773. *Oxidation by Nitrous and Nitric Acid. Part IV.* Spectroscopic Investigation of the Equilibrium between* NO^+ *and Nitrous Acid in Aqueous Perchloric Acid.*

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The disappearance of the absorption spectrum of molecular nitrous acid (weak maxima between λ 3400 and 3900 Å) and the appearance of a strong absorption band ($\varepsilon_{max.} \approx 4200$ at 2600 Å), attributed to NO^+, are perceptible in 45% and complete in 58% (w/w) perchloric acid. Spectrophotometric measurements show that molecular nitrous acid and NO^+ account, within the limits of error (±5%), for the total " analytical " nitrous acid in 1—68% aqueous perchloric acid.

RAMAN lines attributed to NO^+ have been observed by Angus and Leckie [1] in aqueous perchloric acid; the lines were intense in 62%, weak in 48%, and absent in 40% perchloric acid. These Raman lines are also found in solutions of dinitrogen trioxide in sulphuric acid media.[2] A recent note by Bayliss and Watts [3] reported the disappearance of the ultraviolet absorption spectrum of nitrous acid and the concurrent appearance of a broad band ($\lambda \approx 2500$ Å; $\varepsilon \approx 3900$) in aqueous sulphuric acid. These authors attribute this band to NO^+; they plot (without giving details of their method) the composition of their media with respect to molecular nitrous acid and NO^+ against percentage of sulphuric acid and they conclude, from the fact that the two entities do not account for the total, that an appreciable fraction of nitrous acid is converted into a third entity (such as $H_2NO_2^+$) in some of the media.

Preliminary experiments (carried out before the work of Bayliss and Watts had come to our notice) showed that increase in acidity caused similar changes in the absorption spectrum of nitrous acid in aqueous sulphuric and in aqueous perchloric acid. While, however, the positions of the absorption maxima are almost unaffected by change of acidity in aqueous perchloric acid, a marked effect due to the medium is observed in aqueous sulphuric acid; thus the maximum of the broad band attributed to NO^+ moves from $\lambda \approx 2550$ Å to 2300 Å in 60—90% sulphuric acid, and in the more aqueous media appreciable displacements also occur in the region of the maxima of nitrous acid. This feature makes spectrophotometric analysis of the absorption spectra in sulphuric acid media almost impossible. A major experimental difficulty in sulphuric as well as in perchloric acid media arises from the volatility of nitrous acid (except at acidities sufficiently high to convert nitrous acid completely into NO^+). Although the use of closed optical cells effectively prevents appreciable loss of nitrous acid during optical measurements, the concentration of " analytical " nitrous acid (*i.e.*, all entities which diazotise aromatic

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* Part III, *J*, 1956, 1143.

[1] Angus and Leckie, *Proc. Roy. Soc.*, 1935, *A*, **150**, 615.

[2] Millen, *J.*, 1950, 2600.

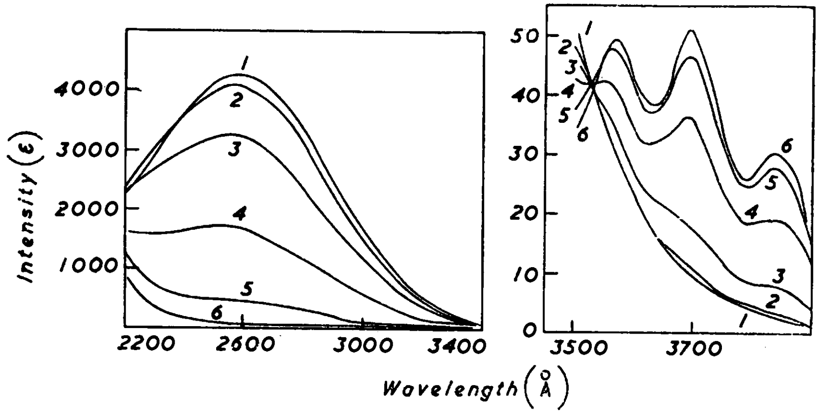
[3] Bayliss and Watts, *Chem. and Ind.*, 1955, 1353.

amines under the conditions of the colorimetric method of analysis used) decreases by 5—10% in the short time between two consecutive withdrawals (by pipette) of samples for analysis from the solutions prepared for spectroscopic measurements. The resultant errors in the determination of the extinction curves were appreciably reduced by a procedure described in the Experimental section.

SUMMARY AND DISCUSSION OF THE RESULTS

The ultraviolet absorption spectra of nitrous acid in 40—60% perchloric acid media are shown in Figs. 1(*a*) and (*b*); extinction coefficients at λ 2600, 3700, 3840, and 3520 Å are listed in the Table. The characteristic bands of molecular nitrous acid (maxima at λ 3700, 3560, and 3840 Å) begin to weaken in approx. 45% perchloric acid and have completely vanished in 58% perchloric acid. The disappearance of these weak maxima is accompanied by the appearance of a broad band (λ ≈ 2600 Å) which reaches its maximum intensity (ε 4240) when the spectrum of molecular nitrous acid has completely disappeared. Further features, not evident from the Table and Figs. 1(*a*) and (*b*) are: the position and intensity of the maximum at 2600 Å do not change appreciably in 58—68% perchloric acid (though the extinction curve drops more steeply between 2600 and 2200 A as acidity increases); the highest peak of molecular nitrous acid ($\lambda_{max.}$ 3700, ε 51·4) does not alter in intensity, and moves gradually towards $\lambda_{max.}$ 3720 Å as the acidity is reduced below 40% perchloric acid.

FIG. 1*a*. FIG. 1*b*.



1, 58%; 2, 55·6%; 3, 53·0%; 4, 50·4%; 5, 47·9%; 6, 41% $HClO_4$.

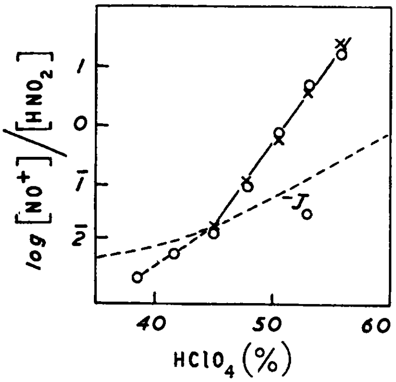
$HClO_4$ (% w/w)	ε_{2600} 1	ε_{3700} 2	ε_{3840} 3	ε_{3520}	100 × $[NO^+]/(HNO_2)$ calculated from ε_{2600}	ε_{3700}	ε_{3840}
60·5	4230	9·1	2·1	46·1	100	100	100
58·0	*4240*	*9·3*	*2·1*	45·0	*100*	*100*	*100*
55·6	4040	10·6	3·5	43·9	95·3	96·8	95·1
53·0	3200	17·2	7·7	42·7	75·5	81·2	80·3
50·4	1650	36·2	19·0	41·6	38·8	36·2	40·5
47·9	447	46·5	27·3	40·6	10·2	11·6	11·3
45·0	130	50·3	30·0	39·6	2·73	2·61	1·76
41·9	46·0	50·6	30·4	38·6	0·73	(0·19)	(0·036)
38·5	25·1	*51·4*	*30·5*	37·5	0·24	*0*	*0*
35·5	17·0	50·7	30·2	36·5	0·052	—	—
31·5	13·9	50·4	29·6	35·5	(−0·021)	—	—
27·5	14·8	49·7	29·3	34·5	*0*	—	—

Values assumed to correspond to 100% and 0% of NO^+ are italicised. Calculated values which are considered as not significant are in parentheses.

The assignment of the broad band at 2600 Å to NO^+, first made by Bayliss and Watts,[3] can be justified by the following arguments : (1) the stability of the nitrous acid solution in concentrated (*i.e.*, >58%) perchloric acid indicates that an ionic entity has been formed; (2) the validity of Beer's law shows that a molecule of this entity is formed from one molecule of nitrous acid; (3) the similarity of the absorption spectra in perchloric and sulphuric acid media indicates that the same entity is formed in both acids; (4) if the entity were $H_2NO_2^+$, one would not expect the spectrum to be almost unchanged in 58—68% perchloric acid, or to persist with undiminished intensity (although shifted towards shorter wavelengths) in up to 90% sulphuric acid.

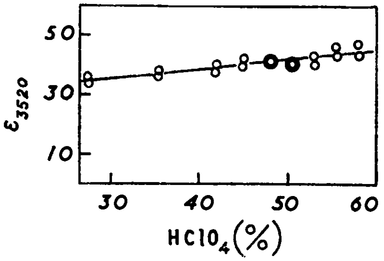
The fraction of " analytical " nitrous acid converted into NO^+ in p% perchloric acid was calculated from $\varepsilon_{2600}(= \varepsilon_1)$ on the assumption that the spectra in 58% and 27·5% acid are, respectively, those of NO^+ and molecular nitrous acid: $[NO^+]/(HNO_2) = [\varepsilon_1(p\%) - \varepsilon_1(27{\cdot}5\%)]/[\varepsilon_1(58\%) - \varepsilon_1(27{\cdot}5\%)]$, where (HNO_2) denotes the concentration of " analytical " nitrous acid.

FIG. 2.



○ *Calc. from* ε_{2600}.
× *Calc. from the mean between* ε_{3700} *and* ε_{3840}.

FIG· 3.



The fraction of molecular nitrous acid converted into other entities was similarly obtained from $\varepsilon_{3700}(= \varepsilon_2)$ and $\varepsilon_{3840}(= \varepsilon_3)$:

$$\{(HNO_2) - [HNO_2]\}/(HNO_2) = [\varepsilon_2(38{\cdot}5\%) - \varepsilon_2(p\%)]/[\varepsilon_2(38{\cdot}5\%) - \varepsilon_2(58\%)]$$

and similarly for ε_3.

The calculations were based on ε values in 58% and 38·5% rather than 27·5% perchloric acid because of a slight displacement of the maxima from 3700 and 3840 Å between 38·5% and 27·5% perchloric acid. The results listed in the last three columns of the Table show that the concentration of NO^+ agrees within the limits of error with the decrease in concentration of molecular nitrous acid. These figures and the appearance of the spectra give no indication of the presence of a third entity such as $H_2NO_2^+$, but they do not exclude the possibility that up to approx. 5% of the " analytical " nitrous acid is converted into a third entity in some of the perchloric acid media.

When the logarithm of the ratio $[NO^+]/[HNO_2]$ ($[HNO_2]$ being the concentration of molecular nitrous acid) calculated from the entries in the Table, is plotted against percentage of perchloric acid, the points lie close to a straight line (Fig. 2) (except at low acidities). One would expect the slope of this line to be similar to that of the $-J_0$ function which governs the dissociation equilibrium for certain indicators in which proton uptake is accompanied by elimination of water. The slope of log $([NO^+]/[HNO_2])$, however, exceeds that of the $-J_0$ function for perchloric [4, 5] acid by a factor of 2·7 (Fig. 2). This surprising feature must be attributed to a strong dependence of the activity coefficients of molecular nitrous

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[4] Hammet and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2734.
[5] Robinson and Baker, *Trans. Proc. Roy. Soc. N.Z.*, 1946, **76**, 250.

acid, and perhaps of NO^+, on the composition of the medium. This is qualitatively supported by two observations : (*a*) addition of sodium perchlorate has a similar (though weaker) effect on the equilibrium as increase of acidity; (*b*) the instability of nitrous acid solutions of a given concentration increases markedly in 35—50% perchloric acid : this must be ascribed to a corresponding increase of the partial pressure (and hence of the activity coefficient) of molecular nitrous acid.

EXPERIMENTAL

Materials.—" AnalaR " perchloric acid (72%) and sodium nitrite were used.

Preparation of solutions. 9 ml. of ice-cooled aqueous perchloric acid of the appropriate strength were added to 1 ml. of aqueous sodium nitrite of the required concentration (10^{-3}M to 5×10^{-2}M). The optical cell was flushed and then filled with part of this solution; samples for determination of the concentration of nitrous acid were taken from the remaining solution (see below). The reference cell was flushed and then filled with a mixture of 9 ml. of aqueous perchloric acid of the same strength and 1 ml. of water.

Determination of the Concentration of Nitrous Acid.—Determination of extinction coefficients requires the knowledge of the concentration of " analytical " nitrous acid in the optical cell. To minimise the error caused by the escape of nitrous acid, samples for analysis were pipetted from the freshly prepared solutions immediately before and after the optical cell had been filled. The nitrous acid content of the first sample usually exceeded that of the second sample by 5—10% (except at high acidities when the two values often agreed closely). The mean between the values obtained for the two samples was taken as the estimate for the concentration of " analytical " nitrous acid in the absorption cell. The constancy of the readings showed that no appreciable loss of nitrous acid from the stoppered 1 cm. cells occurred during the recording of the spectra. 1 ml. samples withdrawn for analysis were added to an excess of alkali, diluted to a suitable volume, and measured by Shinn's colorimetric method[6] (sulphanilamide + *N*-naphthylethylenediamine dihydrochloride). The concentrations of nitrous acid were too low (10^{-4} to 5×10^{-3}M) to permit the use of standard volumetric methods.

Determination of the Extinction Curves.—The spectra were measured on a Hilger " Uvispek " spectrophotometer. The optical cells were kept thermostatically at 25° ± 0·3°. As solutions of different nitrous acid concentrations had to be employed for different parts of the spectrum, and as the error in the estimation of nitrous acid in any given solution was considered to be too high (probably more than ±5%), the following procedure was adopted : in all the media investigated the ratios of the extinction at all wavelengths (ε_λ) to the extinction at 3520 Å were determined; previous experiments had shown that ε_{3520} varied but slowly with acidity. This involved no errors of analysis (although the validity of Beer's law is assumed). For each medium ε_{3520} was then determined repeatedly by the method described above, and the values of ε_{3520} were plotted against % perchloric acid. The ordinates of the " best " straight line drawn through these points (Fig. 3) were regarded as the most reliable estimates for ε_{3520}. Extinction coefficients at other wavelengths were then calculated from the ratios of $\varepsilon_\lambda/\varepsilon_{3520}$. Although this procedure greatly improved reproducibility, substantially similar results for ratios $[NO^+]/(HNO_2)$ and $\{(HNO_2) - [HNO_2]\}/(HNO_2)$ were obtained when the extinction curves were determined by the usual method.

Evaluation of the Extinction Curves.—Calculations of composition were based on the extinction coefficients at 2600, 3700, and 3840 Å. 2600 Å is an obvious choice because the extinction curve at high acidities has a flat maximum of ε 4240 while ε at low acidities is only 15. 3700 Å is the position of the highest peak of molecular nitrous acid in the relevant range of acidities with ε 51·4, while at high acidity $\varepsilon = 9{\cdot}3$. The difference between the extinction at low and high acidities at other wavelengths in the range of the bands of molecular nitrous acid is smaller; results calculated by means of the values of ε at 3840 Å, the position of another peak of molecular nitrous acid (ε 30·5 and 2·1 at low and high acidity, respectively), agree fairly well with those calculated from ε_{3700} (Table).

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[6] Shinn, *Ind. Eng. Chem. Anal.*, 1941, **13**, 33; Kershaw and Chamberlin, *ibid.*, 1942, **14**, 312.