The Kinetics of Oxidation by Nitrous Acid and Nitric Acid. Part II. Oxidation of Formic Acid in Aqueous Nitric Acid.*

By Jean V. L. Longstaff and K. Singer.

[Reprint Order No. 5180.]

The rate of oxidation of formic acid in 0·04—18·4M-nitric acid at 25° is of first order with respect to "analytical" nitrous acid and to formic acid. The second-order velocity constant varies with the concentration of nitric acid; a sharp maximum is reached at [HNO$_3$] = 12·5M. The kinetic results, in conjunction with evidence derived from ultra-violet absorption spectra of solutions of nitrous acid in nitric acid, indicate that the rate-determining step is a bimolecular reaction between formic acid and molecular nitrous acid in less than $\approx$2·5M-nitric acid, and between formic acid and NO$^+$ at higher concentrations of nitric acid.

There are but few reports on the kinetics of oxidation by aqueous nitric acid. The only careful investigation—apart from an early paper by Eckstädt (*Z. anorg. Chem.*, 1902, **29**, 51) on the oxidation of iodide—appears to be that of Abel, Schmid, and Weiss (*Z. physikal. Chem.*, 1930, *A*, **147**, 69) on the oxidation of arsenious acid in up to 2·6M-nitric acid containing nitrous acid, which is of first order with respect to arsenious acid and of second order with respect to nitrous acid. The authors interpret the order by assuming N$_2$O$_3$ (in equilibrium with nitrous acid) to be the oxidising agent. Abel, Schmid, and Babad (*ibid.*, 1928, **136**, 135, 419) also investigated the kinetics and equilibria of the reactions of nitrous acid and of oxides of nitrogen in aqueous nitric acid.

In the present work the oxidation of formic acid in aqueous nitric acid (0·04—18·4M) at 25° was followed by determination of the change of concentration of "analytical" nitrous acid [denoted by (HNO$_2$) and defined as in Part I], and, in some experiments, also by determination of the amount of carbon dioxide formed. In <1M-nitric acid, nitrous acid (<0·04M) decomposes slowly and a correction had to be made by running blank experiments; this was not necessary in >1M-nitric acid. The principal features of the reaction are:

(1) No reaction is detected in the absence of nitrous acid.

(2) The concentration of analytical nitrous acid increases autocatalytically in reaction mixtures containing 1M-nitric acid, it is approximately constant in 1M-nitric acid, and decreases in <1M-nitric acid solutions (Fig. 1).

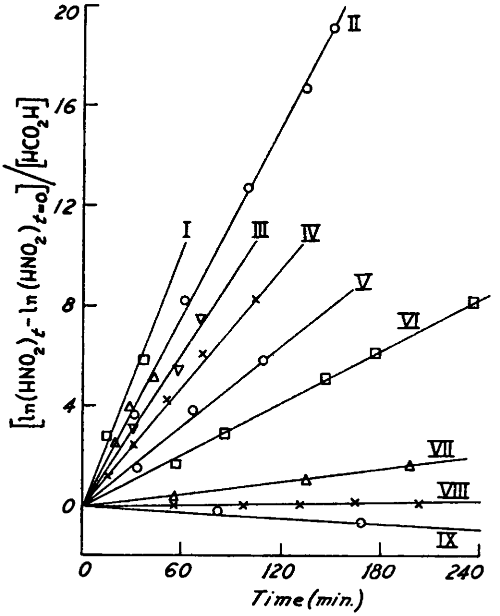
---

* Part I, preceding paper.

(3) The change of concentration of analytical nitrous acid is of first order over the range 10^{-4}—10^{-2}M, and that of formic acid is of first order over the range 0·2—1·2M. Values of the velocity constants $k' = \{d \ln (HNO_2)/dt\}/[H{\cdot}CO_2H]$ (obtained from the slopes of the linear plots of ln (HNO_2) against time) for three concentrations of nitric acid are given in Table 1. Duplicates are included in order to illustrate the reproducibility of the results.

(4) The second-order velocity constant increases slowly between [HNO_3] = 1M and 4M, it increases rapidly (19-fold) between [HNO_3] = 4M and 12·5M, and decreases (5-fold) between [HNO_3] = 12·5M and 18·4M. In <1M-nitric acid the velocity constant is negative (*i.e.*, the concentration of nitrous acid decreases during the reaction) (Table 2, Figs. 1 and 4). The variation of the velocity constant for the formation of carbon dioxide ($k' \times q$) in

FIG. 1. $[\ln (HNO_2)_t - \ln (HNO_2)_{t=0}]/[H{\cdot}CO_2H]$ *plotted against time for experiments in nitric acid.*



Acid strengths are: I, 12·5M; II, 11·1M *and* 14·1M; III, 15M; IV, 16M; V, 8·2M; VI, 18·4M; VII, 3·8M; VIII, 1·0M; IX, 0·1M.

FIG. 2. *The velocity constant for the formation of carbon dioxide plotted against* [H^+] *in different acid media.*

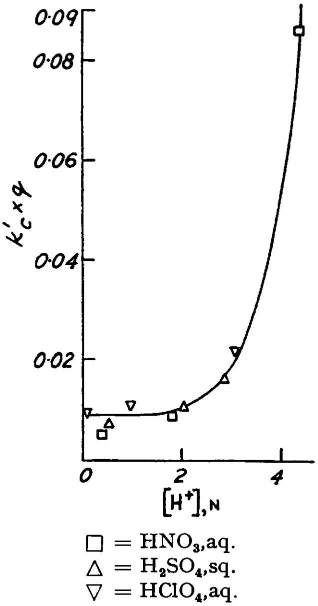


TABLE 1.

[HNO_3] = 7·9 M.								
[$H{\cdot}CO_2H$], M	0·25	0·25	0·61	0·61	1·21	1·21		
k' (min.$^{-1}$ mole^{-1} l.)	0·047	0·047	0·047	0·046	0·056	0·054		
[HNO_3] = 11·0 M.								
[$H{\cdot}CO_2H$], M	0·24	0·25	0·26	0·61	0·61	1·19	1·22	
k' (min.$^{-1}$ mole^{-1} l.)	0·132	0·133	0·138	0·131	0·139	0·151	0·139	
[HNO_3] = 12·5 M.								
[$H{\cdot}CO_2H$], M	0·21	0·22	0·25	0·53	0·53	0·62	0·65	1·13
k' (min.$^{-1}$ mole^{-1} l.)	0·157	0·146	0·148	0·155	0·149	0·158	0·137	0·148

TABLE 2.

[HNO_3], M	0·1	0·44	2·0	3·8	4·2	7·9	9·6	11·0
$k' \times 10^2$	−0·4	−0·8	0·59	0·78	0·85	4·7	9·0	13·0
[HNO_3], M	12·3	13·3	14·1	15·0	16·0	16·7	18·4	
$k' \times 10^2$	16·0	14·8	12·7	10·9	8·2	7·0	3·5	

[The two negative values for k' are not strictly comparable because the initial concentration of nitrous acid in the two experiments was different (see Part I).]

1—6M-aqueous nitric acid (*i.e.*, $\approx$1—4N with respect to $[H^+]$) is quantitatively similar to the change of the corresponding velocity constant ($k_c' \times q$) for the reaction between nitrous acid and formic acid in aqueous sulphuric and perchloric acids in the same range of acidity (Fig. 2). (Values of $k_c' \times q$ are inaccurate owing to the large experimental error in the determination of CO_2.)

(5) The ratio of the amount of carbon dioxide formed to the change of concentration of analytical nitrous acid, $q = \Delta(CO_2)/\Delta(HNO_2)$, varies with the concentration of nitric acid (Table 3).

TABLE 3.

$[HNO_3]$, M	0·04	0·44	1·0	2·0	4·2	8·9	9·4	13·9	15·1
q	−0·5	−0·7	∞	1·3	1·1	1·1	0·9	0·9	0·9

(6) The reaction is accelerated by addition of salts (Table 4).

TABLE 4.

$[H{\cdot}CO_2H] = 0{\cdot}52$M, $[HNO_3] = 3{\cdot}8$M.

Salt added	(None)	1·71M-$NaNO_3$	3·0M-$NaNO_3$	1·13M-Na_2SO_4	2·25M-Na_2SO_4	2·0M-$NaClO_4$
$k' \times 10^2$ ...	0·78	1·24	1·95	1·17	1·97	2·60

DISCUSSION

No reaction appears to take place in the absence of nitrous acid and the value of the second-order velocity constant for the formation of carbon dioxide ($k' \times q$) in aqueous nitric acid is similar to that of the corresponding velocity constant in other mineral acids. Nitric acid therefore cannot take part in the rate-determining step and its function is, presumably, the oxidation of the initial products of the reaction between nitrous acid and formic acid, which are probably NO and H·CO·O or HNO. Possible reaction schemes are therefore :

$$H{\cdot}CO_2H + HNO_2 = H{\cdot}CO{\cdot}O + NO + H_2O \qquad (1)$$

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

$$H{\cdot}CO{\cdot}O + HNO_3 = NO_2 + CO_2 + H_2O \qquad (2b)$$

$$2NO + HNO_3 + H_2O = 3HNO_2 \qquad (3)$$

or

$$H{\cdot}CO_2H + HNO_2 = CO_2 + HNO + H_2O \qquad (4)$$

$$HNO + HNO_3 = 2HNO_2 \qquad (5)$$

If nitric oxide is the initial reduction product, and if α is the fraction of nitric oxide reoxidised according to (3), $q = \Delta(CO_2)/\Delta(HNO_2) = 1/(3\alpha - 2)$. The rate of oxidation of nitric oxide by nitric acid is known to increase with the concentrations of nitric acid (*idem, ibid.*). If the limiting value $\alpha = 0$ were attained in very dilute nitric acid, q should be $-0{\cdot}5$; and as α increases from 0 to 1, q should change from $-0{\cdot}5$ through ∞ to 1. The experimentally observed values of q do in fact exhibit this behaviour (Table 3). Qualitatively similar results would be observed if HNO were the initial reaction product, but in this case the limiting value [pertaining to no reoxidation of HNO by (5)] would be $-1{\cdot}0$. The experimental results therefore indicate that the reaction proceeds by (1), (2*a*), and (3), although initial reduction of nitrous acid to HNO, followed by partial reoxidation of the latter to nitrous acid, cannot be definitely excluded. Measurement of the velocity of oxidation of nitric oxide by nitric acid of different concentrations would permit a more definite distinction between the alternative reaction schemes. The kinetic results for the reaction (3) obtained by Abel, Schmid, and Babad (*loc. cit.*) cannot be used here for quantitative calculations because their experimental conditions were too different.

The Nature of Analytical Nitrous Acid in Nitric Acid.—Equilibria involving aqueous nitric acid, nitrous acid, and oxides of nitrogen have been studied mainly by determining the composition of the vapour phase above the solution (Sanfourche, *Ann. Chim.*, 1924, **10**, 1; Burdick and Freed, *J. Amer. Chem. Soc.*, 1921, **43**, 518; Abel, Schmid, and Stein, *Z. Elektrochem.*, 1930, **36**, 692) and by E.M.F. measurements (Pick, *Z. Elektrochem.*, 1920, **26**, 193; Vetter, *Z. anorg. Chem.*, 1949, **260**, 246). Apart from Vetter, these authors are in general agreement about the qualitative features: in very dilute nitric acid, nitrous acid decomposes according to $3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$, the equilibrium being established only if a constant pressure of nitric oxide is maintained above the solution; in moderately concentrated nitric acid, nitrous acid is largely dehydrated, $2HNO_2 \rightleftharpoons N_2O_3 + H_2O$; and in concentrated nitric acid, nitrous acid is converted into dinitrogen tetroxide: $HNO_2 + HNO_3 \rightleftharpoons N_2O_4 + H_2O$. Oxygen compounds of tervalent nitrogen are stated to be virtually absent in nitric acid of greater concentration than ≈ 11M (Sanfourche, *loc. cit.*; Foerster and Koch, *Z. angew. Chem.*, 1908, **21**, 2171).

Ultra-violet absorption spectra of analytical nitrous acid in nitric acid of different concentrations were measured and are shown in Fig. 3. In up to 6M-nitric acid the extinction curve between $\lambda = 3350$ Å and 4000 Å is quantitatively that of molecular nitrous acid (cf. Part I, Fig. 2); as the concentration of nitric acid is increased from 6 to 14M, the characteristic absorption bands of HNO_2 give way to a strong general absorption which increases towards the short waves. In 15·7M-nitric acid, this general absorption is about 1·5—2 times as intense but otherwise similar to the absorption of dinitrogen tetroxide in carbon tetrachloride in the same region (Fig. 3). Unfortunately, the strong absorption of nitric acid made measurements at $\lambda < 3500$ Å impossible. It seems probable that the strong absorption in nitric acid is caused by dinitrogen tetroxide for the following reasons:

(1) The good first-order dependence over a considerable range of (HNO_2) indicates that at the low concentrations of analytical nitrous acid used in these experiments, only a small fraction could be present as dinitrogen trioxide. This is supported by approximate calculations of the equilibrium $N_2O_3 + H_2O \rightleftharpoons 2HNO_2$ in aqueous solution (J. V. L. Longstaff, Thesis, London, 1953).

(2) There is strong evidence for the formation of molecular compounds between N_2O_4 and HNO_3 in concentrated nitric acid (Bousfield, *J.*, 1919, **115**, 48; Klemenc and Rupp, *Z. anorg. Chem.*, 1930, **194**, 65); this could easily account for enhanced absorption of N_2O_4 in nitric acid (as compared with N_2O_4 in carbon tetrachloride) and for the fact that the absorption continues to increase with increasing concentration of nitric acid above 14M, which cannot be accounted for by further conversion of HNO_2 into N_2O_4.

It is therefore assumed that analytical nitrous acid is present as HNO_2 in up to 6M-nitric acid and that it is progressively converted mainly into N_2O_4 (and NO_2) as the concentration of nitric acid is increased. Since all traces of the HNO_2 absorption maxima have disappeared in 13—14M-nitric acid, it is concluded that conversion into N_2O_4 is complete at this concentration. A rough estimate for the ratio $[N_2O_4]/(HNO_2)$ in different media can be obtained from the prominence of the inflexion of the curve caused by the absorption bands of HNO_2 (Fig. 3). In order to avoid systematic errors in calculations based on these values, two smooth curves were drawn as closely as possible through the estimated lower and upper limits of the ratio $[N_2O_4]/(HNO_2)$, shown in Table 5. The curves were used to calculate upper and lower limits of $[N_2O_4]/(HNO_2)$ for any concentration of nitric acid between 6 and 14M.

TABLE 5.

$[HNO_3]$, M ...	3·75	6·2	8·6	10·4	12·3	12·9	14·0
$[N_2O_4]/(HNO_2)$	0	0·01—0·05	0·10—0·15	0·4—0·6	0·85—0·95	0·93—1·00	1·00

Kinetics.—The following equilibria (not all of which are independent of each other) are known or assumed to exist in aqueous nitric acid containing analytical nitrous acid (cf. Abel, Schmid, and Stein, *loc. cit.*; Goulden and Millen, *J.*, 1950, 2620; Hughes, Ingold, and Reed, *J.*, 1950, 2430):

$$H_2O + HNO_3 \rightleftharpoons H_3O^+ + NO_3^- \quad . \quad (7)$$

$$HNO_2 + HNO_3 \rightleftharpoons N_2O_4 + H_2O \quad . \quad (8)$$

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \quad . \quad (9)$$

$$HNO_2 + H_3O^+ \rightleftharpoons H_2NO_2^+ + H_2O \quad (10)$$

$$H_2NO_2^+ \rightleftharpoons NO^+ + H_2O \quad . \quad (11)$$

$$2HNO_2 \rightleftharpoons H_2O + N_2O_3 \quad . \quad (12)$$

$$N_2O_3 \rightleftharpoons NO + NO_2 \quad . \quad (12a)$$

$$N_2O_4 \rightleftharpoons 2NO_2 \quad . \quad . \quad (13)$$

$$NO^+ + NO_2 \rightleftharpoons N_2O_3^+ \quad . \quad . \quad (14)$$

The entities which may be regarded as possible oxidising agents are therefore HNO_2, NO^+, $H_2NO_2^+$, $N_2O_3^+$, N_2O_3, N_2O_4, NO_2. Attack by N_2O_3 or $N_2O_3^+$ would not lead to the observed first order with respect to analytical nitrous acid.

A rate-determining step involving N_2O_4 would be compatible with the observed order in concentrated nitric acid, where $(HNO_2) \propto [N_2O_4]$ but would lead to second order with respect to (HNO_2) in dilute nitric acid [where N_2O_4 is formed by (13), (12*a*), and (12)]. Attack by NO_2 might lead to first order with respect to (HNO_2) in dilute nitric acid (if no NO accumulates in the reaction mixture; see Part I) and to the order $\frac{1}{2}$ in concentrated nitric acid. It would therefore seem possible that the effective oxidising agents in dilute and in concentrated nitric acid are NO_2 and N_2O_4, respectively. No evidence of a mixed order at intermediate concentrations of nitric acid was, however, observed. Further evidence against the reactivity of N_2O_4 or NO_2 is provided by the similar increase of the rate of the reaction with acidity in nitric acid and in other mineral acids (Fig. 2) although the concentration of N_2O_4 and NO_2 must be greater in nitric acid because of (8). Comparison of the absorption spectra of analytical nitrous acid in >6M-aqueous nitric and other aqueous mineral acids of similar strength shows that the concentration of N_2O_4 is larger in the nitric acid media (Fig. 3 and Part I, Fig. 2).

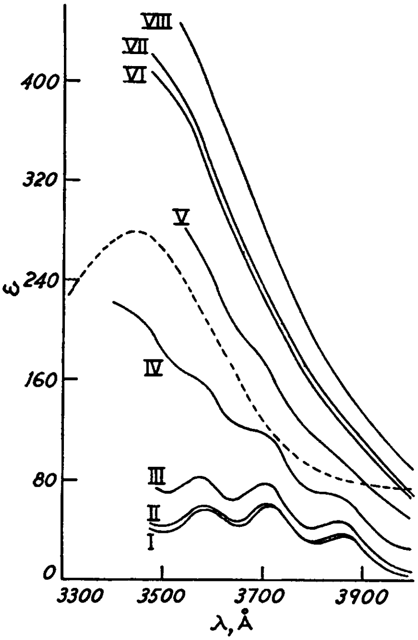


FIG. 3. *Absorption spectra of " analytical " nitrous acid in nitric acid :* I, 3·75M; II, 6·2M; III, 8·2M; IV, 10·4M; V, 12·3M; VI, 12·9M; VII, 13·0M; VIII, 18·7M.
---- Absorption spectrum of dinitrogen tetroxide in carbon tetrachloride.

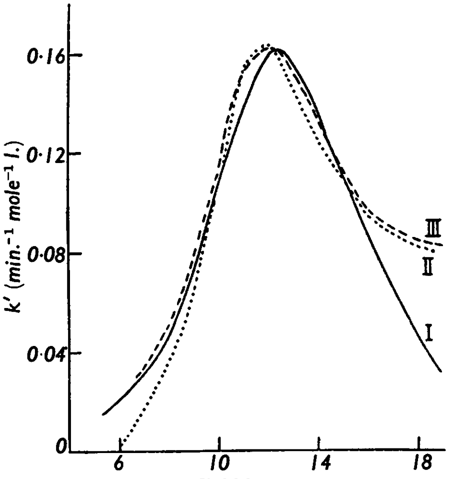
The remaining entities, NO^+, $H_2NO_2^+$, and HNO_2, would give rise to first order with respect to (HNO_2).

The slow increase of the reaction velocity with hydrogen-ion concentration in <2·5M-nitric acid excludes rate-determining steps involving NO^+ or $H_2NO_2^+$ and it is therefore concluded that in these media the rate-determining step is a bimolecular reaction between HNO_2 and $H{\cdot}CO_2H$ (see also Part I, p. 2604).

The 19-fold change of the velocity constant between 4 and 18M-nitric acid seems too great to be accounted for by a possible change of reactivity of HNO_2 (caused by solvent effects) and must be attributed to the appearance of a more reactive entity. The similar increase of the velocity of oxidation with acidity in nitric, sulphuric, and perchloric acids (Fig. 2) at $[H^+] > 2{\cdot}5$M, and the decrease of the concentration of HNO_2 in >6M-nitric acid, indicate that NO^+ and $H_2NO_2^+$ are, respectively, the principal oxidising agents in these solutions.

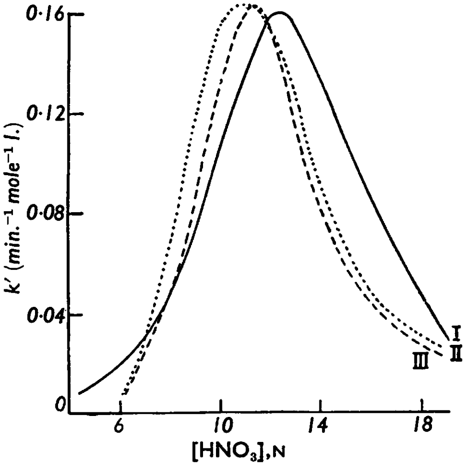
If this is so, the variation of the velocity constant in 4—18M-nitric acid (Fig. 4) should be related to a similar variation of [NO^+] or [$H_2NO_2^+$]. Expressions for the activities of NO^+ and $H_2NO_2^+$ in terms of the activities of HNO_2 and HNO_3 and the equilibrium constants for (7)—(11) can easily be derived (J. V. L. Longstaff, Thesis, London, 1953). The formulæ which are not likely to be seriously affected by the fact that (12), (12*a*), (13), and (14) are disregarded show qualitatively that a_{NO^+} and $a_{H_2NO_2^+}$ tend to zero for both small and large concentrations of nitric acid and must consequently pass through a maximum at some intermediate concentration. Information about the equilibrium constants and activity coefficients necessary for the evaluation of these formulæ is not available. The following features, however, emerge from qualitative considerations: Owing to the operation of the equilibria (10) and (11) [or (10), (8), and (9)] the concentrations of NO^+ and $H_2NO_2^+$ increase with acidity at low concentrations of nitric acid. Since the activity of nitric acid increases more rapidly than the activities of NO_3^- and H_3O^+, the consumption of HNO_2 by the continuing movement of (8) to the right causes (10) to shift to the left. The conversion of HNO_2 into N_2O_4 affects the concentration of NO^+ through (9) and (11) in opposite ways; [NO^+], however, eventually decreases owing to the repression of the dissociation of N_2O_4 by the continued increase of the activity of NO_3^-.

FIG. 4. *Comparison between the observed variation of the velocity constant* (*k*′) *and of the calculated activity of* NO^+ *with* [HNO_3].



I, k'; II, const. a_{NO^+} (lower limit); III, const. a_{NO^+} (upper limit).

FIG. 5. *Comparison between the observed variation of the velocity constant* (*k*′) *and of the calculated activity of* $H_2NO_2^+$ *with* [HNO_3].



I, k'; III, const. $a_{H_2NO_2^+}$ (lower limit); II, const. $a_{H_2NO_2^+}$ (upper limit).

A semiquantitative calculation of the variation of the activities of NO^+ and $H_2NO_2^+$ with [HNO_3] for a given value of (HNO_2) can be carried out by means of: (1) the relations $a_{NO^+} = K_1 a_{N_2O_4}/a_{NO_3^-}$; $a_{H_2NO_2^+} = K_2 a_{NO^+} a_{H_2O}$; (2) the partial pressures of HNO_3 and H_2O above aqueous nitric acid at 25° [obtained by interpolation from Klemenc and Nagel's data (*Z. anorg. Chem.*, 1928, **155**, 257); Wilson and Miles's more recent results (*Trans. Faraday Soc.*, 1940, **36**, 356) could only have been used after some rather inaccurate extrapolation]; and (3) the approximate values for [N_2O_4]/(HNO_2) estimated from the ultra-violet absorption spectra.

Since $a_{H_3O^+} \cdot a_{NO_3^-} \propto a_{H_2O} \cdot a_{HNO_3} \propto p_{HNO_3} \cdot p_{H_2O}$ (where p_{HNO_3} and p_{H_2O} are the partial vapour pressures), the usual (admittedly dubious) assumption $a_{NO_3^-} = a_{H_3O^+}$ leads to $a_{NO_3^-} = a_{H_3O^+} \propto (p_{H_2O} \cdot p_{HNO_3})^{\frac{1}{2}}$.

If it is further assumed that the activity coefficient $f_{N_2O_4}$ does not vary rapidly with [HNO_3], $a_{N_2O_4}$ may be replaced by [N_2O_4] (estimated spectroscopically). Apart from a constant factor, values of $a_{NO^+}/(HNO_2)$ and $a_{H_2NO_2^+}/(HNO_2)$ can be calculated in this way.

To facilitate comparison between the variation of the velocity constant, on the one hand, and $a_{\mathrm{NO^+}}/(\mathrm{HNO_2})$ and $a_{\mathrm{H_2NO_2^+}}/(\mathrm{HNO_2})$, on the other, with the concentration of nitric acid, the constant factors were adjusted so as to make the maxima of k', $a_{\mathrm{NO^+}}/(\mathrm{HNO_2})$, and $a_{\mathrm{H_2NO_2^+}}/(\mathrm{HNO_2})$ numerically equal. Table 6 contains sets of values calculated respectively from the maximum and minimum estimates for $[\mathrm{N_2O_4}]/(\mathrm{HNO_2})$. They are plotted together with k' against $[\mathrm{HNO_3}]$ in Figs. 4 and 5. If the upper limits for $[\mathrm{N_2O_4}]/(\mathrm{HNO_2})$ are used, the maxima for k', $a_{\mathrm{NO^+}}/(\mathrm{HNO_2})$, and $a_{\mathrm{H_2NO_2^+}}/(\mathrm{HNO_2})$ occur at $[\mathrm{HNO_3}] = 12{\cdot}5$, 12·1, and 11·3M, respectively. The lower limits for $[\mathrm{N_2O_4}]/(\mathrm{HNO_2})$ lead to maxima at 12·1M for $a_{\mathrm{NO^+}}$ and 11·6M for $a_{\mathrm{H_2NO}^+}$.

TABLE 6.

$(\mathrm{HNO_3})$, M	Const. $a_{\mathrm{NO^+}}/(\mathrm{HNO_2})$ lower limit	Const. $a_{\mathrm{NO^+}}/(\mathrm{HNO_2})$ upper limit	Const. $a_{\mathrm{H_2NO_2^+}}/(\mathrm{HNO_2})$ lower limit	Const. $a_{\mathrm{H_2NO_2^+}}/(\mathrm{HNO_2})$ upper limit
6·2	2·5	4·6	0·5	0·8
8·6	5·1	6·5	7·6	9·6
10·4	12·0	13·9	14·0	16·1
11·3	15·7	15·5	16·4	16·4
12·3	15·7	16·2	14·5	15·0
12·7	—	16·0	—	13·7
12·9	14·8	15·6	12·5	13·0
13·0	14·8	—	12·1	—
14·0	—	13·1	—	9·2
15·0	10·5	11·3	6·3	6·8
16·0	8·7	9·4	4·5	4·8
17·0	8·3	8·9	3·6	3·9
18·0	7·8	8·5	2·8	3·1

In view of the approximations made in the calculations, the agreement between the general shape and the position of the maximum of the curves for k' and $a_{\mathrm{NO^+}}/(\mathrm{HNO_2})$ is considered satisfactory. At low acidities $a_{\mathrm{NO^+}}$ is considerably smaller than k'; this is consistent with the hypothesis that $\mathrm{HNO_2}$ is the oxidising entity in these media; and the too gradual decrease of $a_{\mathrm{NO^+}}$ to the right of the maximum may well be accounted for by a decrease of $a_{\mathrm{N_2O_4}}$ in this region owing to molecular compound formation or solvation. A more rapid decrease of $a_{\mathrm{NO^+}}$ at high acidities can, in fact, be obtained by allowing for an equilibrium $\mathrm{HNO_3} + \mathrm{N_2O_4} \rightleftharpoons \mathrm{HNO_3,N_2O_4}$ (postulated by Klemenc and Rupp, *loc. cit.*).

Agreement between the curves for $a_{\mathrm{H_2NO_2^+}}$ and k' is less satisfactory; there seems to be no plausible way of accounting for the too rapid decrease of $a_{\mathrm{H_2NO_2^+}}$ to the right of the maximum if $\mathrm{H_2NO_2^+}$ were the oxidising entity.

It is therefore probable that the rate-determining step consists of a bimolecular reaction between $\mathrm{HNO_2}$ and formic acid in 0·1—2·5M-nitric acid, and mainly between $\mathrm{NO^+}$ and formic acid at higher concentrations in up to 18M-nitric acid.

Salt Effects.—The acceleration of the reaction by added salts (Table 4) is probably due to the increase of the concentration of charged entities $\mathrm{NO^+}$, $\mathrm{H_2NO_2^+}$, and to an increase of activity of non-polar entities $(\mathrm{HNO_2})$ with increasing ionic strength. The accelerating effect of added nitrate is perhaps unexpected because of the equilibrium $\mathrm{NO^+} + \mathrm{NO_3^-} \rightleftharpoons \mathrm{N_2O_4}$. However, the experiment was carried out in 3·8M-nitric acid where the concentration of dinitrogen tetroxide is very small, and it is conceivable that in this medium the general salt effect and the effect on the equilibrium (8) (shift to the right) might outweigh the effect caused by the repression of the dissociation of dinitrogen tetroxide by nitrate ion.

Experimental.—The experimental procedures were as described in Part I. Nitric acid was freed from nitrous acid by passage of a current of carbon dioxide or nitrogen for 30 min. in the dark. The concentration of analytical nitrous acid can thus be reduced to 1×10^{-5}M which is sufficient to ensure convenient reaction times in >6M-nitric acid without the addition of sodium nitrite.

Ultra-violet spectra were recorded with a Hilger Uvispek spectrograph in 1-cm. cells. Extinction curves of nitrous acid in nitric acid of different concentrations were measured with nitric acid of the appropriate strength in the solvent cell. The extinction curves in >3M-nitric acid did not change noticeably during the recording of the spectrum (1—2 hr.).

The dinitrogen tetroxide solution was prepared by heating " AnalaR " lead nitrate and by passing the vapour through phosphoric oxide into carbon tetrachloride dried with phosphoric oxide.

We are grateful to Prof. Gwyn Williams for his interest in this work, and we thank the Department of Scientific and Industrial Research for a maintenance grant (to J. V. L. L.). We acknowledge financial assistance from Imperial Chemical Industries Limited and from the Central Research Fund of the University of London.

ROYAL HOLLOWAY COLLEGE (UNIVERSITY OF LONDON),
ENGLEFIELD GREEN, SURREY.

[*Received, March 4th,* 1954.]