496. *The Absorption Spectra of Nitrous Acid in Aqueous Perchloric Acid.*

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Ultraviolet-absorption measurements show that with increasing acidity, molecular nitrous acid, HNO_2, is protonated and dehydrated. The visible-absorption spectra indicate that appreciable amounts of dinitrogen trioxide, N_2O_3, may be present.

PHYSICAL measurements on solutions of " nitrous acid " in aqueous mineral acids show that, in dilute acidic media, " nitrous acid " (by which is meant all the species which are analysed as nitrite on dilution with water) exists as molecular nitrous acid, HNO_2.[1-3] With increasing acidity this is protonated and dehydrated, and in concentrated sulphuric acid the nitrosonium ion, NO^+, is the only entity of importance.[4] There is kinetic evidence for the existence of this ion, and of the nitrous acidium ion, $H_2NO_2^+$, and of dinitrogen trioxide, as intermediates in reactions of " nitrous acid," [5] and the present work was intended to give physical information on the existence of dinitrogen trioxide in acid solutions. Some of our results on the ultraviolet absorption spectra are shown in Table 1 (cf. refs. 1 and 2). In perchloric acid solutions less than *ca.* 7M the spectrum is that of molecular nitrous acid, and very similar to those of alkyl nitrites in organic solvents [6] and of a gaseous mixture of nitrogen dioxide, nitric oxide, and water.[7] For " nitrous acid " of <0·05M-concentration the Beer–Lambert law was obeyed in this region. Addition of sodium nitrate, in amount comparable with that of the nitric acid which could be formed by decomposition of " nitrous acid " during preparation of the solution, had little or no effect on the absorption. Species formed by interaction of " nitrous " and nitric acid therefore do not affect these spectra, which are those of molecular nitrous acid.

In accord with the observations of other workers,[1-3] we find that increase of acidity changes the spectra completely: the fine structure of the absorption band of nitrous acid is replaced by a band rising towards shorter wavelengths.

The molecular extinction coefficients in this wavelength range (3300—3600 Å) in 8—10M-perchloric acid (Table 1) cannot easily be accounted for in terms of molecular nitrous acid and the nitrosonium ion (the spectrum in sulphuric acid being assumed to be that of NO^+) unless there is a very large wavelength shift in the absorption of the nitrosonium ion when the concentrated mineral acid is diluted with water. Bayliss and Watts [2]

[1] Singer and Vamplew, *J.*, 1956, 3971.
[2] Bayliss and Watts, *Chem. and Ind.*, 1955, 1353; *Austral. J. Chem.*, 1956, **9**, 319.
[3] Deschamps, *Compt. rend.*, 1957, **245**, 1432.
[4] Angus and Leckie, *Proc. Roy. Soc.*, 1935, *A*, **149**, 327; 1935, *A*, **150**, 615; Gillespie, Graham, Hughes, Ingold, and Peeling, *J.*, 1950, 2504; Millen, *J.*, 1950, 2600.
[5] Abel, Schmidt, and Schrafonik, *Z. phys. Chem.*, 1931, **148**, 510; Hughes, Ingold, and Ridd, *J.*, 1958, 58, 65, 77, 88; Bunton, Llewellyn, and Stedman, *Nature*, 1955, **175**, 83.
[6] Tarte, *J. Chem. Phys.*, 1952, **20**, 1570; Banus, *J.*, 1953, 3755; Haszeldine and Mattinson, *ibid.*, 1955, 4172.
[7] Porter, *J. Chem. Phys.*, 1951, **19**, 1278.

find a large shift when 98% sulphuric acid is diluted with water, and they suggest that an additional species, the nitrous acidium ion, exists in appreciable quantities in aqueous sulphuric, hydrochloric, and phosphoric acid. Singer and Vamplew [1] observed only a

TABLE 1. *Effect of acid concentration upon the ultraviolet absorption spectra of nitrous acid.*

Solute: sodium nitrite unless otherwise stated.
Absorption maxima italicised: minima in parentheses.

$HClO_4$ (M)	ε_{3300}	ε_{3460}	ε_{3500}	ε_{3560}	ε_{3630}	ε_{3690}	ε_{3780}	ε_{3830}
0·8 [a]	—	*39*	(35)	*56*	(39)	*57*	(26)	*34*
5·1	22	*43*	(41)	*59, 60* [b]	(42)	*61, 62* [b]	(31)	*37, 36* [b]
6·75	70	49	(47)	*56*	(40)	*50*	(26)	*28*
8·0 [c]	182	62	—	29	—	18	—	6
10·0	261	88	—	28	—	9	—	—
98% H_2SO_4	6	3	—	—	—	—	—	—

[a] Addition of sodium perchlorate (6M) to this solution shifts the maxima to slightly shorter wavelengths. [b] These values were obtained with nitrosyl perchlorate (0·02M). [c] A solution of sodium nitrite in a mixture of perchloric acid (7·42M) and sulphuric acid (5·35M) gave slightly lower values of ε.

small wavelength shift when 60% perchloric acid was diluted with water and found no evidence for this additional species. Our results do not differentiate between these two possibilities, although they confirm the view that the Beer–Lambert law is obeyed, and

Visible spectra in 6·9M-perchloric acid. Nitrite = (I) 0·064M, (II) 0·124M, (III) 0·141M (d = 4 cm.).
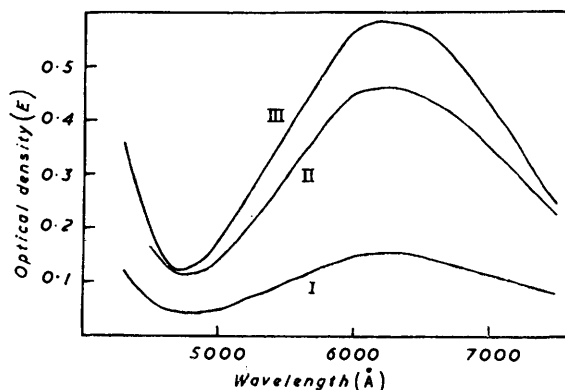
the absorbing species therefore contains one equivalent of nitrite per mole. Bayliss and Watts show that the ratio of supposed nitrous acidium ion to nitrous acid, determined indirectly by spectrophotometry, varies linearly with the activity of sulphuric acid. Their results can be fitted equally well to a near-linear variation with the Hammett acidity function, h_0, which measures the ability of an acidic solution to protonate a neutral base.

Addition of sodium perchlorate slightly increases the absorption in the region 3300—3500 Å (although its effect is partially masked because increase in ionic concentration decreases the fine structure of the absorption). This is because addition of this salt increases the protonating power of the medium,[8] with consequent conversion of molecular nitrous acid into its protonated and dehydrated derivatives. Addition of large (ca. 0·5M) amounts of sodium nitrate increases the absorption over the wavelength range 3000—4000 Å, presumably by formation of dinitrogen tetroxide–nitrogen dioxide.

If the concentration of " nitrous acid " is greater than ca. 5×10^{-2}M the Beer–Lambert law is no longer obeyed; examples are given in Table 2. There is no increased absorption below 3500 Å, and the increase above 3500 Å is not caused by formation of the nitrosonium or nitrous acidium ion. We suppose it to be caused by dinitrogen trioxide. This conclusion is supported by examination of the visible absorption spectra (Figure). These spectra

[8] Long and Paul, *Chem. Rev.*, 1957, **57**, 1.

are characterised by a broad absorption maximum at 6250 Å, which can only be that of dinitrogen trioxide because, although nitrogen dioxide absorbs in the visible region, its absorption overlapping that of dinitrogen trioxide,[9] the ratios of optical densities, for fixed " nitrous acid " concentrations, at various wavelengths are independent of solvent composition. Data illustrating this are shown in the Experimental section. This test

TABLE 2. *Variation of extinction coefficient with concentration of " nitrous acid."*
$[HClO_4] = 5.1M.$

[Nitrite] (M)	ε_{3830}	ε_{3690}	ε_{3560}
0.0208	35.5	62.0	60.2
0.0721	38.1	66.7	66.9
0.151	39.7	69.5	77.2

shows that despite marked changes in the nitrous acid species present, the visible absorption spectrum is that of one species only. Similar behaviour is shown in aqueous sulphuric acid.

Our assumption on the nature of this visible absorption is supported by comparison with the absorption spectra of various *N*-nitroso-compounds.[6] Confirmation comes from a recent demonstration by Dr. Joan Mason [10] that dinitrogen trioxide in toluene has a visible absorption spectrum with $\lambda_{max.}$ 6620 Å (with a half-band width similar to that observed here) and $\varepsilon_{max.}$ 19. If we assume that this value for the molar extinction coefficient in toluene can be used for measurements in perchloric acid we calculate that up to 15% of the " nitrous acid " can exist as dinitrogen trioxide (with $HClO_4$ 6.75M, and nitrite *ca.* 0.15M).

Further confirmation that dinitrogen trioxide exists in appreciable amounts in these perchloric acid solutions comes from the variation of the optical density, E_{6250}, with nitrite concentration; this, for a given perchloric acidity, fits the empirical equation:

$$\log E_{6250} = n \log [\text{nitrite}] + \log C,$$

i.e.,

$$E_{6250} = C[\text{nitrite}]^n$$

Values of n and C have been tabulated for various solvent compositions (Table 3), on the basis of data illustrated in the Experimental section. For a given nitrite concentration, with increasing perchloric acid concentration, E_{6250} first increases (up to 6.7M), then decreases. Values of n show a converse behaviour.

TABLE 3. *Empirical relation between optical density and nitrous acid concentration.*

$[HClO_4]$ (M)	4.2	5.1	6.1	6.75	7.2	7.6
n	1.84	1.72	1.73	1.64	1.70	1.82
C	3.2	7.4	16.6	10.8	4.5	1.1
$10^2 K_c$ (mole^{-1} l.)	5.7	19	49	56	29	36

The increase in E_{6250} corresponds to an increasing dehydration of molecular nitrous acid by the reaction, $2HNO_2 \rightleftharpoons N_2O_3 + H_2O$. When molecular nitrous acid is the bulk component, the concentration of dinitrogen trioxide should follow the relation:

$$[N_2O_3] = K_{N_2O_3}[HNO_2]^2 f^2_{HNO_2}/a_{H_2O} \cdot f_{N_2O_3}$$

The activity coefficient of nitrous acid, f_{HNO_2}, increases with increasing ionic strength,[11] and the activity of water, a_{H_2O}, decreases with increasing acidity.[12] Therefore the concentration of dinitrogen trioxide, and E_{6250}, should increase with increasing perchloric acidity and be proportional to [nitrite]^2, *i.e.*, $n = 2$ when $[HNO_2] \approx [\text{nitrite}]$.

[9] Berl and Winnaker, *Z. anorg. Chem.*, 1933, **212**, 113; Vodar, *Compt. rend.*, 1937, **204**, 1467.
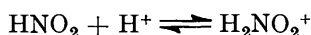[10] J. Mason, personal communication.
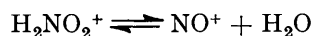[11] Abel and Neusser, *Monatsh.*, 1929, **53/54**, 855.
[12] Robinson and Baker, *Trans. Proc. Roy. Soc.*, N.Z., 1946, **76**, (II), 250.

This is found at low perchloric acid concentrations, but with increasing perchloric acidity the amount of dinitrogen trioxide increases sufficiently for the amount of molecular nitrous acid to be less than the amount of analytical nitrite, and n will then become less than 2. (In the hypothetical case of complete dehydration to dinitrogen trioxide, N_2O_3, n would equal 1.)
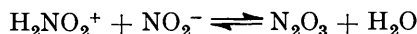
With further increase in perchloric acid concentration both molecular nitrous acid and dinitrogen trioxide are converted into the nitrosonium and possibly nitrous acidium ion by the reactions:
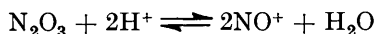
$$HNO_2 + H^+ \rightleftharpoons H_2NO_2^+$$

and

$$H_2NO_2^+ \rightleftharpoons NO^+ + H_2O$$

or

$$H_2NO_2^+ + NO_2^- \rightleftharpoons N_2O_3 + H_2O$$

and

$$N_2O_3 + 2H^+ \rightleftharpoons 2NO^+ + H_2O$$

In the region where these ions are the predominant species ($HClO_4 > 8M$) the absorption at 6250 Å will decrease and n will increase towards 2 with increasing concentration of perchloric acid. Hence dehydration of nitrous acid to dinitrogen trioxide and conversion into the nitrosonium, and possibly the nitrous acidium, ion, occur within the range of perchloric acid concentrations studied, the concentration of these species depending in a predictable manner upon the ionic concentration of the medium. It is possible that some of the apparent discrepancies between ultraviolet absorption measurements in perchloric and sulphuric acid [1,2] may be due to neglect of the possible presence of dinitrogen trioxide in some of the solutions.

It is possible to calculate a classical equilibrium constant, $K_c = [N_2O_3]/[HNO_2]^2$ for the dehydration of nitrous acid. The concentrations of dinitrogen trioxide are from the present work, and those of molecular nitrous acid are calculated from the proportions of nitrous acid and stoicheiometric nitrite determined by Singer and Vamplew.[1] We assume that these proportions of species which contain one equivalent of nitrite per mole will change little with changing nitrite concentration. The values of K_c are tabulated with those of the empirical coefficient C (Table 3). They are independent of the source and concentration of the " nitrous acid ". They increase with increasing perchloric acidity (and decreasing water activity [12] up to *ca.* 7M. Above this, ionic species derived from nitrous acid become important,[1,2,4] and K_c falls slightly.

<div align="center">EXPERIMENTAL</div>

Preparation of Solutions.—Solutions of nitrous acid in aqueous perchloric acid were made up by adding sodium nitrite or nitrosyl perchlorate to the aqueous acid. Allowance was made for the removal of protons by the nitrite ion where this would significantly affect the perchloric acid concentration. The nitrous acid concentration was estimated colorimetrically after addition of a sample to excess of alkali. Solutions were covered with a layer of spectroscopically pure hexane to decrease the decomposition of nitrous acid during spectral measurements; all measurements were made as rapidly as possible. Where the decomposition rate was high ([HNO_2] > *ca.* 0·1M), successive readings of optical density were taken at regular intervals, and extrapolated back to the time of analysis of the nitrous acid.

The ionic strength of the medium, and hence its protonating and dehydrating power, will depend upon the form in which the nitrous acid is added, *i.e.*, as sodium nitrite or nitrosyl perchlorate. This may affect the quantitative significance of the results with the more concentrated solutions of nitrous acid.

Determination of Optical Densities.—Spectra were measured on a Unicam S.P. 500 spectrophotometer, at room temperature, with matched stoppered cells of glass for the visible, and fused silica for the ultraviolet, region.

The independence of the ratio, E_{6250}/E_{7500}, of concentration and environment is shown in Tables (cell length 4 cm.).

Variation of nitrous acid, $[HClO_4] = 6.9M$.

[Nitrite] (M)	0.0639	0.124		0.141	0.0734 [a]	0.0834 [b]
E_{6250}/E_{7500}	2.08	2.16	2.13	2.15	2.08	2.17

[a] $[NaClO_4] = 1.64M$. [b] $[NaNO_3] = 1.07M$.

Variation of perchloric acid.

$[HClO_4] = 4.2M$: E_{6250}/E_{7500} (mean) = 2.03.
$[HClO_4] = 8.0M$: E_{6250}/E_{7500} (mean) = 2.18.

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