938. *Oxidations of Organic Compounds with Quinquevalent Vanadium. Part VIII.*[1] *The Oxidation of Oxalic Acid.*

By J. R. Jones and William A. Waters.

Bobtelsky and Glasner[2] reported that the rate of oxidation of oxalic acid by quinquevalent vanadium is diminished by the addition of mineral acid, reaches a minimum value at about 3·5M-[H$^+$] and thereafter increases. A kinetic study confirms this observation and shows that oxalic acid must form with vanadium(v) a number of complexes of different stabilities. In the absence of mineral acid a complex, vanadium(v),$(H_2C_2O_4)_2$, readily oxidises further oxalic acid. In acid solutions this complex breaks down; in concentrated mineral acid the oxidation becomes a bimolecular reaction between the ion $V(OH)_3^{2+}$ and $H_2C_2O_4$.

Previous investigations of this series have shown that oxidations of organic compounds by quinquevalent vanadium occur only in acid solution and involve cations, such as VO_2^+ or $V(OH)_3^{2+}$, which first combine with organic substrates to form co-ordinated complexes; these then decompose homolytically, yielding a derivative of quadrivalent vanadium and an organic radical. In general, these oxidations exhibit acid catalysis, the ion $V(OH)_3^{2+}$ being a much more potent oxidant than VO_2^+, and they are of the first order with respect to the organic substrate.

Bobtelsky and Glasner,[2] however, reported that the rate of oxidation of oxalic acid by quinquevalent vanadium can be diminished by addition of hydrochloric or sulphuric acid, reaching a minimum value at about 3·5M-hydrogen ion concentration. They also found that the oxidation was of the first order with respect to vanadium(v), but approximately of the second order with respect to oxalic acid. Since, both the negative acid catalysis and the reaction order with respect to the oxalic acid, appeared to be unique, we have investigated this oxidation in greater detail. Our results, which accord with the account given by Bobtelsky and Glasner, show that the unusual kinetic features of the reaction are due to the formation of a seriex of complexes between vandium(v) and oxalic acid, the stabilities of which are pH-dependent.

Results

The stoicheiometry of the overall reaction accords with the equation

$$2V^{V} + H_2C_2O_4 = 2V^{IV} + H_2O + 2CO_2$$

but we have been unable to adduce any experimental evidence of the transient formation of organic radicals, or of radical-ions such as $HC_2O_4\cdot$, $\cdot C_2O_4^-$ or $\cdot CO_2^-$, since the mixture formed during this oxidation of oxalic acid, unlike those given by manganic salts[3] or by Fenton's reagent,[4] does not promote the chain reaction between oxalic acid and mercuric chloride or

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[1] Part VII, *J.*, 1961, 630.

[2] Bobtelsky and Glasner, *J. Amer. Chem. Soc.*, 1942, **64**, 1462.

[3] Drummond and Waters, *J.*, 1953, 2836.

[4] Weiss, *Discuss. Faraday Soc.*, 1947, **2**, 188.

the polymerisation of vinyl cyanide. However, we do not consider that this negative evidence of radical formation necessarily indicates that a 2-electron oxidation, such as

$$V^{V} + H_2C_2O_4 \xrightarrow[\text{Slow}]{} V^{III} + 2H^+ + 2CO_2$$

$$V^{III} + V^{V} \xrightarrow[\text{Fast}]{} 2V^{IV}$$

is involved; the oxalic acid radical may be oxidised so rapidly by V^V that its independent existence cannot be demonstrated by the tests mentioned above.

The oxidations of oxalic acid by vanadium(v) were all carried out in solutions in which

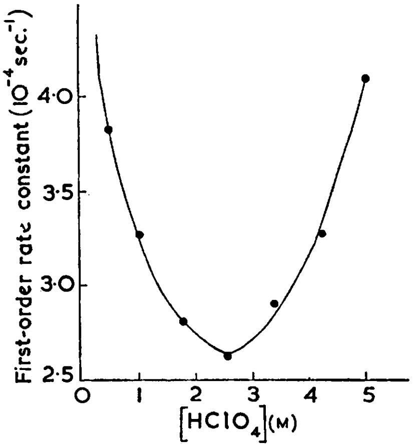


FIG. 1. Oxidation of oxalic acid in perchloric acid at 50°.
$[V^V] = 0{\cdot}05$M. $[H_2C_2O_4] = 0{\cdot}122$M. Ionic strength = 5·1.

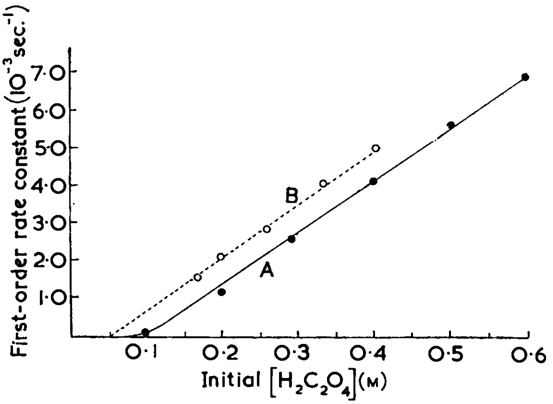


FIG. 2. Oxidation of oxalic acid at 40° in the absence of mineral acid.
Ionic strength = 2·1. (A) Initial $[V^V] = 0{\cdot}05$M. (B) Initial $[V^V] = 0{\cdot}025$M.

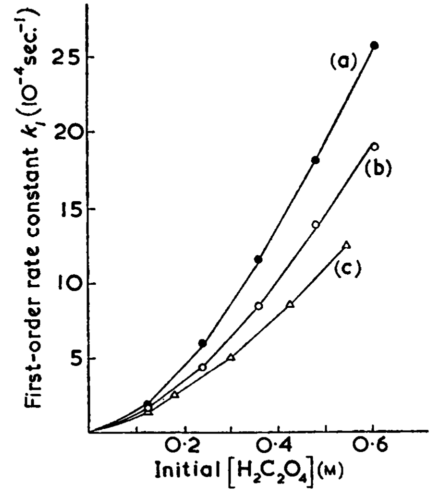


FIG. 3. Oxidation of oxalic acid at 40° in dilute perchloric acid.
Initial $[V^V] = 0{\cdot}05$M. (a) $[HClO_4] = 0{\cdot}50$M; ionic strength = 3·1. (b) $[HClO_4] = 1{\cdot}00$M; ionic strength = 3·1; (c) $[HClO_4] = 1{\cdot}45$M; ionic strength = 3·55.

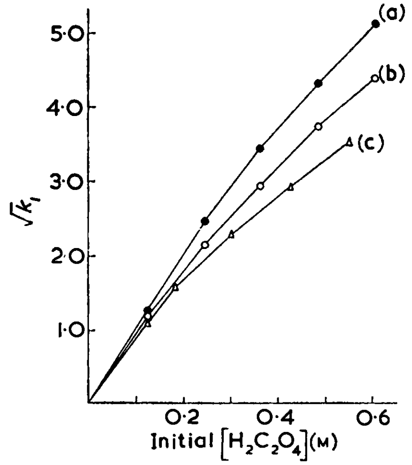


FIG. 4. Curves of Fig. 3 plotted to show the approximation to a second-order rate-dependence on oxalic acid.

oxalic acid was present in large excess over vanadium and were all found to follow strict first-order kinetics with respect to the vanadium for at least 85% of the oxidation.

The general trend of the oxidation in the presence of perchloric acid is shown by Fig. 1. Fig. 2 shows the relation between the rate of oxidation and the initial concentration of the oxalic acid in solutions made up from ammonium metavanadate with no added mineral acid; the curves of Fig. 3 show corresponding rates of oxidation in the presence of 0·5M-, 1·0M-, and 1·45M-perchloric acid respectively. Fig. 4 shows that the results plotted in Fig. 3 correspond approximately to a reaction having second-order kinetics with respect to total oxalic acid concentration, especially at the lower values, and explains how Bobtelsky and Glasner came to their conclusions mentioned above.

Table 1 shows that, in the absence of mineral acid, ammonium oxalate can replace oxalic acid and also that the addition of 0·10M-perchloric acid has very little effect on the oxidation rate. Table 2, however, shows how slightly larger amounts of perchloric acid decrease the oxidation rate when an excess of oxalic acid is present.

It is clear, from Fig. 2, that in the pH range 1—2 a complex of vanadium(V) with two molecules of oxalic acid must be reacting with a third molecule of oxalic acid before any vanadium(IV) is formed, but the potentiometric titration of oxalic acid with alkali in the presence of ammonium metavanadate (Fig. 5) shows that the complex formation effects no significant pH change in this region.

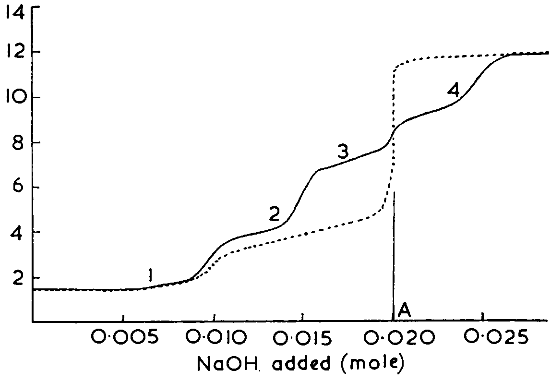


FIG. 5. Potentiometric titration of oxalic acid and its vanadium(V) complexes.

Full line: The initial solution contained 0·01 mole of oxalic acid (0·20M) and 0·0025 mole of ammonium metavanadate (0·05M). Broken line: The initial solution contained 0·01 mole of oxalic acid (0·20M) only. The titration was carried out with 1·0M-sodium hydroxide.

Fig. 3 indicates that the vanadium(V)–oxalic acid complex, formed in neutral solution, breaks down gradually to other complexes as the acidity of the medium is increased; and finally Table 3 indicates that at high acidity (4·2M) the reaction approaches one of first order

TABLE 1.

Oxidation of oxalic acid by aqueous ammonium metavanadate (0·05M) at 40°. Ionic strength of all solutions, 2·1.

	First-order rate constants, k_1 (10^{-3} sec.$^{-1}$)		
Oxalic acid (M)	Only $NaClO_4$ added	$(NH_4)_2C_2O_4$ added (0·05M)	$HClO_4$ added (0·10M)
0·101	0·125	0·320	0·22
0·201	1·18	1·77	1·08
0·401	4·15	—	4·17

TABLE 2.

Effect of varying perchloric acid concentrations in the range 0·0—1·0M.

$[V^V]$ = 0·05M. $[H_2C_2O_4]$ = 0·121M. Ionic strength = 2·1. Temp. = 40°.

$[HClO_4]$ (M)	0·00	0·10	0·20	0·30	0·40	0·50	0·80	1·0
10^4k_1 (sec.$^{-1}$)	3·17	2·92	2·50	2·22	1·98	1·83	1·60	1·44

TABLE 3.

Reaction order with respect to oxalic acid in 4·2M-perchloric acid at 50°.

$[V^V]$ = 0·05M. Ionic strength = 5·1.

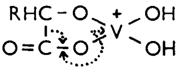
Oxalic acid (M)	0·024	0·049	0·073	0·097	0·122
$10^3k_2 = k_1/[H_2C_2O_4]$	2·17	2·29	2·42	2·60	2·71

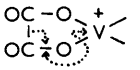
with respect to oxalic acid even at low concentrations of the latter. As Fig. 1 shows, the oxidation then becomes an acid-catalysed process, just as would be expected for a reaction involving $V(OH)_3^{2+}$ rather than VO_2^+.

DISCUSSION

Other studies [1,3] of oxidations of organic molecules by vanadium(V) have indicated that formation of a cyclic transition complex (*e.g.*, I) favours the movement of an electron to a positively charged vanadium centre. Consequently, for oxidation of oxalic acid one

(I)

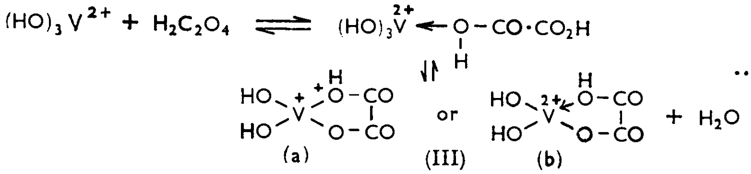




(II)

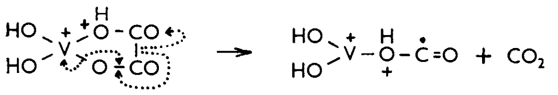
may suggest that the oxidisable complex is more likely to contain the cyclic group (II) than a linear group HO·CO·CO·V$\lessgtr$ in which there is no structural assistance to 1-electron movement.

Now at acidities over 4N with respect to hydrogen ion the oxidation of oxalic acid appears to be a reaction of normal type, *i.e.*, of the first order with respect to both $[H^+]$ and [Oxalic acid]. Under these conditions it is rational to consider that the active oxidant



..... (A)

is the uncomplexed ion $V(OH)_3^{2+}$, to write the equilibria as annexed (A), and to suggest that the doubly charged cation (IIIa or b), formed to a slight extent only, can readily undergo the 1-electron redistribution (B) to a compound of vanadium(IV) having a bound radical, ·CO·O⁻, which would very easily reduce another ion of vanadium(V).

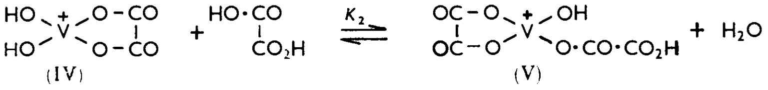


..... (B)

As the acidity is lowered the cation (III), being a strong acid, would lose proton giving a complex (IV) which can also be formed by combination of oxalic acid and the abundantly present ion VO_2^+. Since VO_2^+ is but a feeble oxidant, the ion (IV) can be regarded as a stable complex, whilst again the equilibrium constant K_1, which must be acid-dependent, may be small at hydrogen-ion concentrations over 1·0N.

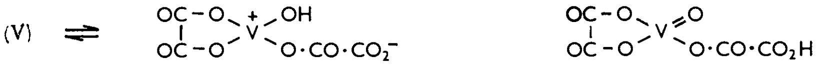
$$VO_2^+ + H_2C_2O_4 \overset{K_1}{\rightleftharpoons} (IV)$$

However, at lower acidities the hydroxyl groups of the ion (IV) may react with a further molecule of oxalic acid, and, since the carboxyl group is electrophilic, complex (V) would be less stable than complex (IV) and may decompose as shown.



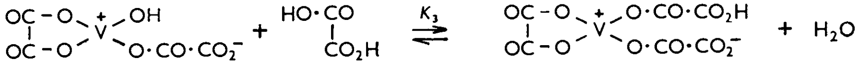
Under conditions in which both K_1 and K_2 are small, we have $[(IV)]$ = approx. $K_1[VO_2^+][H_2C_2O_4]$ and $[(V)]$ = approx. $K_1K_2[VO_2^+][H_2C_2O_4]^2$, so that the decomposition of the complex ion (V) could appear to be roughly of the second order with respect to oxalic acid. More exactly, however, the kinetics appertaining to the slow decomposition of the complex (V) would accord with the experimental data shown in Fig. 3.

As the acidity is lowered still further, oxalic acid would begin to ionise, and so likewise would the acid complex (V); the latter would then give an electrically neutral complex



(VI) (VII)

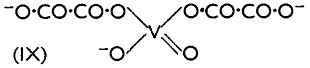
(VI or VII) in which the electron-attracting properties of the vanadium atom would be very small. The tendency of this complex to lose oxalic acid would also diminish as the environment becomes more neutral. However, it may combine with yet another molecule of oxalic acid:



(VI) (VIII)

and since Fig. 2 shows that a complex of formula $(H_2C_2O_4)_2,V^V$ is an oxidant of oxalic acid it may be concluded that a cyclic ternary complex such as (VIII) easily decomposes to a compound of vanadium(IV). This is rational since complex (VIII), unlike (VII), necessarily has a positively charged vanadium at its centre.

Our present evidence indicates that oxidation of oxalic acid is possible down to pH 2, but does not occur at still lower acidities. The potentiometric titrations (Fig. 5) indicate that the dissociation constant of a complex (VI) is of the same order as that of oxalic acid, but that in the pH range 2—6 another complex, *e.g.*, (IX) is formed which consumes two equivalents of alkali in decomposing to free oxalate, $C_2O_4^{2-}$, and metavanadate, VO_3^-, anions which are present at the equivalence point A. This neutralisation (part 3 of the curve) can be represented as:



(IX) $+ 2OH^- \longrightarrow 2C_2O_4^{2-} + VO_3^- + H_2O$

Since in this pH range there is no reduction of vanadium(V), the complex (IX) must be stable to reduction by oxalate anions. The four sections of the potentiometric titration curve thus represent:

(1) $H_2C_2O_4 + OH^- \rightleftharpoons HC_2O_4^- + H_2O$

$(VII, VI) + 3OH^- \rightleftharpoons (IX) + 2H_2O$

(2) $2HC_2O_4^- + 2OH^- \rightleftharpoons 2C_2O_4^- + 2H_2O$

(3) $(IX) + 2OH^- \rightleftharpoons 2C_2O_4^- + VO_3^- + H_2O$

(4) $VO_3^- + OH^- \rightleftharpoons HVO_4^{2-}$

$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$

EXPERIMENTAL

Standardised solutions of " AnalaR " oxalic acid were used. Vanadium(V) solutions were made up, as in previous work, from " AnalaR " ammonium metavanadate and " AnalaR " perchloric acid; " recrystallised grade " sodium perchlorate (Hopkin and Williams) was used for adjustment of ionic strengths.

Reactions, carried out in a thermostat regulated within ±0·1°, were followed titrimetrically as in Part I,[5] but care was taken not to expose solutions containing ferric oxalate (formed by the quenching of V^V with Fe^{2+}) to direct sunlight in which this salt quickly decomposes regenerating Fe^{2+}. If such solutions had to be retained for more than a few minutes they were stored in the dark. The rates of the direct oxidations of oxalic acid by vanadium(V) were not affected by exclusion of light.

Potentiometric titrations were made at room temperature with a Doran pH meter with one glass electrode and one saturated calomel electrode in the titration vessel.

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[5] Littler and Waters, *J.*, 1959, 1299.