747. *A Potentiometric Study of the Reaction between Nitrous Acid and Hydriodic Acid.*

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Nitrous acid and hydriodic acid, liberated from their salts by hydrochloric acid, interact in two ways simultaneously:

$$2HNO_2 + 2HI \longrightarrow I_2 + 2NO + 2H_2O \quad . \quad . \quad . \quad (1)$$

$$2HNO_2 + 4HI \longrightarrow 2I_2 + N_2O + 3H_2O \quad . \quad . \quad . \quad (2)$$

If potassium iodide is added to nitrous acid in 10—15N-sulphuric acid, reaction (1) occurs, but in 2—7·5N-sulphuric acid both (1) and (2) occur. Similar addition in hydrochloric acid solution leads to (1) and (2) unless the concentration of hydrochloric acid is $\geqq$ 5N, in which case two successive reactions occur:

$$HI + 2HNO_2 + HCl \longrightarrow ICl + 2H_2O + 2NO \quad . \quad . \quad (3)$$

$$HI + ICl \longrightarrow HCl + I_2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The dissociation constant of nitrous acid at 20° is 7×10^{-4}.

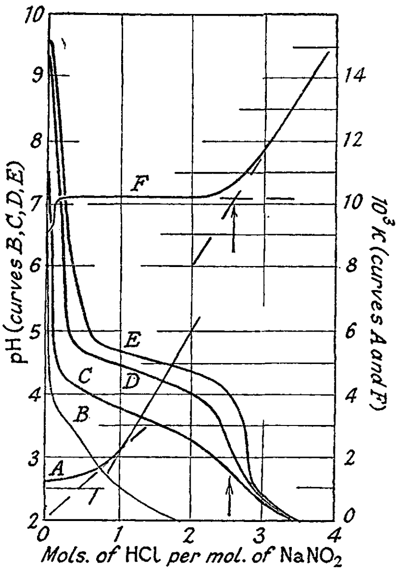
The object of this work was to study the reaction between nitrous and hydriodic acids in solutions of hydrochloric acid and sulphuric acid at different concentrations. As the formation of nitrous acid from sodium nitrite by a strong acid was followed with the glass electrode, the dissociation constant of nitrous acid was calculated from the pH values observed as it was gradually released; as this constant had not hitherto been determined potentiometrically, the values obtained are recorded.

EXPERIMENTAL

Dissociation Constant of Nitrous Acid.—This was calculated from the pH values as determined with the glass electrode at 20° during the titration of (*a*) 100 c.c. of 0·0125M-sodium nitrite with 0·0883N-hydrochloric acid, (*b*) 50 c.c. of 0·05M-nitrite with 0·0883N-acid. In the table, (*a*) and (*b*), are recorded some of the observed pH values and the values of pK_a and K_a calculated therefrom. As the accuracy of the observed pH values is of the order of ±0·01 pH unit and as no correction has been made for the activity coefficients of the ions, the agreement between the two mean values of K_a, 7·1 × 10^{-4} and 7·2 × 10^{-4}, is considered satisfactory. These values are slightly higher than those previously published, which were derived from measurements of electrical conductivity, kinetics, solubility of carbon dioxide in sodium nitrite solutions, and pH values estimated by means of indicators. The values so obtained vary from 4·0 to 6·2 × 10^{-4} at 15—18° (Klemenc and Hayek, *Monatsh.*, 1929, **53**, 407; Arndt, *Z. physikal. Chem.*, 1903, **45**, 574; Ray, Dey, and Ghosh, *J.*, 1917, **111**, 416; Schmidt, *Z. Elektrochem.*, 1936, **42**, 582; *Angew. Chem.*, 1936, **49**, 378; Klemenc and Pollak, *Z. physikal. Chem.*, 1922, **101**, 157; Bauer, *ibid.*, 1906, **56**, 215; Dhar and Datta, *Z. Elektrochem.*, 1913, **19**, 407; Blanchard, *Z. physikal. Chem.*, 1902, **41**, 706).

(*a*) HCl, c.c.	pH	pK_a	K_a × 10^4	(*b*) HCl, c.c.	pH	pK_a	K_a × 10^4
1·0	4·30	3·15	7·08	1·0	4·59	3·15	7·08
3·0	3·77	3·14	7·24	5·0	3·80	3·15	7·08
5·0	3·47	3·15	7·08	10·0	3·43	3·15	7·08
7·0	3·24	3·14	7·24	15·0	3·12	3·14	7·24
9·0	3·05	3·15	7·08	20·05	2·83	3·13	7·41
11·0	2·87	3·16	6·92	25·05	2·54	3·13	7·41
	Mean	3·15	7·1 × 10^{-4}			3·14	7·2 × 10^{-4}

FIG. 1.



Reaction between Nitrous and Hydriodic Acids.—(i) *In hydrochloric acid solution.* (*A*) Curve *B* in Fig. 1 gives the change in pH as nitrous acid is displaced from sodium nitrite by hydrochloric acid; it is a glass-electrode titration curve of 100 c.c. of 0·0125M-nitrite with 1·09N-acid. Curve *A* illustrates the change in specific conductivity during the same titration at 20°. Curves *C*, *D*, and *E* show the effect on the pH values of inserting increasing concentrations of potassium iodide in the sodium nitrite solutions when titrated with 1·09N-hydrochloric acid. These refer respectively to the titrations of 100 c.c. of 0·0125M-nitrate + *x*M-iodide, where *x* = 0·075, 0·75, and 1·50 for the respective curves. Curve *F* is the conductometric titration graph of the same solution as used for *C* with 1·09N-hydrochloric acid. The initial pH of solution *C* was 7·57, that of *D* 9·38, and that of *E* 9·44.

When solutions of the separate salts were mixed, a little iodine was liberated and made the solutions yellow. Hence some interaction must have occurred between the nitrite and iodide ions and so rendered the solutions alkaline. Curves *D* and *E* show that the solutions remained above pH 7 during the addition of 0·25 mol. of hydrochloric acid. Had no reaction occurred between the nitrite and iodide ions, the pH curves *C*, *D*, and *E*, would have been identical with curve *B*, as is the case when mixtures of sodium nitrite and potassium bromide, and of sodium nitrite and potassium chloride, are treated with hydrochloric acid. Moreover, the conductometric graph *F* would have been similar in form to *A*.

The inflections of curves *C*, *D*, and *E* show that 2·60, 2·61, and 2·75 mols. respectively of acid per mol. of sodium nitrite were required to bring the reactions between nitrite and iodide ions to completion, and these amounts are confirmed by the "breaks" in the corresponding conductometric graphs; *e.g.*, that of *F* confirms the location of the poorly-defined inflection in *C*. These curves show that in addition to the 1 mol. of hydrochloric acid needed to displace the nitrous acid from its salt, 1·60—1·75 mols. of acid were required to release equivalent amounts of hydriodic acid from the iodide which must have immediately reacted with the nitrous acid.

To account for such quantities it is evident that the interaction did not occur according to a single equation but to at least two equations, *viz.*, (1) and (2) (above) to different extents. The greater amount of hydrochloric acid required in titration *E* suggests that a relatively high concentration of iodide tends to favour reaction (2).

Whichever of these reactions occurs when an alkali nitrite is mixed with an alkali iodide in solution, hydrogen ions must be the essential reactants, for it is their removal from the water and reaction with nitrite and iodide ions, *e.g.*, $4H^{\bullet} + 2NO_2' + 2I' \longrightarrow I_2 + 2H_2O + 2NO$, that render the solution alkaline, as shown by the initially high pH values in titrations *E*, *D*, and *C*.

(*B*) The redox titration curves of 100 c.c. of 0·025M-sodium nitrite + xN-hydrochloric acid with 2N-potassium iodide at 18° are plotted in Fig. 2, the values of x being recorded on the respective curves, but the upper of the two curves marked 2·5 relates to 100 c.c. of 0·0375M-nitrite. When read from left to right, the inflections reveal that 1·25, 1·25, 1·25, 1·15, 1·00, and 1·00 mols. of hydriodic acid had reacted with one mol. of nitrous acid. Hence in 5·0—7·5N-hydrochloric acid solutions nitric oxide was the sole product of reduction of nitrous acid, whereas in 0·27—2·5N-solutions of the acid, a little nitrous oxide was also formed.

(ii) *In sulphuric acid solution.* Fig. 3 gives the redox titration curves, obtained with bright platinum electrodes, of 100 c.c. of 0·0125M-sodium nitrite + xN-sulphuric acid with N-potassium iodide at 18°. The values of x, *viz.*, 1—15, are marked on the respective curves. The mid-points of the inflections being taken as indicating the number of mols. of hydriodic acid that reacted with 1 mol. of nitrous acid, these values are found to be : in 1N-acid, 1·28; in 5N, 1·18; in 7·5N, 1·14; in 10N, 1·00; and in 15N, 1·00. Hence in 10—15N-solutions of sulphuric acid, nitrous acid is quantitatively reduced according to equation (1) to nitric oxide by hydriodic acid, whereas lower concentrations of sulphuric acid lead to the production of some nitrous oxide as well through the reaction of some hydriodic acid with nitrous acid, according to equation (2).

FIG. 2.

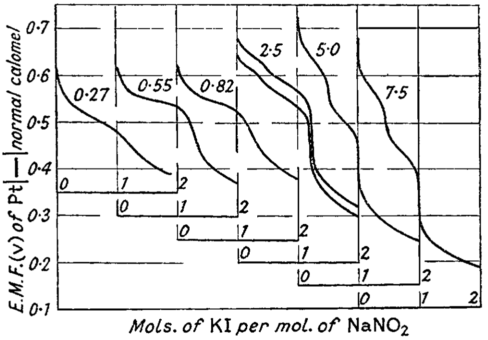
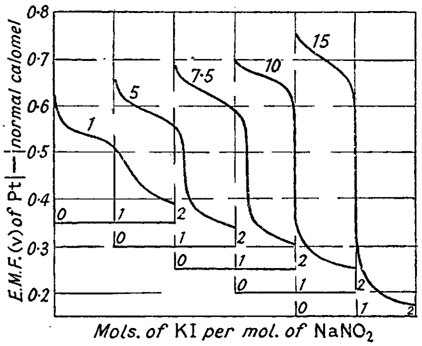


FIG. 3.



DISCUSSION

Neither the redox curves of the sulphuric acid solutions of nitrous acid in Fig. 3 nor the first three curves referring to 0·27—0·82N-hydrochloric acid solutions in Fig. 2 are divided into two sections. The two curves for 2·5N-hydrochloric acid, however, are clearly thus divided, the first section terminating when slightly less than 0·5 mol. of iodide had been added. The higher concentrations of hydrochloric acid, 5 and 7·5N, cause the initial sections to be quite well defined with almost vertical inflections with 0·5 mol. of potassium iodide. As the first 0·5 mol. of potassium iodide was added, the solutions acquired the pale yellow colour of iodine monochloride but immediately after the inflections the orange-red colour of iodine appeared. The first sections of the 5N and the 7·5N curve can therefore be explained by the equation (3), and the second sections by (4).

Unlike the interaction of nitrous and hydriodic acids in fairly concentrated sulphuric acid solutions, equation (1) provides no information regarding the mechanism of the interaction in the presence of hydrochloric acid; in this case equation (1) is composite in that it represents the sum of the two successive reactions (3) and (4). In 2·5N-hydrochloric acid some iodine monochloride is formed as judged from the pale yellow colour during the first part of the titration ending with rather less than 0·5 mol. of potassium iodide. It thus appears that at this concentration the total reaction consists of reactions given by equations (1), (2), (3), and (4).

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