Visible spectrum of dinitrogen trioxide in aqueous solution

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The visible absorption spectrum of N_2O_3 has been measured by stopped-flow mixing of solutions of $NaNO_2$ and HNO_3. It has a maximum at 630 nm, $\varepsilon = 29.3$ dm^3 mol^{-1} cm^{-1}. The spectrum is similar to that reported for solutions of N_2O_3 in anhydrous organic solvents at low temperatures. Comparison with the blue species observed for solutions of $NaNO_2$ in moderately concentrated $HClO_4$ and HNO_3 shows that although the spectra are very similar there must be an additional species present in these very acidic media, possibly $N_2O_3H^+$.

This paper is concerned with the very different values for the formation constant of N_2O_3 from HNO_2 [equilibrium (1)]

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O \qquad (1)$$

obtained by spectrophotometric measurements in moderately concentrated perchloric acid[1,2] and those from UV measurements in very much less acidic aqueous media, a difference already noted in the literature.[3] The classic work of Hammett[4] and of Ridd and co-workers[5] established that dinitrogen trioxide, N_2O_3, is an important electrophilic nitrosating agent in aqueous solutions, and it has since been found[6,7] to be the active species in many organic and inorganic reactions of nitrous acid usually at relatively low acidities, pH > 0. In order to understand its chemistry properly a knowledge of its formation constant, $K_1 = [N_2O_3]/[HNO_2]^2$, is necessary.

Dinitrogen trioxide is a deep blue coloured species whose spectrum was first studied photographically by Berl and Winnaker.[8] More recent work by Mason[9] and by Shaw and Vosper[10] on solutions of N_2O_3 in a range of anhydrous organic solvents at low temperatures has shown the blue colour to be due to a weak peak, $\varepsilon \approx 10$–20 dm^3 mol^{-1} cm^{-1}, in the region 620–700 nm. Spectrophotometric measurements of the blue solutions of HNO_2 at six acidities in the range 4.2–7.6 mol dm^{-3} perchloric acid showed[1] a peak at 625 nm, and by using a value of $\varepsilon = 19$ dm^3 mol^{-1} cm^{-1} (the value for toluene as solvent) a mean value of $K_1 = 0.32$ dm^3 mol^{-1} was estimated. Turney, on the basis of spectrophotometric and partition experiments suggested[2] a figure of *ca.* 0.2 dm^3 mol^{-1}, while Schmid and Krenmayr[11] refined the calculation and proposed a value of 0.15 dm^3 mol^{-1}. In contrast to these values a calculation using the rate constants for the forward and back reactions of equilibrium (1) leads[6] to $K_1 \simeq 7.5 \times 10^{-3}$ dm^3 mol^{-1}, while a UV study by Schwarz *et al.*,[3] when combined with pulse radiolysis data, yielded $K_1 \simeq 3 \times 10^{-3}$ dm^3 mol^{-1}. This last figure seems to be commonly accepted by kineticists.[7] Schwarz suggested that the higher figure of 0.2 dm^3 mol^{-1} might be due to the presence of species such as $N_2O_3H^+$ in moderately concentrated mineral acid. The obvious gap in the evidence is the absence of any data on the visible spectrum of N_2O_3 in dilute aqueous acid, the conditions used by Schwarz. An extinction coefficient obtained for solutions in toluene may be unreliable in predicting concentrations in aqueous media. The present work was planned to remedy this deficiency.

Results and discussion

Solutions of nitrous acid in dilute aqueous mineral acid appear virtually colourless, and in order to get measurable absorbances in the visible region it is necessary to work with high concentrations of nitrite to drive equilibrium (1) to the right. This brings with it the attendant disadvantages of instability and the evolution of gas bubbles of NO which make manual spectrophotometry impracticable. One solution is to use stopped-flow spectrophotometry to mix relatively concentrated solutions of sodium nitrite and nitric acid. Nitric acid was used as the acidifying agent in preference to perchloric acid to minimise decomposition as it is a product of the disproportionation of HNO_2, and also because dissociation constants for solutions of HNO_2 in $NaNO_3$ are available in the literature. In a closed system losses of NO to the atmosphere do not occur, and it was found that a stable absorbance reading could be obtained for several seconds after mixing before bubbles of nitric oxide appeared in the light beam. From the known rate constants[6] for the forward and back reactions of equilibrium of (1) it can be calculated that the half-life for the approach to equilibrium should be just over 1 ms under our conditions, so equilibrium should be maintained during the 1–2 s observation period. A further advantage of the stopped-flow method is that small absorbances can be measured quite accurately. The visible absorption spectrum of the resulting solution was obtained by a series of repeat mixing experiments made at selected wavelengths from 420 to 800 nm. The resulting spectrum is shown in Fig. 1 together with a spectrum for the blue species observed for solutions of $NaNO_2$ in 6.5 mol dm^{-3} nitric acid. The two spectra are very similar.

The results of a set of stopped-flow measurements of the absorbance A at 630 nm with a range of concentrations of nitrous acid at ionic strength I are shown in Table 1. Even at concentrations as high as $[HNO_2] = 0.8$ mol dm^{-3} there is a

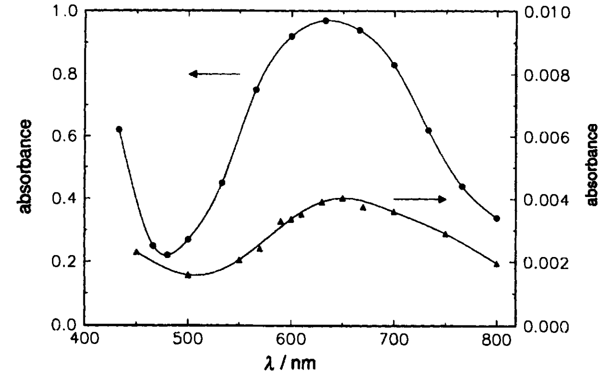

Fig. 1 Spectra of N_2O_3 in dilute acid aqueous solution (▲) and the blue species in 6.5 mol dm^{-3} nitric acid (●)

Table 1 Absorbances for solutions of HNO_2 at 630 nm

$[NaNO_2]$/ mol dm^{-3} [a]	$[HNO_3]$/ mol dm^{-3} [a]	I/mol dm^{-3}	$A/10^{-4}$	σ[b]$/10^{-4}$	ε/dm^3 mol^{-1} cm^{-1} [c]	ε/dm^3 mol^{-1} cm^{-1} [d]
0.4	1.0	0.5	4.3	0.8	—	30.3
0.6	1.0	0.5	10.7	0.9	—	25.4
0.8	1.0	0.5	25.8	0.8	26.8	30.0
1.0	1.0	0.5	39.0	2.2	28.8	31.0
1.2	1.2	0.6	57.1	1.2	29.0	30.5
1.4	1.4	0.7	82.7	0.5	30.7	31.8
1.6	1.6	0.8	110	4.0	31.2	32.0

[a] Concentration in stopped-flow reservoirs. [b] Standard deviation for A. [c] Extinction coefficient for N_2O_3 after correcting for ionisation of HNO_2. [d] Extinction coefficient if 0.0003 is added to absorbance A.

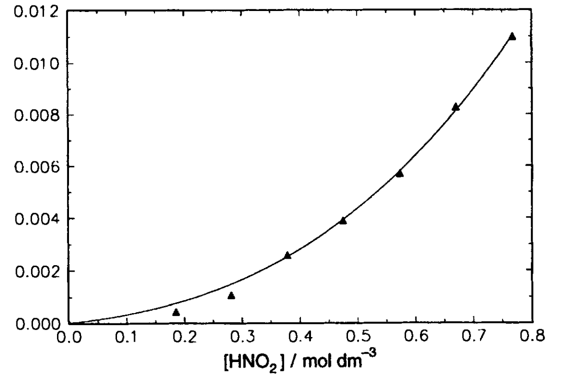

Fig. 2 Variation of absorbance at 630 nm with $[HNO_2]$, path length = 2 mm

Table 2 Absorbance of solutions of $NaNO_2$ in 6.1 mol dm^{-3} $HClO_4$ at 625 nm

[Nitrite]/mol dm^{-3}	A[a]	K_1/dm^3 mol^{-1}
0.0738	0.165	0.280
0.110	0.373	0.297
0.113	0.388	0.293
0.130	0.380	0.213
0.180	0.923	0.292
0.192	0.971	0.270
0.201	0.990	0.250
0.235	1.41	0.271
0.263	1.68	0.261

[a] Path length = 4 cm.

small amount of ionisation of nitrous acid; a correction was calculated from the pK_a data of Tummavuori and Lumme.[12] Fig. 2 shows the steep increase in A with $[HNO_2]$. A plot of log A *versus* log $[HNO_2]$ (corrected for ionisation) gives a slope of 2.2 for the concentration range $[HNO_2]$ = 0.4–0.8 mol dm^{-3}. The points at the two lowest nitrous acid concentrations lie significantly below the line and have been left out of the calculation. Their absorbance values are very small. To obtain the extinction coefficient at 630 nm the equilibrium constant of $K_1 = 3 \times 10^{-3}$ dm^3 mol^{-1} was used to calculate $[N_2O_3]$ and the ε values are listed in the sixth column of Table 1 giving a mean value of 29.3 dm^3 mol^{-1} cm^{-1}. It can be seen that there is a small trend in these values. The absorbance values depend upon a measured small change in the voltage derived from the photomultiplier output compared with the value used to set 100% transmission. The solution of sodium nitrite was used to set the 100% reading but this may not be a perfect match for the reaction solution after mixing which is $HNO_2 + NaNO_3$. If the absorbance values were low by 0.0003 units then the extinction coefficients would be essentially constant over the whole range of nitrous acid concentrations, as shown in the last column of Table 1. Using the alternative value of 7.5×10^{-3} dm^3 mol^{-1} for K_1 would change the absolute magnitude of ε to 11.7 dm^3 mol^{-1} cm^{-1}, but would not alter the apparent trend in K_1. As the effects are so small we do not ascribe any chemical significance to the variation in ε in column six. Both of these values, 29.3 and 11.7 dm^3 mol^{-1} cm^{-1}, are close to the range of extinction coefficients N_2O_3 in anhydrous organic solvents reported by Mason[9] and by Shaw and Vosper.[10]

Turning now to the interpretation of the spectra in moderately concentrated mineral acid the similarity of the spectra in aqueous media and in 6.5 mol dm^{-3} HNO_3 suggests a similar species. Using ε = 29.3 dm^3 mol^{-1} cm^{-1} for aqueous media in preference to the value of 19 for toluene solutions, values of K_1 have been recalculated for one of the sets of data originally studied by Bunton. The results are in Table 2 and it is apparent that K_1 is approximately constant. To compare it with the value of Schwarz it is necessary to obtain K_1^* corrected for the activity of water, a_w, and the activity coefficients of HNO_2 and N_2O_3, f_1 and f_2, respectively [eqn. (2)]. Values of a_w are known

$$K_1^* = K_1 a_w f_2/f_1^2 \qquad (2)$$

and Schmid and Krenmayr have proposed values for f_1 for nitrous acid in perchloric acid,[11] but values for f_2 are not known. If we set $f_2 = 1$, then for 6.1 mol dm^{-3} $HClO_4$, K_1^* = 0.035 dm^3 mol^{-1}. This is an order of magnitude greater than the value of Schwarz. The discrepancy will be greater than this if $f_2 > 1$. Use of the higher value for K_1 of 7.5×10^{-3} dm^3 mol^{-1} does not help; it leads to a lower extinction coefficient for N_2O_3 which in turn increases the value of $[N_2O_3]/[HNO_2]^2$ calculated from the data in Table 2. The agreement is no better. We conclude that even with an extinction coefficient for N_2O_3 measured for aqueous solutions the results obtained in moderately concentrated $HClO_4$ are not consistent with those deducted for low acidity aqueous media. Schwarz has suggested that in the acidic media $N_2O_3H^+$ may be present, and this is certainly consistent with the earlier observation [1] that plots of log A_{625} *versus* log [nitrite] have slopes as low as 1.64 in 6.75 mol dm^{-3} perchloric acid suggesting a sizeable fractional conversion of HNO_2 to a species formed from two (or more) molecules of nitrous acid. The surprising feature is that such a species has a very similar spectrum in the visible region as that of N_2O_3.

An alternative approach (also used by Turney[2]) is to combine the mass balance [eqn. (3)] with $K_1 = [N_2O_3]/[HNO_2]^2$ to yield

$$[\text{Nitrite}] = [HNO_2] + 2[N_2O_3] \qquad (3)$$

eqn. (4). Using the Beer–Lambert law, this can be converted to

$$[\text{Nitrite}] = [N_2O_3]^{\frac{1}{2}}/K_1^{\frac{1}{2}} + 2[N_2O_3] \qquad (4)$$

an expression with the absorbance at 625 nm, A, as a variable, eqn. (5). A plot of [nitrite]/A *versus* $A^{-\frac{1}{2}}$ for the 6.1 mol dm^{-3}

$$[\text{Nitrite}]/A = (\varepsilon l K_1)^{-\frac{1}{2}} A^{-\frac{1}{2}} + 2/\varepsilon l \qquad (5)$$

$HClO_4$ data yields a good straight line with an intercept for which an effective coefficient of 23.8 dm^3 mol^{-1} cm^{-1} can be obtained, and a K_1 value of 0.35 dm^3 mol^{-1}. The ε value is close to the figure obtained for dilute acid aqueous media, but the K_1 value again is much higher than the Schwarz figure. The results still clearly require the formation of a substantial fraction of the nitrite to be converted to a dimeric species. If Schwarz's suggestion of $N_2O_3H^+$ is accepted as a very plausible interpretation, then the present work requires that the visible spectrum of $N_2O_3H^+$ and N_2O_3 are very similar.

Mason has proposed that the visible spectrum is due to a n_N–π^* transition similar to that observed for monomeric nitrosoalkanes.[9] This suggests that the site of protonation in $N_2O_3H^+$ is not on the nitroso fragment of the molecule, but must be on the nitro fragment. In view of the fact that K_1^* for 6.1 mol dm^{-3} perchloric acid is approximately 10 times greater than the dilute acid value of 3×10^{-3} dm^3 mol^{-1} it is likely that the ratio $[N_2O_3H^+]/[N_2O_3]$ is quite large, around a factor of 10. If we use the Hammett Acidity Function as a measure of acidity, this corresponds to a pK_a value for $N_2O_3H^+$ of around -1.8.

We have looked for other evidence from the literature that is consistent with the existence of $N_2O_3H^+$. Bunton *et al.*[13] measured the rate of the nitrous acid catalysed exchange of ^{18}O between nitric acid and water at 0 °C in systems in chemical equilibrium. At low nitric acid concentration, $[HNO_3] = 4.2$ mol dm^{-3}, the rate of tracer exchange is first-order with respect to $[HNO_2]$, and is very close to the known rate of formation and hydrolysis of N_2O_4 [equilibrium (6)]. Again in 12.5 mol dm^{-3}

$$H^+ + HNO_2 + NO_3^- \rightleftharpoons N_2O_4 + H_2O \qquad (6)$$

nitric acid the rate of exchange has an order of 1.1 with respect to [nitrite]. Under these conditions the bulk component of nitrite is N_2O_4, and so presumably one is again observing equilibrium (6). At intermediate concentrations of nitric acid the order of reaction increases, and is 1.8, 2.0 and 2.0 at $[HNO_3] = 9.45$, 10.25 and 10.9 mol dm^{-3}, respectively. When the concentration of nitrite is greater than *ca.* 0.05 mol dm^{-3} the solutions in nitric acid show the same characteristic blue colour as observed in perchloric acid with an essentially identical spectrum. Plots of log *A* *versus* log [nitrite] have slopes in the range 1.81–1.88 and the maximum absorbance is observed at $[HNO_3] \approx 10.5$ mol dm^{-3} as shown in Fig. 3. This is just where the nitrous acid catalysed exchange of tracer between nitric acid and water shows second-order kinetics. Using the extinction coefficient of 23.8 dm^3 mol^{-1} cm^{-1} and allowing for the fractional conversion of nitrous acid to dinitrogen tetraoxide we calculate $K_1 \simeq 0.43$ dm^3 mol^{-1}, very comparable to the classical formation constant for 'N_2O_3' in perchloric acid. It seems very likely that the same blue species is involved, probably $N_2O_3H^+$.

Exchange of ^{18}O between nitrous acid and water is very rapid by the formation and hydrolysis of NO^+ so that N_2O_3 and $N_2O_3H^+$ will be in isotopic equilibrium with the solvent. There is already a pathway for nitrite–nitrate exchange *via* the formation and hydrolysis of N_2O_4 so the results require an additional pathway that is second-order with respect to [nitrite]. The fact that second-order kinetics occur at the same nitric acid concentration as the maximum in the blue colour due to $N_2O_3H^+$ leads us to suggest equilibria (7)–(9) as possible pathways. Rate

$$N_2O_3 \rightleftharpoons NO + NO_2 \qquad (7)$$

$$N_2O_4 \rightleftharpoons 2NO_2 \qquad (8)$$

$$N_2O_3H^+ \rightleftharpoons NO + NO_2 + H^+ \qquad (9)$$

constants at 20 °C for the forward and reverse reactions in equilibria (7) and (8) are known,[6] but no data are available for equilibrium (9). The obvious alternative mode of fission of $N_2O_3H^+$ to $HNO_2 + NO^+$ would not lead to nitrite–nitrate exchange. Pathways involving a bimolecular reaction with oxygen transfer from N_2O_4 to N_2O_3 would lead to nitrite–nitrate exchange, but are rejected as they would require kinetics that are third-order with respect to [nitrite].

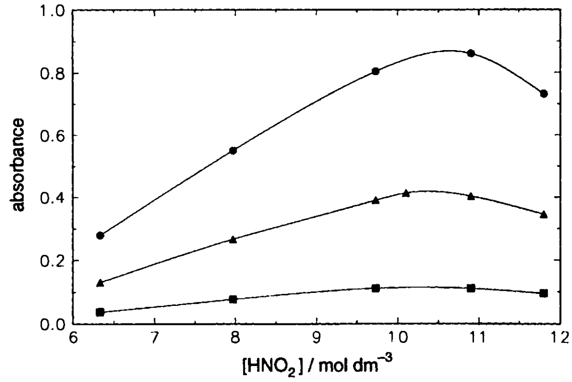

Fig. 3 Spectra of solutions of $NaNO_2$ in HNO_3. Absorbance at 630 nm interpolated for [nitrite] = 0.1 (■), 0.2 (▲) and 0.3 (●) mol dm^{-3}.

Conclusions

Dinitrogen trioxide in dilute acid aqueous solution has a peak at 630 nm with an extinction coefficient of *ca.* 29 dm^3 mol^{-1} cm^{-1}. The blue species observed for solutions of nitrous acid in moderately concentrated perchloric and nitric acids has a very similar visible spectrum, but is probably $N_2O_3H^+$ with the proton located on the nitro group in N_2O_3.

Experimental

Materials

All chemicals were AnalaR grade, and were used without further purification.

Stopped-flow measurements

These were made on a Hi-Tech instrument with a 2 mm path length cell. Equal volumes of $NaNO_2$ and HNO_3 were mixed and the absorbance measured over a 5 s scan. Normally five repeat experiments provided a mean value and a standard deviation for the absorbance.

Absorption spectra in nitric acid solution

In these experiments nitric acid was added to solid sodium nitrite and the resulting solution added to a 4 cm cell and stabilised by floating a layer of hexane on the surface, which reduces loss of nitric oxide to the atmosphere. Even so the absorbance slowly decayed and measurements were taken with time. The total concentration of nitrite ($[\text{nitrite}] = [HNO_2] + 2[N_2O_3] + 2[N_2O_3H^+] + \frac{1}{2}[NO_2] + [N_2O_4]$) was measured by removing an aliquot and quenching in excess NaOH solution. This was then made up to a known volume, mixed and analysed colorimetrically. A 5 cm^3 portion was added to 5 cm^3 of solution A (0.1 g sulfanilic acid, 10 g sodium bromide and 13 cm^3 60% perchloric acid made up to 500 cm^3). Diazotisation was complete within 5 min and an azo dye was formed quantitatively by adding 10 cm^3 of solution B (1 g of 'R' salt, 20 g borax made up to 1 dm^3). The absorbance was measured at 490 nm. The absorbance–time data were plotted and extrapolated to the time at which the aliquot was quenched.

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