The Kinetics of Oxidation by Nitrous Acid and Nitric Acid. Part I. Oxidation of Formic Acid by Nitrous Acid.

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[Reprint Order No. 5179.]

The kinetics of the reaction between formic acid and nitrous acid in aqueous sulphuric acid and in aqueous perchloric acid have been investigated. The reaction is approximately of first order with respect to formic acid and of first order with respect to "analytical" nitrous acid at constant initial concentration of analytical nitrous acid. The kinetic data indicate that the rate-determining step is a bimolecular reaction between formic acid and molecular nitrous acid in dilute acid media, and between formic acid and NO^+ or $H_2NO_2^+$ in more acidic media.

COMPARATIVELY little work has been reported on the kinetics of oxidation by nitrous acid. Abel and his co-workers recognised the essential rôle of nitrous acid in oxidation by nitric acid and investigated the oxidation of arsenious acid (Abel, Schmid, and Weiss, *Z. physikal. Chem.*, 1930, **147**, 76) and of sulphurous acid (Abel and Proisl, *Monatsh.*, 1935, **66**, 6) by aqueous nitrous acid. They also made a careful study of the kinetics of the reversible self-decomposition of nitrous acid in dilute nitric acid and in other mineral acids (Abel and Schmid, *Z. physikal. Chem.*, 1928, **132**, 55; **134**, 279; Abel, Schmid, and Babad, *ibid.*, 1928, **136**, 55). In dilute mineral acid, nitrous acid disproportionates according to the equation

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

In their kinetic work on oxidation by nitrous acid, Abel and his co-workers found it necessary to repress this reaction by shaking the reaction mixture in an atmosphere of nitric oxide in order to obtain reproducible results. Bobtelsky and Kaplan (*Z. anorg. Chem.*, 1930, **189**, 234) found the reaction between potassium iodide and nitrous acid to be of first order with respect to both reactants.

In the present work the oxidation of formic acid by nitrous acid was investigated in aqueous sulphuric acid (0·1—6M), aqueous perchloric acid (1—6M), and in water. The oxidation in aqueous nitric acid is described in Part II (following paper). Concentrations of less than 10^{-2}M-nitrous acid were used and under these conditions the rate of self-decomposition of nitrous acid is slow compared with the rate of oxidation and can be allowed for. All kinetic experiments were carried out at 25°. Dissolved oxygen was initially removed from the reactant solutions and the reaction mixture was screened from light. The course of the reaction was followed by colorimetric estimation of nitrous acid and, in some experiments, also by determination of the amount of carbon dioxide formed by oxidation of formic acid.

The initial concentration of nitrous acid was varied between 10^{-4} and 10^{-2}M and the reaction was followed up to about 70% consumption of the nitrous acid. The initial concentration of formic acid was varied between 0·5M and 1M and did not change measurably during a run. The following features were observed:

(1) The reaction is of first order with respect to the concentration of "analytical" nitrous acid in all runs; typical graphs of ln (HNO_2) against time, from which the first-order velocity constant k can be obtained, are shown in Fig. 1 [(HNO_2) denotes the concentration of "analytical" nitrous acid which comprises all molecular entities which diazotise aromatic amines under the conditions of the colorimetric method of analysis used]. Limited data indicate that in aqueous solution and in up to 4M-aqueous sulphuric acid the reaction is of first order with respect to formic acid (Table 1). In aqueous perchloric acid there are considerable deviations from first-order dependence on formic acid (Table 1), perhaps owing to inaccuracy caused by the subtraction of a relatively large blank decomposition.

TABLE 1.

Expt.	H·CO$_2$H, M	10^4k (min.$^{-1}$)	10^4k_b (min.$^{-1}$)	10^4k_c (min.$^{-1}$)	$10^4k_c'$ (min.$^{-1}$ mole^{-1} l.)
		2·8M-H$_2$SO$_4$; Initial (HNO$_2$) = 1 × 10^{-3}M.			
239*a*	0·51	48	14	34	67
239*b*	1·02	92	14	78	76
255	1·31	95	4	91	69
		2·8M-HClO$_4$; Initial (HNO$_2$) = 4 × 10^{-5}M.			
72	0·22	58	32	26	120
73	0·55	53	25	28	51
74	1·10	119	25	94	85
75	1·65	184	32	152	92

$k = -\mathrm{d}\ln(\mathrm{HNO_2})/\mathrm{d}t$; $k_b = -\mathrm{d}\ln(\mathrm{HNO_2})/\mathrm{d}t$ for blank run; $k_c = k - k_b$; $k_c' = k_c/[\mathrm{H{\cdot}CO_2H}]$.

For the reaction between formic acid (1·2M) and nitrous acid in the absence of mineral acid k_c' was equal to 0·0060 (min.$^{-1}$ mole^{-1} l.).

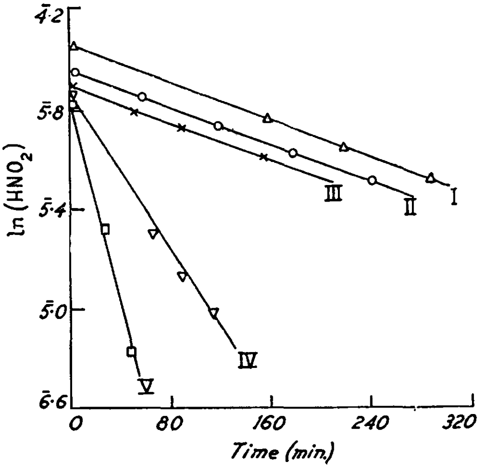


FIG. 1. ln (HNO$_2$) *plotted against time for experiments in aqueous sulphuric acid.* I, 0·11M; II, 1·0M; III, 2·0M; IV, 3·5M; V, 4·0M.

(2) The rate of the reaction is approximately independent of acidity in media up to 2·5N with respect to H$^+$ but increases rapidly with acidity above [H$^+$] = 3N (Tables 2 and 3).

TABLE 2. *Experiments in aqueous sulphuric acid.* Initial (HNO$_2$) = 1 × 10^{-3}M.

[H$_2$SO$_4$], M	0·1	1·0	2·0	2·8	3·5	4·0
$10^3k_c'$ (min.$^{-1}$ mole^{-1} l.)	6·0	6·0	5·5	7·2	29·5	101

TABLE 3. *Experiments in aqueous perchloric acid.* Initial (HNO$_2$) = 4 × 10^{-5}M.

[HClO$_4$], M	0·1	0·46	0·9	1·9	2·8	3·1	3·9	6·0
$10^3k_c'$ (min.$^{-1}$ mole^{-1} l.)	5·1	4·9	4·9	5·9	8·5	9·0	30·0	67·0

(3) The ratio of amount of carbon dioxide formed to the change in concentration of "analytical" nitrous acid in a given reaction time corrected to allow for the self-decomposition of nitrous acid, $q = [\Delta(\mathrm{CO_2})/\Delta(\mathrm{HNO_2})]_{\mathrm{corr.}}$, is approximately -1 in >2·8M-sulphuric acid, and $-0·5$ in <2·0M-sulphuric acid (Table 4). In aqueous perchloric acid, $q \approx -0·5$ in <1·0M- and $\approx$ 1—1·5 in >3M-solution.

TABLE 4.

[H$_2$SO$_4$], M	0·44	0·55	2·0	2·8	2·8	3·6
$-q$	0·61	0·50	0·68	1·13	1·0	0·97

(4) Although satisfactory first-order constants with respect to "analytical" nitrous acid are obtained in any given run, the velocity constants increase with the initial concentration of nitrous acid (Table 5).

TABLE 5. $[H_2SO_4] = 2{\cdot}8$M.

Initial (HNO_2), M × 10^3	0·7	0·9	2·7	12·6
$10^3k_c'$ (min.$^{-1}$ mole^{-1} l.)	7·6	6·7	11·5	16·5

(5) Formate ion appears to be less reactive than formic acid (see p. 2608).

DISCUSSION

The Course of the Reaction.—The oxidation of formic acid to carbon dioxide may proceed by two one-electron transfers, *e.g.*,

$$HNO_2 + H{\cdot}CO_2H = NO + H_2O + H{\cdot}CO{\cdot}O \qquad (2a)$$

$$H{\cdot}CO{\cdot}O + HNO_2 = NO + H_2O + CO_2 \qquad (2b)$$

or by a two-electron transfer,

$$HNO_2 + H{\cdot}CO_2H = HNO + CO_2 + H_2O \qquad (3)$$

with possible further reaction between nitroxyl and formic acid. The presence of $H{\cdot}CO{\cdot}O$ radicals and of HNO radicals in reaction mixtures has variously been postulated (Hart, *J. Amer. Chem. Soc.*, 1951, **73**, 68; Style and Ward, *J.*, 1952, 2125; Andrussow, *Ber.*, 1926, **59**, 458; *Z. angew. Chem.*, 1926, **39**, 332; 1935, **48**, 593; Baudisch, *Ber.*, 1921, **54**, 410; Raschig, *Z. angew. Chem.*, 1904, **17**, 1410; Gray and Style, *Trans. Faraday Soc.*, 1952, **48**, 1137). The fact that some reduction of mercuric chloride occurs in mixtures of nitrous and formic acids, but not in either acid alone, affords some evidence for the presence of free radicals in the reaction mixture (cf. Wieland and Zilg, *Annalen*, 1937, **530**, 257).

Possible reduction products of nitrous acid are nitric oxide (Winkler, *Ber.*, 1901, **34**, 1412), hyponitrous acid ($H_2N_2O_2$), nitrous oxide, and hydroxylamine (cf. Raschig, *Z. angew. Chem.*, 1904, **17**, 1411; *Z. anorg. Chem.*, 1926, **155**, 225). Direct identification of the reduction product proved to be too difficult because of the small initial concentration of nitrous acid in the reaction mixtures. Some indirect evidence, however, may be obtained from the ratio q (see p. 2605). If the final reduction product is nitric oxide, $q = -0{\cdot}5$; reduction to HNO, $H_2N_2O_2$, or N_2O would give $q = -1{\cdot}0$; and reduction to $NH_2{\cdot}OH$, $q = -2{\cdot}0$. The observed values (Table 4) suggest that the final reduction product is nitric oxide in dilute acid media and N_2O, $H_2N_2O_2$, or HNO in stronger acid, but do not permit a distinction between the mechanisms (2*a*), (2*b*), and (3), since HNO formed by (3) could subsequently be oxidised to nitric oxide : $HNO + HNO_2 = 2NO + H_2O$.

The participation of atmospheric oxygen, which was not rigorously excluded during the runs, in the reaction (*e.g.*, by oxidation of nitric oxide) would invalidate deductions based on the observed values of q, but this possibility is discounted for the following reasons. The procedure used led to reproducible results, which would be unlikely unless the reaction involving atmospheric oxygen were to go to completion. It seems unlikely that sufficient oxygen to reoxidise the nitric oxide or nitroxyl would have been available. Moreover the change of $-q$ with increasing acidity from 0·5 to 1·0 implies that oxidation of NO or HNO to NO_2 by oxygen would be complete in the more acidic media and completely absent in less acidic media. This, again, is very improbable, particularly since the solubility of non-polar gases in aqueous solutions is known to decrease with increasing concentration of electrolyte.

The Nature of " Analytical " Nitrous Acid.—The dissociation constant of nitrous acid is $5{\cdot}0 \times 10^{-4}$ at 25° (Schmid, *Angew. Chem.*, 1936, **49**, 378); no appreciable amounts of nitrite ion can therefore be present in the mineral acid media used.

In a recent paper on the kinetics of the gas-phase reaction between N_2O_3, NO, NO_2, and H_2O, Wayne and Yost (*J. Chem. Phys.*, 1950, **18**, 767), using data obtained by Abel and Neusser (*Monatsh.*, 1929, **54**, 855), Verhoek and Daniels (*J. Amer. Chem. Soc.*, 1931, **53**, 1250), and Forsythe and Giauque (*ibid.*, 1942, **64**, 48), have given reliable estimates of the constants for the equilibria $2HNO_2 \rightleftharpoons N_2O_3 + H_2O$, $N_2O_3 \rightleftharpoons NO + NO_2$, and $HNO_2(aq.) \rightleftharpoons HNO_2(g)$. If one assumes that the Bunsen absorption coefficient of NO_2 in water is of the same order of magnitude as that of NO, the constants for the equilibria between NO, NO_2, N_2O_3, and HNO_2 in aqueous solution can be calculated from the gas-phase equilibrium constants. It is found that in the relevant range the concentrations of NO, NO_2, and N_2O_3 are each less than 1% of the concentration of analytical nitrous acid.

More direct evidence on the nature of analytical nitrous acid was obtained experimentally. According to Abel and his co-workers (*locc. cit.*), the disproportionation of nitrous acid (1) proceeds in two steps:

$$4HNO_2 \rightleftharpoons N_2O_4 + 2NO + H_2O \text{ (rapid)} \quad (4)$$

and

$$N_2O_4 + H_2O \longrightarrow HNO_2 + HNO_3 \text{ (rate-determining)} \quad (5)$$

If an appreciable amount of nitrous acid were transformed into dinitrogen tetroxide in the equilibrium (4) the amount of nitrous acid determined by diazotisation would not correspond to the amount of sodium nitrite introduced. No such discrepancy was observed. Further, the ultra-violet absorption spectra of dinitrogen tetroxide in carbon tetrachloride and of aqueous acidic solutions of nitrous acid were recorded, and no trace of the absorption band of dinitrogen tetroxide was detected in the nitrous acid solutions. The extinction curves of nitrous acid (0·04M) in 0·05M-HNO_3, 4M-$HClO_4$, and 4M-H_2SO_4 between $\lambda = 3350$ Å and 4000 Å are almost identical (Fig. 2) and similar to the spectrum obtained by Kortüm (*Z. physikal. Chem.*, 1939, **43**, *B*, 418) for nitrous acid dissolved in 0·05N-hydrochloric acid. By comparing the spectra of gaseous mixtures of NO, NO_2, and H_2O, and NO, NO_2, and D_2O, Porter (*J. Chem. Phys.*, 1951, **19**, 1278) has proved conclusively that the four absorption maxima between 3400 Å and 3900 Å are due to molecular nitrous acid.

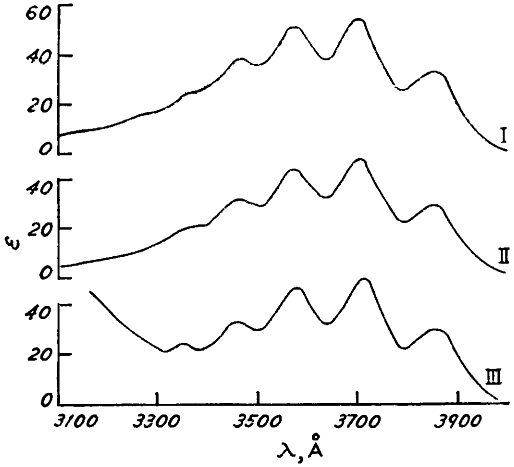


FIG. 2. *Absorption spectrum of "analytical" nitrous acid in different acid media.* I, in 4M-sulphuric acid; II, in 4M-perchloric acid; III, in 0·05M-nitric acid.

It is therefore concluded that, in the acid media used in the present work, the bulk of analytical nitrous acid is molecular nitrous acid.

Kinetics of the Reaction.—The first order of the reaction with respect to analytical nitrous acid and to formic acid can be accounted for by a rate-determining step which consists of either (1) a bimolecular reaction between $H{\cdot}CO_2H$ or $H{\cdot}CO{\cdot}O^-$ and HNO_2, or (2) a bimolecular reaction between $H{\cdot}CO_2H$ or $H{\cdot}CO{\cdot}O^-$ and a molecular entity X in equilibrium with molecular nitrous acid in the stoicheiometric ratio 1 : 1. The relevant equilibria known or believed to exist in aqueous solutions of nitrous acid are:

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O \quad (6)$$

$$HNO_2 + H_3O^+ \rightleftharpoons H_2NO_2^+ + H_2O \quad (7)$$

$$H_2NO_2^+ \rightleftharpoons NO^+ + H_2O \quad (8)$$

$$NO^+ + NO_2 \rightleftharpoons N_2O_3^+ \quad (9)$$

$$N_2O_3 \rightleftharpoons NO + NO_2 \quad (10)$$

$$2NO_2 \rightleftharpoons N_2O_4 \quad (11)$$

$$N_2O_4 + H_2O \rightleftharpoons HNO_2 + HNO_3 \quad (12)$$

The possible oxidants are N_2O_3, $N_2O_3^+$, NO^+, $H_2NO_2^+$, N_2O_4, NO_2, and HNO_2. Of these only those stoicheiometrically related to HNO_2 in the ratio 1 : 1 are admissible on kinetic grounds. N_2O_3 and $N_2O_3^+$ must be excluded for this reason. It may be noted that second-order kinetics with respect to nitrous acid have been reported and attributed to attack by N_2O_3 in a number of reactions (cf. Austin, Hughes, Ingold, and Ridd, *J. Amer. Chem. Soc.*, 1952, **74**, 555; Abel, Schmid, and Weiss, *loc. cit.*). [Abel (*Monatsh.*, 1952, **83**, 1103) has proposed a mechanism for the diazotisation of amines in which attack by N_2O_3 may lead to first-order kinetics under certain conditions; it is considered unlikely that these conditions apply here.]

The concentration of NO_2 is determined by the equilibria (10) and (6); two cases have to be considered: (i) if NO accumulates as a reaction product, then $[NO_2] = K[HNO_2]^2/[NO]$ from (10) and (6) and, since $[HNO_2] \approx (HNO_2)$, $[NO_2]$ is not proportional to (HNO_2); (ii) if NO is not formed by a reaction other than (10), $[NO] = [NO_2] \propto [N_2O_3]^{\frac{1}{2}} \propto (HNO_2)$, and attack by NO_2 would give rise to first order with respect to (HNO_2). NO_2 can, however, be excluded as a possible oxidising agent for the following reasons: (1) if NO_2 dimerises according to (11) to an appreciable extent, $[NO_2]$ will not be proportional to (HNO_2); and (2) the rate of oxidation of formic acid in nitric acid media is similar to that of oxidation in perchloric and sulphuric acid solutions of similar acidity (see Part II). If NO_2 were the oxidising agent, the reaction in nitric acid should be faster than that in other mineral acids since, owing to the equilibrium (12), the ratio $[NO_2]/(HNO_2)$ in nitric acid solution must be larger than in other media.

The concentrations of NO^+ and $H_2NO_2^+$ are proportional to $[HNO_2]$ and $[H^+]$. The velocity constant of a bimolecular reaction between NO^+ or $H_2NO_2^+$ and formic acid would therefore depend on $[H^+]$; such a process cannot be the rate-determining step in media up to 3N with respect to H^+, but participation by NO^+ or $H_2NO_2^+$ may well account for the increase of the velocity constants at higher acidities.

Reaction between NO^+ or $H_2NO_2^+$ and formate ion would lead to the observed order as well as to independence of the velocity constant of acidity, since $[NO^+]$ or $[H_2NO_2^+]$ is proportional to $[H^+]$, and $[H{\cdot}CO{\cdot}O^-]$ to $[H^+]^{-1}$. This would therefore account for the observed rate in media for which $[H^+] \leqslant 3$N, but it is difficult to reconcile this interpretation with the very rapid increase of the reaction rate at $[H^+] > 3$N. Also, some experimental evidence for the non-reactivity of formate ions towards nitrous acid was obtained by comparing the velocities of the reaction in the following two solutions:

	(HNO_2), M	$[NO_2^-]$, M	$[H{\cdot}CO_2H]$, M.	$[H{\cdot}CO{\cdot}O^-]$, M	$[H^+]$, M	k_c'
(A)	$4{\cdot}11 \times 10^{-4}$	$4{\cdot}67 \times 10^{-4}$	1·2	0·6	$3{\cdot}5 \times 10^{-4}$	0·0012
(B)	$8{\cdot}54 \times 10^{-4}$	$2{\cdot}4 \times 10^{-5}$	1·19	$1{\cdot}45 \times 10^{-2}$	$1{\cdot}45 \times 10^{-2}$	0·0060

The velocity constant in (A) is one-fifth of that in (B). Although this may be due to the lower value of $[H^+]$, or possibly to the increase in $[NO_2^-]$, the result is hardly compatible with the assumption that the formate ion is the reactive entity since its concentration in (A) is approximately 40 times that in (B).

It is therefore concluded that in the acidity range $[H^+] = 0{\cdot}1$—$3{\cdot}0$N, the rate-determining step is a bimolecular reaction between HNO_2 and $H{\cdot}CO_2H$. The rapid increase of the reaction velocity at $[H^+] \approx 3$N is probably due to the increase in concentration of the more reactive oxidising agents NO^+ or $H_2NO_2^+$ in the more acidic media (an increase in the reactivity of HNO_2 or $H{\cdot}CO_2H$ owing to changes in the medium could hardly account for the magnitude of the observed effect).

Insufficient data were obtained to permit a definite interpretation of the observed dependence of the second-order velocity constant on the initial concentration of nitrous acid, but a possible explanation would be a two-step reaction such as

$$H{\cdot}CO_2H + HNO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H{\cdot}CO_2H,HNO_2 \xrightarrow{k_2} H{\cdot}CO{\cdot}O + NO + H_2O$$

which might give rise to approximately first order with respect to nitrous acid for moderate changes of concentration, but at sufficiently low concentrations of nitrous acid the first rather than the second step might become rate-determining.

EXPERIMENTAL

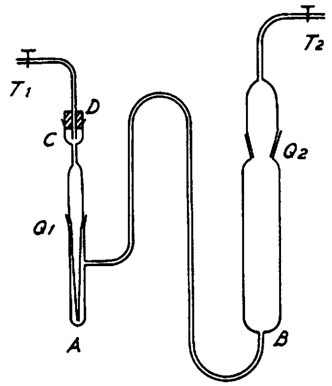
Materials.—" AnalaR " sulphuric acid, perchloric acid, sodium nitrite, and formic acid were used without further purification. Experiments showed that redistillation of the formic acid had no effect on the kinetic results.

Removal of Dissolved Oxygen.—A current of nitrogen, freed from oxygen by a solution of vanadous sulphate in contact with zinc amalgam (Meites and Meites, *Analyt. Chem.*, 1948, **20**, 984) and from carbon dioxide by a solution of barium hydroxide, was passed through the solutions from which the reaction mixture was prepared (*i.e.*, sulphuric or perchloric acid, formic acid, and sodium nitrite solution).

Preparation of the Media.—Sulphuric or perchloric acid solutions were standardised by titration with sodium hydroxide. Media of the required composition were prepared by mixing calculated volumes of sulphuric or perchloric acid, formic acid solution, and sodium nitrite solution in a volumetric flask (100 or 200 ml.) and diluting to the mark with water.

Determination of Nitrite.—The concentration of analytical nitrous acid was determined by the colorimetric method described by Shinn (*Ind. Eng. Chem. Anal.*, 1941, **13**, 33) and modified by Kershaw and Chamberlin (*ibid.*, 1942, **14**, 312), the colour being measured on a Hilger " Spekker " photoelectric absorptiometer. Nitrite concentrations in the range 10^{-3}—10^{-4} mg. of nitrite nitrogen/c.c. are estimated by this method; more concentrated solutions are determined after suitable dilution. The reagents are stable for several weeks, and nitrate and formic acid do not interfere. Calibration curves can be used for several days.

FIG. 3.



Determination of Carbon Dioxide.—The procedure was based on a turbidimetric method (Snell and Snell, " Colorimetric Methods of Analysis," Vol. II, Van Nostrand, New York, 1949). As some of the carbon dioxide formed during the reaction escapes from the liquid phase, the reaction and the subsequent analysis were carried out in glass vessels of the type shown in Fig. 3. The two arms *A* (a tube 1·5 cm. in diam., 12 cm. long) and *B* (a tube 2 cm. in diam., 17 cm. long) are joined by a capillary tube. The capacity of the portion of *A* below the side-arm is a little more than 10 ml. *A* carries the joint Q_1 which is fitted with an air-leak, a fairly wide capillary extending almost to the bottom of the vessel. The upper end of Q_1 is joined through a short piece of capillary tube to the vessel *C* (1·5 cm. in diam., 2—3 cm. long). *C* is closed by a rubber bung *D*, carrying a tube leading to the nitrogen supply, which is controlled by the tap T_1. The right-hand arm *B* carries the joint Q_2 connected to the two-way tap T_2, which can be opened to the atmosphere or to a water-pump. The capillary joining *A* and *B* is constricted at the junction with *B* in order to reduce the size of the gas bubbles rising through the barium hydroxide solution and thus to ensure complete absorption of carbon dioxide. A calibration curve was obtained in the following manner:

After passage of nitrogen through the empty vessel for 15 min., Q_2 is removed and 30 ml. of 0·2N-barium hydroxide are transferred to *B* from a burette; the current of nitrogen is reduced, and Q_2 replaced. Next, Q_1 is removed and the required volume of standard sodium carbonate solution ($\approx 7 \times 10^{-4}$M) is pipetted into *A*, the nitrogen current is turned off, and Q_1 replaced. *D* is then removed, about 3 ml. of dilute hydrochloric acid are transferred to *C*, and *D* is replaced. A slow current of nitrogen is turned on and gentle suction is applied simultaneously by opening T_2 to the pump. In this way the acid is drawn from *C* into *A* and the liberated carbon dioxide is swept into the barium hydroxide solution in *B*. After 15 min. the contents of *B* are emptied into a 4-cm. cell, covered by a glass lid, and the optical density of the barium carbonate suspension is measured on the " Spekker " (Wratten neutral filters are used). The optical density seems to be somewhat dependent on the characteristics of the reaction vessel; separate calibration curves for each vessel had therefore to be used; even so, the average agreement between duplicates was only about 7%. Up to $3·5 \times 10^{-6}$ mole of carbon dioxide can be estimated by this method.

Kinetic Experiments.—A 200-ml. volumetric flask and five carbon dioxide vessels (Fig. 3) were used in runs in which both nitrous acid and carbon dioxide were determined. Nitrogen was passed through the mineral acid and sodium nitrite solutions for 30 min. At the same time the carbon dioxide vessels were flushed with nitrogen and charged with barium hydroxide as described above. The joints Q_2 were then replaced by Quickfit stoppers, the taps T_1 closed, and the vessels placed in the thermostat (25°). The calculated volumes of the reactants were mixed in the 200-ml. volumetric flask and placed in the thermostat; 5-ml. portions of the reaction mixture were pipetted rapidly into the arm *A* of each carbon dioxide vessel (opened for this purpose by lifting Q_1). For the nitrite estimation, 5-ml. samples, taken from the 200-ml. flask at suitable intervals, were added to an excess of cooled sodium hydroxide; the resultant solution was almost neutralised with hydrochloric acid and made up to a standard volume. The colorimetric determination of nitrite (p. 2609) was carried out on a suitable aliquot part of this solution.

After corresponding time intervals, carbon dioxide vessels were in turn taken from the thermostat; the reaction was quenched by placing the arm *A* in ice, and carbon dioxide was determined after sweeping the carbon dioxide into the barium hydroxide solution and turbidimetric measurement of the precipitate as described above.

A blank experiment was carried out at the same time: nitrous acid was estimated in samples taken from a solution of the same composition as the reaction mixture but containing no formic acid.

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[*Received, March 4th* 1954.]