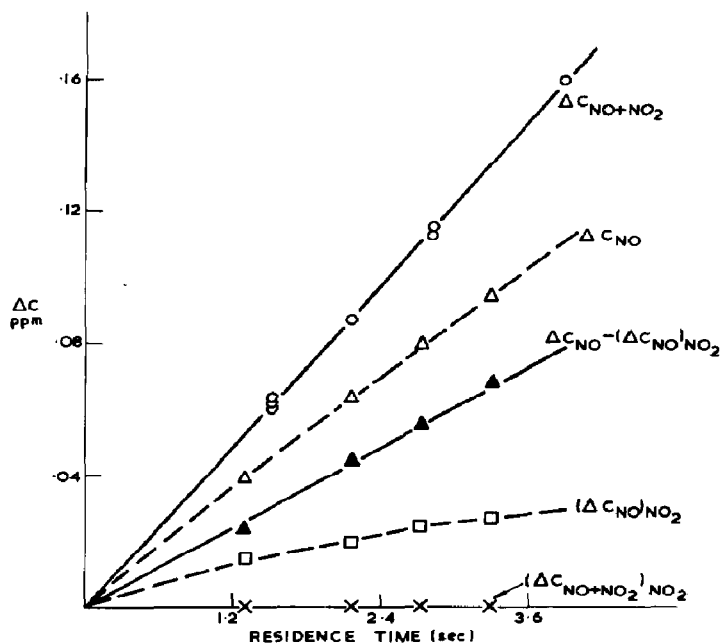*There was, as expected, no measurable change in the total NO + NO_2 when mixtures of NO and NO_2 were photolyzed.

Fig. 2. Effect of reactor residence time on the observed concentration changes in the photolysis of HNO_2–NO–NO_2 and NO–NO_2 mixtures. Initial concentrations in the two mixtures were HNO_2 = 3.24 ppm, NO = 0.56 ppm, NO_2 = 0.44 ppm, and NO = 0.56 ppm, NO_2 = 0.39 ppm respectively. ○,△ = measurements made on mixture containing HNO_2; ×,□ = measurements made on mixture containing only NO + NO_2. Filled triangles show formation of NO from HNO_2 photolysis.

flow rates through the photolysis cell. Figure 2 shows ΔC_{NO}, ΔC_{NO+NO_2}, $(\Delta C_{NO})_{NO_2}$ and $[\Delta C_{NO}-(\Delta C_{NO})_{NO_2}]$ plotted against reactor residence time, τ, for the photolysis of a mixture containing initially 3.24 ppm HNO_2, 0.56 ppm NO and 0.44 ppm NO_2. It will be seen that although the production of NO from NO_2 was non-linear the values of ΔC_{NO+NO_2} and $\Delta C_{NO}-(\Delta C_{NO})_{NO_2}$ increased linearly up to $\tau \simeq 3$ s. For most rate determinations standard flow conditions giving τ = 2.2 s were employed.

The incident light intensity in the cell was estimated from measurement of the rate of photolysis of NO_2 (18 ppm) in 1 atm. N_2. The specific absorption rate (k'_a) for NO_2, derived from the rate of NO_2 photolysis, was 2.8 × $10^{-2}s^{-1}$ which corresponds to a photon flux of 5.4 × 10^{16} quanta/s. However, subsequent checks showed that the lamp output varied considerably (up to 30%) from day to day and, since the light intensity was not monitored during the experiments, a correction for these variations could not be made. Short term fluctuations in intensity were much less (< 3% per hour).

Oxygen (breathing grade; >99.5% O_2,~0.5% Ar; 20 ppm C (mainly CO_2 and CH_4), CO = nil) and nitrogen (oxygen free grade, CO = nil, CO_2 < 5 ppm, hydrocarbon < 5 ppm) were taken directly from cylinders. Nitric oxide was obtained from a cylinder containing a mixture of NO (130 ppm) in nitrogen. The sodium nitrite, sodium hydroxide and water were Analar grade.

TABLE 1

Rates of formation of NO and NO_2 in the photolysis of gaseous HNO_2

Initial concentrations (ppm)			Formation rates (ppm $s^{-1} \times 10^2$)	
HNO_2	NO	NO_2	R_{NO}	R_{NO_2}
18.33	1.96	2.31	10.22	12.20
16.05	1.96	3.39	9.75	8.10
9.13	0.873	0.542	5.81	6.12
9.00	1.54	1.16	6.23	4.43
8.86	0.608	0.900	6.58	4.73*
8.46	1.53	1.26	5.41	3.77
8.18	0.390	1.33	5.98	4.93*
3.24	0.595	0.461	1.98	2.17
2.76	0.101	0.582	2.05	1.42*
2.64	0.557	0.463	1.32	1.60
2.00	0.214	0.156	1.14	1.46
1.29	0.183	0.113	0.653	0.775
1.06	0.090	0.102	0.608	0.686
0.98	0.102	0.095	0.593	0.636
0.87	0.102	0.100	0.435	0.556
1.31	0.124	0.116	0.698	0.833
1.29	0.183	0.113	0.616	0.775†
1.25	0.272	0.111	0.476	0.715†
1.19	0.440	0.110	0.360	0.650†
0.835	0.078	0.060	0.428	0.571
0.807	0.180	0.058	0.295	0.551†
0.793	0.330	0.055	0.215	0.410†
0.775	0.971	0.054	0.041	0.321†

*Runs with [NO]/[NO_2] reduced by the addition of ozone to the original mixture.
†Runs with additional NO.

Results and Discussion

Table 1 shows a summary of the rates of formation of NO and NO_2 in the photolysis of mixtures containing initially between 0.8 and 18.5 ppm HNO_2. The concentrations of HNO_2, NO and NO_2 are mean values of the measured concentrations at the inlet and outlet of the photolysis cell. The maximum conversion of HNO_2 was approximately 3% and therefore the concentrations are close to those present initially. The R_{NO} and R_{NO_2} values are averages of at least three determinations for each mixture, corrected for the NO formation by photolysis of NO_2.

Most experiments were carried out with an initial HNO_2 concentration of approximately 80 - 85% of the "total NO_x", the remainder being NO and NO_2. In a few of these runs (marked *) the NO/NO_2 ratio was reduced by the addition of a little ozone to the reservoir. The last eight rows in Table 1 show the results for experiments in which increasing amounts of NO were ad-

ded to mixtures containing approximately constant concentrations of HNO_2 and NO_2.

It will be seen from Table 1 that both NO and NO_2 are formed at comparable rates in the photolysis of HNO_2 and the experiments with added NO show clearly that the photolysis is inhibited by NO. These observations are qualitatively consistent with the simple photolysis mechanism, comprising the following reactions:

$$HNO_2 \qquad \rightarrow OH + NO \qquad\qquad\qquad (A)$$

$$OH + NO + M \quad \rightarrow HNO_2 + M \qquad\qquad\qquad (1)$$

$$OH + NO_2 + M \quad \rightarrow HNO_3 + M \qquad\qquad\qquad (2)$$

$$OH + HNO_2 \qquad \rightarrow H_2O + NO_2 \qquad\qquad\qquad (3)$$

However, this mechanism requires that $R_{NO} > R_{NO_2}$ for all conditions except $[NO_2] = 0$ when $R_{NO} = R_{NO_2}$. This is inconsistent with the data in Table 1 where it will be seen that there was a tendency for R_{NO_2} to be greater than R_{NO}, particularly in experiments with added NO when the difference $R_{NO_2}-R_{NO}$ was far too large to be attributed to experimental error.

There are several possible explanations of the "excess" NO_2 formation. For example, if a fraction of the OH radicals produced in reaction (A) react with a fourth component to yield H or HO_2, NO_2 could be formed in the reaction:

$$HO_2 + NO \qquad \rightarrow NO_2 + OH \qquad\qquad\qquad (4)$$

This seems unlikely, however, since the rates of reactions (1) - (3) at pressures near 1 atm. are very rapid ($k \lesssim 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}) and impurity gases which can react with OH to give HO_2 (e.g. H_2, CO, CH_4) were not present in the diluent N_2 and O_2 at sufficient concentration to compete for OH under the experimental conditions. Alternatively, NO_2 may be produced in a reaction of HNO_2 with active species produced in the photolysis of NO_2 [i.e $O(^3P)$, O_3] e.g.

$$O + HNO_2 = OH + NO_2 \qquad\qquad\qquad (5)$$

At the NO_2 concentrations employed (up to 3 ppm) the maximum steady-state concentration of $O(^3P)$ (resulting from the photolysis of NO_2) was ~ 5 × 10^7 molecules/cm^3. For reaction (5) to account for 10% of the HNO_2 removal, the quantity $k_5[O]$ is required to be 8 × 10^{-4} s^{-1} i.e. $k_5 \gtrsim 10^{-11}$ cm^3 $molecule^{-1}s^{-1}$. Abstraction reaction of $O(^3P)$ are normally very much slower than this and therefore a significant contribution by reaction (5) seems unlikely. Experimental tests showed that ppm concentrations of O_3 and HNO_2 do not react at a measurable rate over a period of hours.

In our preliminary report [3] it was suggested that the "excess" NO_2 may result from the occurrence of the alternative photodissociation process:

$$HNO_2 = H + NO_2 \qquad\qquad \lambda < 366\ nm \qquad\qquad (B)$$

followed by:

$$H + O_2 + M = HO_2 + M \tag{6}$$

and reaction (4). For each dissociation by process (B), two molecules of NO_2 are formed and one molecule of NO removed. The present data do not allow a rigorous test for the occurrence of process (B) but it is postulated in the absence of any reasonable alternative explanation of the unexpectedly high rates of NO_2 formation.

Steady state analysis of the mechanism, comprising the two primary dissociation processes (A) and (B) and reactions (1) - (4) and (6), yields the following expressions for the rates of formation of NO and NO_2:

$$\frac{R_{NO}}{[HNO_2]} \left\{ (\Phi_A - \Phi_B)k_a - (\Phi_A + \Phi_B)k_a \left(\frac{k_1[NO]}{k_1[NO] + k_2[NO_2] + k_3[HNO_2]} \right) \right\} \tag{i}$$

$$\frac{R_{NO_2}}{[HNO_2]} \left\{ 2\Phi_B k_a + (\Phi_A + \Phi_B)k_a \left(\frac{k_3[HNO_2] - k_2[NO_2]}{k_1[NO] + k_2[NO_2] + k_3[HNO_2]} \right) \right\} \tag{ii}$$

where k_1 and k_2 are the effective bimolecular rate constants for reactions (1) and (2) with $M = N_2 + O_2$ at 1 atm. and Φ_A and Φ_B are the quantum efficiencies for processes (A) and (B). k_a is the absorption rate per unit HNO_2 concentration. These complex functions cannot be used for direct graphical test of the data but they may be simplified for certain limiting conditions, if the rate constants k_1, k_2 and k_3 are of similar magnitude (see later). If the quantity $k_x[NO_x]$ is substituted for $(k_1[NO] + k_2[NO_2] + k_3[HNO_2])$ eqn. (i) becomes:

$$\frac{R_{NO}}{[HNO_2]} = (\Phi_A - \Phi_B)k_a - (\Phi_A + \Phi_B)k_a \frac{k_1[NO]}{k_x[NO_x]} \tag{iii}$$

For the limiting condition $[NO] \to 0$, and with a constant ratio $[NO_2/[HNO_2]]$, the slope of a plot of $R_{NO}/[HNO_2]$ against $[NO]/[NO_x]$ is equal to the quantity:

$$(\Phi_A + \Phi_B)k_a \left(\frac{k_1}{k_x(NO \to 0)} \right)$$

where $k_x(NO \to 0)$ is the "mean" rate constant for the removal of OH by reactions (2) and (3). The intercept at $[NO] = 0$ gives the quantity $(\Phi_A - \Phi_B)k_a$.

A plot of the experimental values according to eqn. (iii) for an approximately constant ratio $[NO_2]/[HNO_2] = 0.08$ ($\pm$ 0.01) is shown in Fig. 3. The results for the two sets of experiments in which increasing amounts of NO were added to mixtures containing 0.8 ppm and 1.2 ppm HNO_2 are seen to lie on the same curve. The curvature is ascribed to a change in the effective value of k_x as the relative proportion of NO in the mixture increases. The
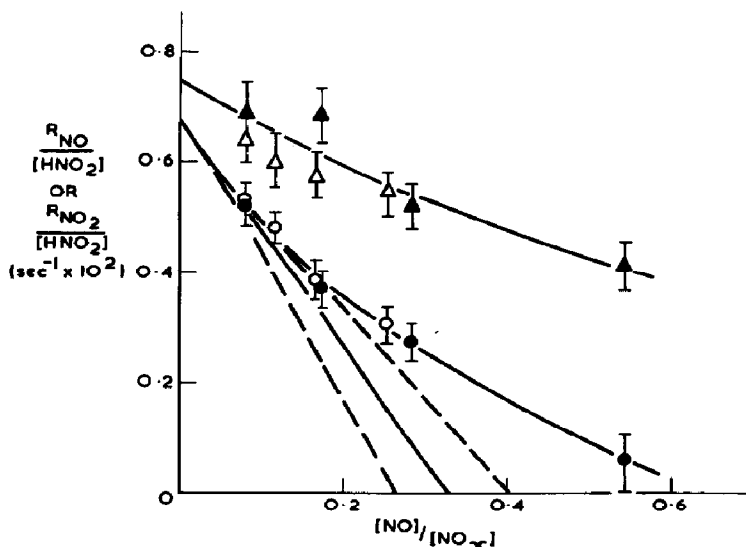
Fig. 3. Plot of $R_{NO}/[HNO_2]$ ($\bigcirc$, $\bullet$) and $R_{NO_2}/[HNO_2]$ ($\triangle$, $\blacktriangle$) against $[NO]/[NO_x]$ (= $NO + NO_2 + HNO_2$) in the photolysis of nitrous acid. Solid symbols = 0.8 ppm HNO_2; open symbols = 1.25 ppm HNO_2.

values of the limiting slope (S) and intercept (I) at $[NO] = 0$, estimated graphically from this plot are $S = 2.08 \pm 0.42 \times 10^{-2} \ s^{-1}$ and $I = 0.68 \pm 0.02 \times 10^{-2} \ s^{-1}$ respectively.

If the quantity $r = [NO_2]/[NO_x]$ then $[HNO_2]/[NO_x] = 1-r$ for $[NO] = 0$ and the following equations can be derived involving the limiting slope and intercept of the plot of eqn. (iii):

$$(\Phi_A + \Phi_B)k_a = S\left(\frac{k_2}{k_1}\right) r + \left(\frac{k_3}{k_1}\right)(1-r) \qquad \text{(iv)}$$

$$(\Phi_A - \Phi_B)k_a = I \qquad \text{(v)}$$

Equations (v)–(iv) gives:

$$-2\Phi_B k_a = I - S\left(\frac{k_2}{k_1}\right) r + \left(\frac{k_3}{k_1}\right)(1-r) \qquad \text{(vi)}$$

An expression for $2\Phi_B k_a$ may also be derived from eqn. (ii). When $[NO] = 0$, eqn. (ii) becomes:

$$I' = \qquad \text{(vii)}$$

$$\frac{R_{NO_2}}{[HNO_2]} (NO \to 0) = 2\Phi_B k_a + (\Phi_A + \Phi_B)k_a \cdot \frac{k_1}{k_x}\left(\frac{k_3}{k_1}\frac{[HNO_2]}{[NO_x]} - \frac{k_2[NO_2]}{k_1[NO_x]}\right)$$

Since $(\Phi_A + \Phi_B)k_a \times k_1/k_x = S$, the following equation is obtained:

$$2\Phi_B k_a = I' - S\left(\frac{k_3}{k_1} (1-r) - \frac{k_2}{k_1} r\right) \qquad \text{(viii)}$$

Figure 3 also shows the values of $R_{NO_2}/[HNO_2]$ plotted against $[NO]/[NO_x]$ for the experiments with added NO. A simple functional dependence of these variables is not expected but the plot may be used to derive a value of $R_{NO_2}/[HNO_2]$ at $[NO] = 0$ (*i.e. I'*). The data show some scatter which reflects both the less accurate determination of R_{NO_2} (compared to R_{NO}) and also the variations in $[NO_2]/[NO_x]$ which can have a marked effect on $R_{NO_2}/[HNO_2]$. The estimated value of I' is $0.75 \pm 0.05 \times 10^{-2}$ s^{-1}.

From the values of I, S, I' and r eqns. (vi) and (viii) can be solved to obtain the ratio k_3/k_1 *i.e.*

$$\frac{k_3}{k_1} = \frac{I' + I}{2S(1-r)} = 0.37$$

The uncertainty in this ratio is approximately $\pm$ 20% arising mainly from the uncertainty in S.

In order to calculate the dissociation rates $\Phi_A k_a$ and $\Phi_B k_a$ a knowledge of the ratio k_2/k_1 is necessary. From our preliminary study of the photolysis of HNO_2 it was estimated that $k_2/k_1 \simeq 1.0 \pm 0.2$ [3]. No other experimental determinations of this ratio at 1 atm. pressure and 300 K seem to have been reported, although estimates have been made at higher temperatures. In studies of the reaction of NO_2 with H_2 Rosser and Wise [5] concluded that reactions (1) and (2) had "essentially equal" rate constants at 600 - 700 K with M = H_2. From a study of the thermal reaction between H_2O_2 and NO, Asquith [6] found $k_2/k_1 = 1.0 \pm 0.5$ at 550 K and 100 Torr pressure. Maximum and minimum limits for the ratio at 1 atm. and 300 K can be estimated from recent measurements of the absolute rate constants of reactions (1) and (2) at lower pressures. On the basis of low pressure data [up to 30 Torr for reaction (1) and 300 Torr for reaction (2)], Morley and Smith [7] estimate high pressure limiting values of $k_1 = 1.7 \times 10^{-10}$ and $k_2 = 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (*i.e.* for the bimolecular reactions OH + NO_x = HNO_x). The value of $k_1 = 1.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, calculated from the third order rate constant determined for reaction (1) with M = 30 Torr H_2 [7] gives a lower limit for this rate constant at 1 atm. Combining these data with those of Simoniatis and Heicklen [8] for the indirect determination of $k_2 = 5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for M = 1 atm. N_2 at 300 K, it can be concluded that: $0.1 < k_2/k_1 < 5$. Table 2 shows the values of $\Phi_A k_a$ and $\Phi_B k_a$ calculated from eqns. (v) and (vi) using the values of $k_2/k_1 = 1$, 0.1 and 5. It will be seen that the choice of k_2/k_1 within these limits does not influence $\Phi_A k_a$ greatly but can make an appreciable difference to the derived value of $\Phi_B k_a$.

With a knowledge of the ratios k_3/k_1 and k_2/k_1, it is possible to calculate values of $\Phi_A k_a$ and $\Phi_B k_a$ from all of the experimental data in Table 1. If $k_3/k_1 = 0.37$ and $k_2/k_1 = 1$, the following equations may be derived from eqns. (i) and (ii):

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

TABLE 2

Primary dissociation rates in the photolysis of HNO_2

k_2/k_1 assumed value	Dissociation rates $(s^{-1} \times 10^{-2})$*	
	$\Phi_A k_a$	$\Phi_B k_a$
0.1	0.728	0.023
1.0	0.775	0.091
5.0	0.991	0.308

*Calculated for $I = 0.68 \times 10^{-2}\,s^{-1}$, $I' = 0.750 \times 10^{-2}\,s^{-1}$, $S = 2.08 \times 10^{-2}\,s^{-1}$; see text.

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

where

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

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

Solution of these simultaneous equations gives $\Phi_A k_a$ and $\Phi_B k_a$ from the measured R_{NO} and R_{NO_2} values in a given mixture of HNO_2, NO and NO_2. The dissociation rates are, of course, subject to the uncertainty in k_2/k_1.
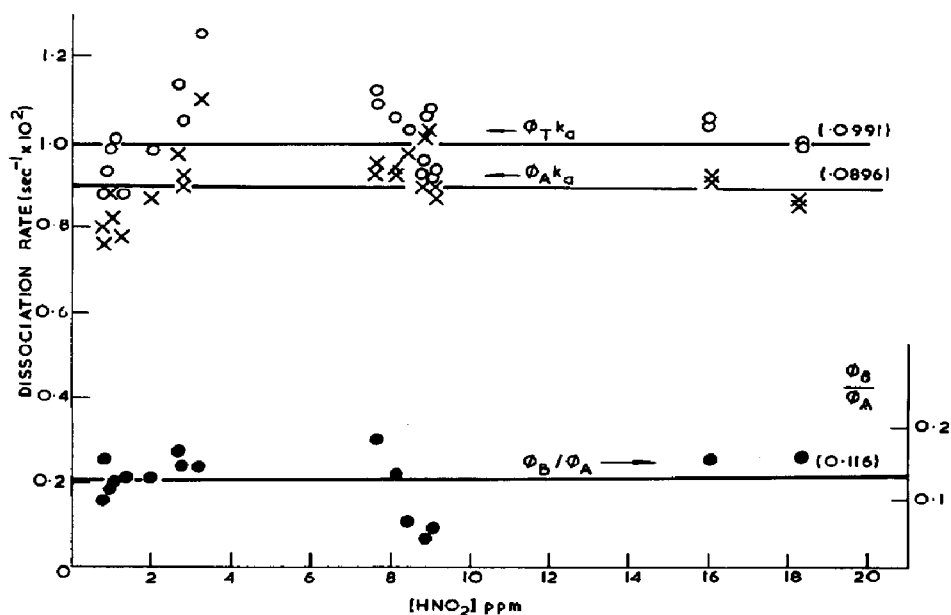

Fig. 4. Calculated values of the total primary dissociation rate, $\Phi_T k_a$, the dissociation rate $\Phi_A k_a$ and the ratio Φ_B/Φ_A plotted against the concentration of nitrous acid. Mean values given in parentheses.

Figure 4 shows a plot of the quantities $\Phi_A k_a$, $\Phi_T k_a$ [$= (\Phi_A + \Phi_B) k_a$, the total photodissociation rate] and Φ_B/Φ_A as a function of the concentration of HNO_2. The values of $\Phi_A k_a$ showed considerable variation but there was no significant trend over the 20 fold change in HNO_2 concentration. The variations are ascribed mainly to fluctuations in the light intensity. The ratio Φ_B/Φ_A also showed no overall trend with HNO_2 concentration but some of the values in the middle of the concentration range were significantly less than the mean value of 0.116. These differences are rather greater than expected from the estimated experimental error which possibly suggests that the mechanism involving process (B) is incorrect. However, we cannot find any reasonable alternative description of the average behaviour of the system at the present time. Some support for the mechanism and numerical values for the rate parameters adopted comes from the consistency in the Φ_A and Φ_B values, calculated by eqns. (ix) and (x), for the results at high [NO] / [NO_x] (see Table 3).

TABLE 3

Calculated values of $\Phi_A k_a$ and $\Phi_B k_a$ from experiments with added NO

| HNO_2	$\dfrac{NO}{NO_x}$	($s^{-1} \times 10^2$)	
		$\Phi_A k_a$*	$\Phi_B k_a$*
0.83	0.080	0.756	0.113
1.31	0.080	0.773	0.096
1.29	0.115	0.803	0.088
1.25	0.167	0.768	0.105
0.81	0.172	0.811	0.130
1.19	0.253	0.841	0.113
0.79	0.280	0.780	0.086
0.77	0.540	0.960	0.111

*Calculated using $k_3/k_1 = 0.37$ and $k_2/k_1 = 1.0$.

It is of interest to compare the dissociation rate, $\Phi_T k_a$, with the estimated absorption rate of HNO_2 in the photolysis cell. The latter may be derived from the measured absorption rate of NO_2 ($k_a' = 2.8 \times 10^{-2}$ s^{-1}) and a consideration of the extinction coefficients ϵ_{NO_2} and ϵ_{HNO_2} in the wavelength region 330 - 380 nm. The average value of ϵ_{NO_2} in this region is close to 145 l mol^{-1} cm^{-1} [9]. The absorption spectrum of HNO_2 shows a diffuse structure in this region [4] and evaluation of ϵ_{HNO_2} from the available data is difficult. Asquith and Tyler [10] have estimated that ϵ_{HNO_2} lies between 50 and 150 l mol^{-1} cm^{-1} at 368 nm (the maximum absorption in this region). The average ϵ_{HNO_2} for the range 340 - 380 nm is estimated to be roughly one-half the maximum and therefore $\epsilon_{HNO_2} \simeq 50 \pm 25$ l mol^{-1} cm^{-1}. Thus for weak absorption by both gases :

$$k_a (HNO_2) = k_a'(NO_2) \times \frac{50(\pm 25)}{145} = 0.97 \pm 0.45 \times 10^{-2} \ s^{-1}$$

The average value of $\Phi_T k_a$ was $0.991 \times 10^{-2}\,s^{-1}$ and therefore $0.7 < \Phi_T < 1.9$. When the uncertainties are taken into account it is probable that the quantum yield for HNO_2 dissociation is close to unity. If $\Phi_T = 1$, it follows that $\Phi_A \simeq 0.9$ and $\Phi_B \simeq 0.1$ (assuming that $k_2/k_1 \simeq 1$). It is concluded, therefore, that the predominant process following absorption by nitrous acid in the near u.v is dissociation to give $OH + NO$. A small fraction ($\sim 10\%$) of the HNO_2 molecules appear to undergo dissociation to give $H + NO_2$ but more evidence is required to confirm this result. A study of the photolysis of nitrous acid using selected wavelengths above and below the energy threshold for H atom production would provide useful information on this matter.

The experimental value of the rate constant ratio k_3/k_1 ($= 0.37 \pm 0.06$) shows that the rate of abstraction of an H atom from HNO_2 is of the same magnitude as the addition of OH to NO and NO_2 (if $k_2 \simeq k_1$) at 1 atm. pressure. If $k_1 \simeq k_2 = 5 \times 10^{-12}\,cm^3\ molecule^{-1}\ s^{-1}$, $k_6 = 1.8 \times 10^{-12}\,cm^3\ molecule^{-1}\ s^{-1}$, which is more than an order of magnitude faster than the analogous reaction [7, 11]:

$$OH + HNO_3 = H_2O + NO_3 \quad [7]; \quad (k_7 = 1.3 \times 10^{-13}\,cm^3\ molecule^{-1}\ s^{-1})$$
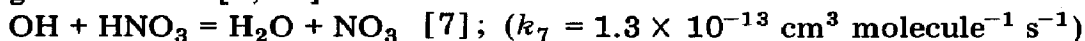
If the reactions have similar pre-exponential factors, reaction (3) must have a considerably lower activation energy than reaction (7). A possible explanation of this arises from the unusual properties of the *cis* rotational isomer of HNO_2, which exists in equilibrium with the more stable *trans* isomer with $[trans\text{-}HNO_2] \simeq 2.5[cis\text{-}HNO_2]$ at 300 K. It has been shown [12] that the H–O bond is unusually long and possesses a low vibrational frequency compared with other simple polyatomic molecules such as H_2O, HCOOH, HNO_3, $trans\text{-}HNO_2$, etc. On this basis the abstraction of an H atom from $cis\text{-}HNO_2$ might be expected to have a lower activation energy than from HNO_3.

Acknowledgement

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