833. *The Nitrous Acid–Dinitrogen Trioxide Equilibrium in Aqueous Perchloric Acid.*

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The equilibrium constant for the reaction $2HO{\cdot}NO \rightleftharpoons N_2O_3 + H_2O$ has been redetermined by spectroscopic and distribution methods. The combined methods establish K_a as $0{\cdot}20 \pm 0{\cdot}05$ at 20°.

Apart from an estimate of the equilibrium constant by a thermodynamic cycle [1] and a spectrophotometric study by Bunton and Stedman,[2] no quantitative work has been done on the equilibrium $2HO{\cdot}NO \rightleftharpoons N_2O_3 + H_2O$. In the latter estimation it was necessary to take an approximate value for the extinction coefficient of dinitrogen trioxide. There is also a trend in the K_c values which is probably associated with a change in the water activity of the solutions. If the K_c values are each multiplied by the appropriate water activity then the mean value of K_a is $0{\cdot}19 \pm 0{\cdot}08$.

In the present work the equilibrium constant has been redetermined spectrophotometrically, a graphical method being used to obtain $\varepsilon_{N_2O_3}$. An independent estimate of K has been made by distributing dinitrogen trioxide between toluene and aqueous perchloric acid.

A preliminary examination of the spectrum of "blue" nitrous acid in 46% (w/w) perchloric acid showed almost no trace of the nitrosyl ion, and a calculation of the proportion from the equilibrium $HO{\cdot}NO + H^+ \rightleftharpoons NO^+ + H_2O$ using the mean value of pK (8·3) found from Turney and Wright's [1] and Singer and Vamplew's [3] values, combined with J_0 values found by Deno *et al.*,[4] showed that the proportion of nitrosyl ion should be less than about 3%. Since all measurements were made in perchloric acid more dilute than 46% (w/w) no further account was taken of this equilibrium.

For the equilibrium

$$\underset{c_2}{2HO{\cdot}NO} \rightleftharpoons \underset{c_1}{N_2O_3} + \underset{a_W}{H_2O}$$

$K_1 = c_1a_W/c_2^2$, whence $c_2 = a_W^{\frac{1}{2}}c_1^{\frac{1}{2}}/K_1^{\frac{1}{2}}$ (where c_1 and c_2 are in molar concentration

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[1] Turney and Wright, *J.*, 1958, 2415.

[2] Bunton and Stedman, *J.*, 1958, 2440.

[3] Singer and Vamplew, *J.*, 1956, 3971.

[4] Deno, Berkheimer, Evans, and Peterson, *J. Amer. Chem. Soc.*, 1959, **81**, 2344.

units and the water activity a_w is the relative vapour pressure of the solutions, given by P/P_0); also $c_{NO_2^-} = c_2 + 2c_1 = a_W^{\frac{1}{2}}c_1^{\frac{1}{2}}/K_1^{\frac{1}{2}} + 2c_1$, but for the blue solution $D = \varepsilon c_1$ for a 1-cm. cell, where ε is the extinction coefficient of the blue solution. Whence $c_{NO_2^-}/D = (1/K_1^{\frac{1}{2}}\varepsilon^{\frac{1}{2}})(a_W/D)^{\frac{1}{2}} + 2/\varepsilon$, and a plot of the left-hand side against $(a_W/D)^{\frac{1}{2}}$ should be a straight line of slope $1/K_1^{\frac{1}{2}}\varepsilon^{\frac{1}{2}}$ and intercept $2/\varepsilon$.

All experiments were carried out by measuring D at 6563 Å. From the value of K so found, and by measuring c/D at different wavelengths, it is possible to evaluate ε and hence the spectrum of dinitrogen trioxide.

Since Mason's experiments [5] indicate that the spectrum of dinitrogen trioxide in toluene shows no nitrous acid structure, the next set of experiments were carried out by distributing dinitrogen trioxide between toluene and water. Under these conditions, we have the equilibria (where subscripts W and T refer, respectively, to water and toluene)

$$(N_2O_3)_W \rightleftharpoons (N_2O_3)_T$$

$$H_2O + (N_2O_3)_W \rightleftharpoons 2(HO{\cdot}NO)_W$$

for which we have

$$K_1 = c_{N_2O_3(W)}/c_{N_2O_3(T)} \text{ and } K_2 = c^2_{HO\cdot NO(W)}/c_{N_2O_3(W)}a_W$$

Again, in the aqueous layer

$$c_{NO_2^-} = c_{HO\cdot NO(W)} + 2c_{N_2O_3(W)}$$

whence, $c_{NO_2^-(W)}/c_{N_2O_3(T)} = (K_1K_2a_W)^{\frac{1}{2}}/\sqrt{c_{N_2O_3(T)}} + 2K_1$.

EXPERIMENTAL

(a) *Spectrophotometric measurements.* In expts. 1—14 the total nitrous acid in all forms was determined by adding the solution to sodium hydroxide and measuring the optical density of the nitrite. In expts. 15—21 the total nitrite was determined by addition to acidified potassium permanganate; after $\frac{1}{2}$ hr. the excess of permanganate was determined, through potassium iodide, with thiosulphate. The table gives the molar concentration of nitrite ion, the optical density, D (1 cm.), and a_W.

Expt.	$c_{NO_2^-}$	D	a_W	Expt.	$c_{NO_2^-}$	D	a_W	Expt.	$c_{NO_2^-}$	D	a_W
15	0·191	0·157	0·469	17	0·0720	0·0468	0·469	2	0·0368	0·0073	0·596
18	0·175	0·155	0·469	9	0·0625	0·0186	0·575	7	0·0361	0·0109	0·575
19	0·134	0·0759	0·469	12	0·0572	0·0264	0·512	3	0·0348	0·0067	0·575
16	0·119	0·0820	0·469	21	0·0450	0·0194	0·469	4	0·0291	0·0042	0·670
20	0·0930	0·0325	0·469	10	0·0450	0·0095	0·575	8	0·0271	0·0054	0·575
6	0·0865	0·0318	0·575	13	0·0435	0·0165	0·512	14	0·0264	0·0078	0·512
11	0·0745	0·0365	0·512	1	0·0425	0·0085	0·635	5	0·0262	0·0031	0·630

In each case nitrite was added to make the perchloric acid solution of the desired strength; this was then shaken until a reasonably stable blue solution was obtained. There was much effervescence with evolution of nitrous fumes and the solutions were never entirely stable.

(b) *Distribution measurements.* Reagent-grade toluene (25 ml.) was shaken with aqueous perchloric acid (25 ml.) (a_W 0·571) in each of four funnels. Successive increasing amounts of solid sodium nitrite were added. Again there was much effervescence and evolution of nitrous fumes. The mixtures were shaken and set aside for about $\frac{1}{2}$ hr. to reach equilibrium. Duplicate samples were drawn from the upper and lower layers and analysed by addition to excess of acidified standard permanganate as before. A typical result was

c_W (g. of nitrite per 25 ml.)	0·300	0·398	0·469	0·516
c_T (g. of nitrite per 25 ml.)	0·0469	0·0743	0·0891	0·1042
c_W/c_T	6·40	5·36	5·26	4·95

the collected results being

c_W/c_T	7·80	6·76	6·54	6·40	6·20	5·80	5·76	5·36	5·26	4·95	4·50
$1/\sqrt{2c_T}$	3·48	3·01	2·49	3·27	2·56	2·33	2·24	2·53	2·37	2·19	2·24

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[5] Mason, *J.*, 1959, 1288.

These results are in terms of g. of nitrite per 25 ml.; to convert the slope and intercept found on this basis to quantities in the formula, multiply c_W/c_T by 2 and $1/\sqrt{2c_T}$ by 2·17.

RESULTS AND DISCUSSION

The spectrophotometric results can be expressed by

$$c/D = 0{\cdot}536(a_W/D)^{\frac{1}{2}} + 0{\cdot}1033$$

for which ε_{6563} is 19·4 and K is $0{\cdot}18 \pm 0{\cdot}04$. From measurements of the absorption of a solution of total nitrite concentration 0·175M in perchloric acid (a_W 0·469) and by use of the above value of K, we obtain the absorption spectrum:

λ (Å)	5000	5500	6000	6500	7000	7500	8000
D (1 cm.)	0·0518	0·0960	0·142	0·151	0·122	0·0880	0·0615
ε	5·8	10·2	15·2	17·1	12·9	9·4	6·6

The value of ε at 6563 Å given by this spectrum is less than that found by interpolation and is a measure of the extent to which these data deviate from the best straight line found above.

The results from distribution experiments can be expressed by

$$c_{NO_2^-(W)}/c_{N_2O_3(T)} = 1{\cdot}896/[c_{N_2O_3(T)}]^{\frac{1}{2}} + 2{\cdot}756$$

from which we calculate a value of $K = 0{\cdot}22 \pm 0{\cdot}04$. If we accept all results as equally admissible, *viz.*, Bunton and Stedman's, the present spectrophotometric and the present distribution results, we then estimate a final value of $K = 0{\cdot}20 \pm 0{\cdot}05$.

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