238. *The Kinetics of Oxidation by Nitrous and Nitric Acid. Part III.* Oxidation of Oxalic Acid by Nitrous Acid.*

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The velocity of the reduction of nitrous acid in aqueous solution containing oxalic acid and oxalate is of first order with respect to " analytical " nitrous acid and of approximately first order with respect to mono-oxalate ion ($HC_2O_4^-$). Between 35° and 55° the second-order constant equals $5{\cdot}05 \times 10^{14}$ exp $(-26{,}900/\mathbf{R}T)$ l. mole^{-1} sec.$^{-1}$.

It was hoped to measure the rate of oxidation of oxalic acid in media containing nitric and/or nitrous acid over a range of conditions similar to those under which the oxidation of formic acid had been studied.[1,2] This proved to be impossible because of the slowness of the reaction in the accessible range of concentrations of oxalic acid. Satisfactory velocities were only obtained when an appreciable fraction of the oxalic acid in the reaction mixture was ionised, *i.e.*, mainly between pH 1 and 2.

The reaction was followed by measuring the rate of disappearance of " analytical " nitrous acid † (initial concentration usually $4{\cdot}7 \times 10^{-3}$M) in media containing 0·3—0·7M-oxalic acid partly neutralised by lithium hydroxide and made up to an ionic strength approx. 0·9M by addition of lithium perchlorate. The disappearance of nitrous acid was also measured in blank experiments, *i.e.*, in media containing no oxalic acid but equalling the corresponding reaction mixtures in acidity, ionic strength, and initial nitrous acid concentration.

Table 1. Initial (HNO_2) = $4{\cdot}7 \times 10^{-3}$M. Total ionic strength : approx. 0·9M.

				Calc. from K' = 0·05			Calc. from K' = 0·1		
Total oxalate * (M)	LiOH (M)	$k' \times 10^3$ (min.$^{-1}$)	$k_b \times 10^3$ (min.$^{-1}$)	[H$^+$] (M)	[HOx$^-$] (M)	$k \times 10^3$ (l. mole^{-1} (min.$^{-1}$)	[H$^+$] (M)	[HOx$^-$] (M)	$k \times 10^3$ (l. mole^{-1} min.$^{-1}$)
	At 35°.								
0·58	0·54	1·55	0·25	0·003	0·54	2·87	0·005	0·545	2·82
0·80	0·64	1·81	0·225	0·012	0·65	2·78	0·01	0·65	2·79
0·80	0·44	1·55	0·282	0·035	0·48	3·22	0·03	0·47	3·29
0·80	0·29	1·26	0·281	0·06	0·35	3·59	0·10	0·39	3·23
0·78	0·128	0·915	0·267	0·11	0·24	3·71	0·165	0·29	3·16
	At 45°.								
0·58	0·54	5·15	0·75	0·003	0·54	9·5	0·005	0·545	9·4
0·80	0·68	7·19	0·74	0·008	0·69	10·4	0·015	0·70	10·3
0·58	0·32	4·40	0·51	0·03	0·35	12·6	0·05	0·37	11·8
0·80	0·41	5·47	0·58	0·04	0·45	12·1	0·06	0·47	11·5
0·80	0·29	4·92	0·39	0·06	0·35	14·0	0·10	0·39	12·6
0·80	0·10	3·54	0·42	0·13	0·23	15·4	0·17	0·27	13·1
	At 55°.								
0·51	0·48	17·1	0·99	0·002	0·48	35·6	0·005	0·49	34·9
0·61	0·38	19·3	1·17	0·03	0·41	47·0	0·03	0·41	47·0
0·60	0·30	17·0	0·94	0·05	0·35	48·6	0·06	0·36	47·3
0·80	0·31	17·9	1·18	0·06	0·37	48·5	0·10	0·41	43·7
0·68	0·14	12·6	0·97	0·09	0·23	54·8	0·14	0·28	45·0
0·80	0·10	12·6	0·58	0·13	0·23	54·8	0·17	0·27	46·7
0·68	0·086	11·3	0·86	0·12	0·21	53·9	0·17	0·26	43·5

* Concn. of oxalic acid + concn. of oxalate ions.

(1) Reproducible linear plots of log (HNO_2) *versus* time were obtained for reaction mixtures and controls in all cases; the slope of the former ($k_{exp.}$) usually exceeded that of

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* Part II, *J.*, 1954, 2610.

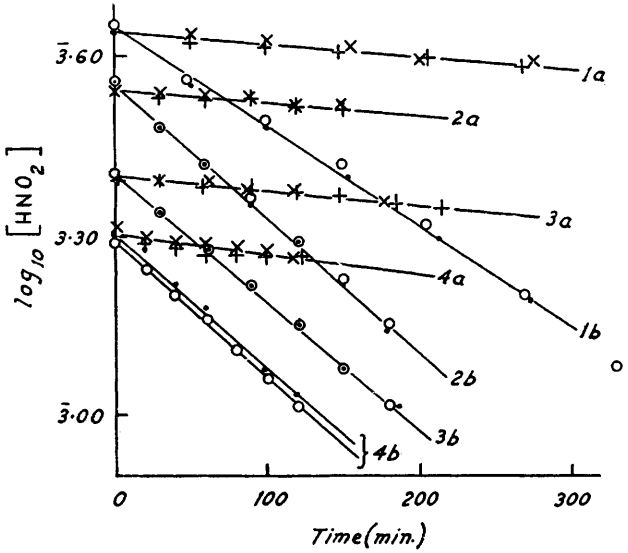
† The concentration of " analytical " nitrous acid, denoted by (HNO_2), is the sum of the concentrations of all molecular entities which diazotise aromatic amines under the conditions of the colorimetric method used.

[1] Part I, Longstaff and Singer, *J.*, 1954, 2604.

[2] Part II, *idem*, *ibid.*, p. 2610.

the latter (k_b) by a factor of more than five. Some typical plots are shown in Fig. 1. Since the self-decomposition of nitrous acid by disproportionation ($3HNO_2 = HNO_3 + 2NO + H_2O$) has been shown to be of the fourth order with respect to " analytical " nitrous acid,[3] it seems probable that the nitrous acid in the blank experiments disappeared by evaporation. If one assumes that the rate of evaporation of nitrous acid in the reaction mixtures and in the blank experiments is approximately equal, the first-order constant for the reduction of nitrous acid (k') is given by $k' = k_{exp.} - k_b$. Results obtained at 35°, 45°, and 55° at initial (HNO_2) $= 4\cdot7 \times 10^{-3}$M and ionic strength 0·9M (approx.) are shown in Table 1. In contrast to the reduction of nitrous acid by formic acid, k' shows no trend with initial concentration of nitrous acid (Table 2).

FIG. 1.



○ Runs at 45°. ● Duplicate runs at 45°. + × Corresponding blanks.

The ordinate scale of plots 2*a*—*b*, 3*a*—*b*, and 4*a*—*b* is displaced downwards by 0·1, 0·2, and 0·3 unit respectively.

Run	Total oxalate (M)	LiOH (M)	Initial (HNO_2) (M × 10^3)
1	0·75	0·10	4·70
2	0·65	0·29	4·70
3	0·42	0·32	4·00
4	0·31	0·54	4·00

TABLE 2.

No $LiClO_4$ added.

	Total oxalate (M)	LiOH (M)	Initial (HNO_2) (M × 10^3)	$k' \times 10^3$ (min.$^{-1}$)	Calc. from $K' = 0\cdot1$ [H^+] (M)	 [HOx^-] (M)	 $k \times 10^3$ (min.$^{-1}$)
At 35°	0·66	0·64	4·0	1·54, 1·59	0·003	0·64	2·44
	0·66	0·64	2·0	1·52, 1·54	0·003	0·64	2·40
	0·66	0·64	1·0	1·51, 1·50	0·003	0·64	2·35
At 45°	0·52	0·48	4·0	5·94, 6·06	0·07	0·49	1·22
	0·52	0·48	2·0	5·33, 5·34	0·07	0·49	1·09
	0·52	0·48	1·0	5·79, 5·47	0·07	0·49	1·15

(2) Comparison between columns 3 and 4 of Table 1 suggests that k' may be proportional to the concentration of mono-oxalate ion ($HC_2O_4^- = HOx^-$). The dissociation constant of oxalic acid and the activity coefficients of $H_2C_2O_4$, H^+, and $HC_2O_4^-$ at the required ionic

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[3] Abel and Schmid, *Z. phys. Chem.*, 1928, **132**, 55; **134**, 279.

strength and temperatures are not known. When the concentration of mono-oxalate is calculated from $K' = K \cdot f_{H_2Ox}/f_{H^+} \cdot f_{HOx^-}[H^+][HC_2O_4^-]/[H_2C_2O_4] = 0{\cdot}05$, which is the value[4] of the thermodynamic dissociation constant of oxalic acid at zero ionic strength and 25°, the second-order constant $k = k'/[HC_2O_4^-]$ increases slowly with acidity. Approximately constant values for k are obtained when the calculation is carried out for all temperatures with $K' = 0{\cdot}1$ (a value which in view of the high ionic strength is not unreasonable) (Table 1). The low values of k at the lowest acidities can be ascribed to partial dissociation of nitrous acid (dissociation constant at 25° $= 5 \times 10^{-4}$ and quite possibly higher at the prevailing temperatures and ionic strengths). Thus, if $K_{HNO_2} = 5 \times 10^{-4}$ and $[H^+] = 7 \times 10^{-3}$, approximately 7% of the nitrous acid is dissociated.

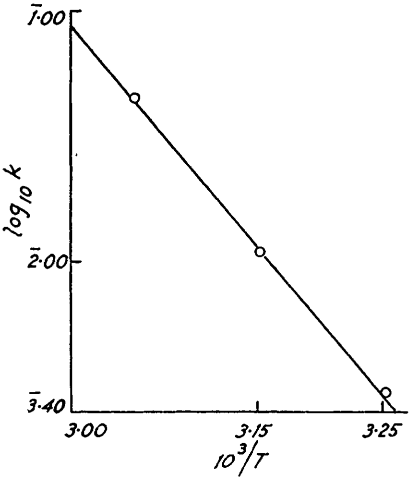
TABLE 3.

No $LiClO_4$ added.

	Total oxalate (M)	LiOH (M)	$k' \times 10^3$ (min.$^{-1}$)	Calc. from $K' = 0{\cdot}1$ $[H^+]$ (M)	$[HOx^-]$ (M)	$k \times 10^3$ (min.$^{-1}$)
At 35°	0·66	0·64	1·56	0·003	0·64	2·46
	0·58	0·53	1·55	0·004	0·53	2·92
At 45°	0·58	0·53	5·89	0·004	0·53	11·1
	0·58	0·32	4·63	0·03	0·35	13·2

(3) The omission of lithium perchlorate from the reaction mixture has no marked effect on k (Tables 2 and 3).

FIG. 2.



(4) A plot of log k (35°, 45°, and 55°) *versus* $1/T$ gave a straight line. For each temperature the mean was taken of the values of k shown in Table 1, except the value obtained at the lowest acidity. It is found that $k = 5{\cdot}05 \times 10^{14} \exp(-26{,}900/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$.

(5) Efforts to determine the stoicheiometry of the reaction by measuring the ratio of carbon dioxide formed to nitrous acid consumed were unsuccessful. Some results were however obtained showing that this ratio was not greater than 2 and not smaller than 1.

Discussion.—Since analytical nitrous acid in the reaction mixtures consists almost entirely of molecular nitrous acid (except at the lowest acidities employed), the first-order dependence on "analytical" nitrous acid excludes N_2O_3 or NO_2 as possible oxidising entities; oxidation by N_2O_3 would lead to the second order with respect to (HNO_2), while oxidation by NO_2 would be compatible with a first-order reaction only in the initial stages of the reaction when $[NO_2] \propto (HNO_2)^2/[NO]$ and $[NO_2] = [NO]$, but not, as was observed, up to 70% conversion of nitrous acid. Oxidation of oxalate ion by NO^+ must be excluded

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[4] Parton and Gibbons, *Trans. Faraday Soc.*, 1939, **35**, 542.

because of the slow (if any) variation of k with acidity and with ionic strength. This leaves molecular nitrous acid as the probable oxidising agent.

EXPERIMENTAL

" AnalaR " perchloric acid, sodium nitrite, oxalic acid, and B.D.H. lithium hydroxide were used without further purification.

Dissolved oxygen was removed as described in Part I.

Reaction mixtures were prepared by mixing solutions of known strengths of oxalic acid and of dilithium oxalate (prepared from oxalic acid and lithium hydroxide) in the required proportions, checking the excess of oxalic acid by alkalimetric titrations, adding calculated amounts of stock solutions of lithium perchlorate and of sodium nitrite, and diluting to 100 ml. with water.

It was found that a large volume of gas phase in contact with reaction mixture leads to appreciable loss of nitrous acid, *i.e.*, large and not always reproducible values for k_b. By using 100 ml. volumetric flasks as reaction vessels the volume of gas phase is kept sufficiently small—even after withdrawal of eight 2 ml. samples—to ensure small and reproducible values of k_b.

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