54. *Oxidations of Organic Compounds by Quinquevalent Vanadium. Part XII.*[1] *Oxidation of Propionaldehyde, n-Butyraldehyde, and Isobutyraldehyde.*

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

Oxidation of isobutyraldehyde is an acid-catalysed reaction of zero order with respect to vanadium(v); the rate-determining reaction is shown, by comparison with bromination and iodination, to be enolisation of the aldehyde. Propionaldehyde and n-butyraldehyde are oxidised more slowly than they enolise and the empirical rate equation is of the form

$$-d[V^v]/dt = k[V^v][\text{Aldehyde}]/(1 + K[\text{Aldehyde}])$$

indicating rapid, reversible formation and slow breakdown of an equimolar complex of the reactants.

Oxidation of aliphatic aldehydes by 1-electron-abstracting reagents, such as potassium ferricyanide,[2] manganic pyrophosphate,[3] and the radical $\cdot O\cdot N(SO_3K)_2$,[4] has been reported to occur at rates which are of zero order with respect to the oxidant: these reactions have been considered to proceed by attack on the enolic forms of the aldehydes or on the enolate anions. For analogous reactions of ketones it now appears that a distinction must be made between the alkaline or weakly acid oxidants mentioned above and strongly acidic reagents such as cobaltic and manganic sulphates or quinquevalent vanadium in perchloric acid.[5,6] There is clearly a great difference between the ease of electron release from an enolate anion to give a neutral mesomeric radical $R\cdot CH{:}CH\cdot O\cdot \longleftrightarrow \cdot CHR\cdot CHO$ and the ease of hydrogen loss from an enol molecule, $R\cdot CH{:}CH\cdot OH$; consequently there

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[1] Part XI, *J.*, 1962, 2068.
[2] Speakman and Waters, *J.*, 1955, 40.
[3] Drummond and Waters, *J.*, 1953, 440.
[4] Allen and Waters, *J.*, 1956, 1132.
[5] Hoare and Waters, *J.*, 1962, 971.
[6] Littler, *J.*, 1962, 832.

might be mechanistic differences in the modes of oxidation of aliphatic aldehydes under (i) alkaline and (ii) strongly acid conditions. Indeed Shorter's study[7] of oxidation by ceric sulphate indicated that oxidation of acetaldehyde proceeds to the extent of 90% to give formic acid, presumably *via* the enol, and the rest more directly to give acetic acid; and Bawn and White[8] have suggested that cobaltic sulphate oxidises acetaldehyde to acetic acid *via* the acetyl radical.

A comparative study of oxidation rates by acid solutions of vanadium(v) and of acid-catalysed enolisation rates has therefore been made for propionaldehyde, n-butyraldehyde, and isobutyraldehyde; its results, though not conclusive, are given below.

RESULTS

Stoicheiometry.—In M-sulphuric acid at 25° the maximum amounts of vanadium(v) reduced per mole of aldehyde were propionaldehyde 3·9 mol., n-butyraldehyde 8·1 mol., and isobutyraldehyde 2·7 mol. Acetaldehyde was not attacked under these conditions. In all cases a small amount of insoluble material, presumably a polymer, was formed. This information indicates that the overall reactions approach:

$$\mathrm{Me{\cdot}CH_2{\cdot}CHO + 4V^V \longrightarrow Me{\cdot}CHO + H{\cdot}CO_2H}$$
$$\mathrm{Me{\cdot}CH_2{\cdot}CH_2{\cdot}CHO + 8V^V \longrightarrow Me{\cdot}CHO + 2H{\cdot}CO_2H}$$
$$\mathrm{Me_2CH{\cdot}CHO + 4V^V \longrightarrow Me_2CO + H{\cdot}CO_2H}$$

Acetone and formic acid were identified as oxidation products of isobutyraldehyde. Propionic and butyric acid cannot be the immediate oxidation products of the other two aldehydes since they are not attacked by vanadium(v) under these conditions.

Kinetics.—Precipitation of insoluble polymers occurred to a slight extent in all the oxidations, but did not appear immediately on mixing of the reactants. With propionaldehyde and butyraldehyde there were indications of a short induction period and, when the aldehyde was in excess, the disappearance of vanadium(v) followed first-order kinetics for about 50% of the reaction. With isobutyraldehyde there was no induction period, and vanadium(v) disappeared at a constant rate for >90% of the reaction. The oxidations proceeded at the same rate under nitrogen as they did in air; but under nitrogen precipitation of polymers did not begin until after partial oxidation.

Table 1 shows that the initial rate of oxidation of isobutyraldehyde is of the first order with respect to the aldehyde, and Fig. 1 shows that it is of the first order with respect to the acidity of the solution up to about 3M. In Fig. 1 there is also a comparison of the rates of oxidation of isobutyraldehyde by vanadium(v) with the rates of its reactions with bromine and iodine. The two last are complex, for aqueous solutions of halogens act to some extent as oxidising agents by reactions which are of the first order with respect to the halogen:

TABLE 1.

Oxidation of isobutyraldehyde with vanadium(v) at 25°. (1·0M-perchloric acid; ionic strength, 3·1M).

[Aldehyde] (M)	0·088	0·176	0·220	0·440
10^6k_0 (moles of V^V sec.$^{-1}$ l.$^{-1}$)	0·84	1·63	1·95	3·75
10^6k_0/[Aldehyde]	9·5	9·3	8·9	8·5

$$\mathrm{R{\cdot}CHO + Br_2 + H_2O \longrightarrow R{\cdot}CO_2H + 2HBr}$$

However, Fig. 1 shows that at acidities over about 1·2N, in which the formation of the very active oxidants, hypobromous and hypoiodous acid, would be suppressed, the acid-dependence of all three reactions is the same. If it is assumed that the rate of oxidation by halogen is independent of acid concentration in this range, it follows that oxidation by vanadium(v) occurs at the same rate as substitution by iodine and bromine, *i.e.*, at a rate controlled by the velocity of enolisation.

For the straight-chain n-aldehydes the evidence is not so conclusive. For the first half

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[7] Shorter, *J.*, 1950, 3425.

[8] Bawn and White, *J.*, 1951, 349.

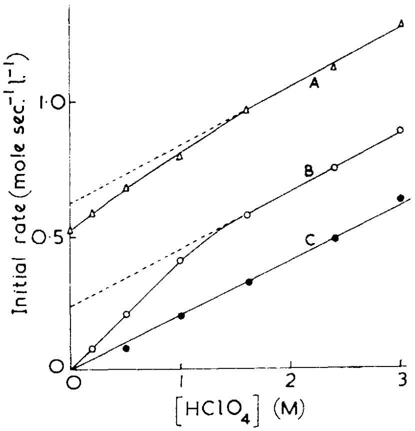


FIG. 1. Reactions of isobutyraldehyde with (A) 0·05N-bromine, (B) 0·05N-iodine, and (C) 0·05N-vanadium(V) at 25°. Dependence of the reaction rate on acidity: isobutyraldehyde = 0·22M; ionic strength maintained at 3·2M.

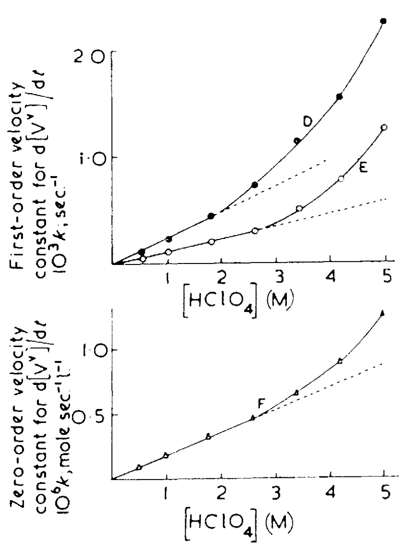


FIG. 2. Dependence on acid concentration of the rates of oxidation of aldehyde by vanadium(V) at 25°. Ionic strength maintained at 5·1M. First-order rate constants for (D) 0·220M-propionaldehyde and (E) 0·110M-n-butyraldehyde. Zero-order rate constant for (F) 0·220M-isobutyraldehyde.

of their reactions the rate was of the first order with respect to vanadium(V); later it decreased slightly. Table 2 shows that the rate dependence on aldehyde concentration fits the empirical

TABLE 2.

Oxidations of n-aldehydes with vanadium(V) at 25°: dependence of first-order rate constants on aldehyde concentration.

$1/k_1 = a/[\text{Aldehyde}] + b$. Initial $[V^V]$ = 0·050M.

(i) Propionaldehyde in 1·0M-perchloric acid; ionic strength = 3·1M.

[Aldehyde] (M)	0·069	0·104	0·138	0·176	0·220	0·264	0·308	0·352	0·460
$10^5 k_1$ (sec.⁻¹)	3·37	4·68	6·53	7·88	9·25	10·60	11·50	13·00	15·08
$10^5 k_1$/[Aldehyde]	48·8	45·1	47·3	44·8	42·0	40·2	37·3	36·9	34·3
$10^{-3} a$ (when $b = 2·60 \times 10^3$)	1·87	1·95	1·75	1·77	1·80	1·80	1·87	1·79	1·80

(ii) Propionaldehyde in 3·0M-perchloric acid; ionic strength = 3·1M.

[Aldehyde] (M)	0·069	0·104	0·138	0·176	0·264	0·352
$10^5 k_1$ (sec.⁻¹)	9·85	13·7	17·0	20·2	28·7	36·7
$10^5 k_1$/[Aldehyde]	142	132	123	115	109	104
$10^{-3} a$ (when $b = 1·50 \times 10^3$)	0·60	0·59	0·60	0·61	0·52	0·43

(iii) n-Butyraldehyde in 1·0M-perchloric acid; ionic strength = 3·1M.

[Aldehyde] (M)	0·088	0·131	0·175	0·219
$10^5 k_1$ (sec.⁻¹)	3·50	4·92	6·33	7·42
$10^5 k_1$/[Aldehyde]	39·8	37·5	36·2	33·9
$10^{-3} a$ (when $b = 3·0 \times 10^3$)	2·24	2·27	2·24	2·29

(iv) n-Butyraldehyde in 3·0M-perchloric acid; ionic strength = 3·1M.

[Aldehyde] (M)	0·088	0·131	0·175	0·219
$10^5 k_1$ (sec.⁻¹)	9·33	13·2	17·1	20·3
$10^5 k_1$/[Aldehyde]	106	101	97·7	92·7
$10^{-3} a$ (when $b = 1·0 \times 10^3$)	0·85	0·86	0·85	0·86

equation $1/k_1 = a/[\text{Aldehyde}] + b$, which could indicate that the reactions involve rapid, reversible formation and slow decomposition of an equimolar complex:

$$\text{Aldehyde} + \text{Vanadium(v)} \overset{K}{\rightleftharpoons} \text{(Complex)} \xrightarrow{k} \text{Products}$$

for which, if [Aldehyde] $\gg$ [Vanadium(v)], we have

$$-\mathrm{d}[\mathrm{V^v}]/\mathrm{d}t = k[\mathrm{V^v}][\text{Aldehyde}]/(1 + K[\text{Aldehyde}])$$

which is of the form of the empirical rate equation given above.

Fig. 2 shows the acidity dependence of the three aldehydes in perchloric acid solutions of constant ionic strength (5·1M). At low acidities (2·5N-acid) the rates are proportional to the acid concentration, $[H_3O^+]$; and the experimental measurements cannot be correlated with Hammett's h_0 function, for $h_0 > [H_3O^+]$ in the 1—2N-acidity range. For propionaldehyde the results can be fitted to an empirical equation of the form $-\mathrm{d}[\mathrm{V^v}]/\mathrm{d}t = \text{Constant} + \mathrm{a}[H^+]^2$.

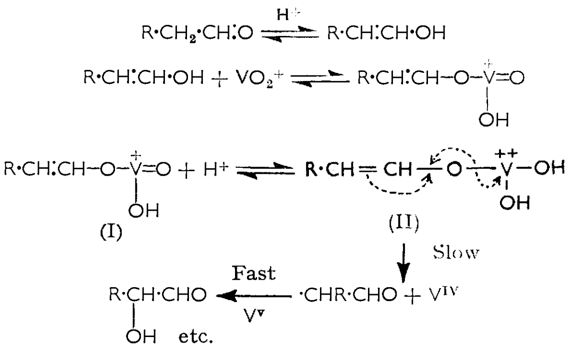
The reactions of propionaldehyde and n-butyraldehyde with iodine were found to be reversible and therefore unsuitable for the estimation of enolisation rates, and their reactions with bromine had both first- and zero-order components in both 1·0N- and 3·0N-acid. A graphical estimate has been made of the zero-order reaction rates (the enolisation rates) for both aldehydes; it was 4—5 times their rates of oxidation by vanadium(v).

DISCUSSION

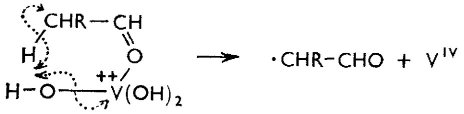
The rate of oxidation of isobutyraldehyde is independent of the concentration of vanadium(v) and can be ascribed satisfactorily to a rapid attack on the enol of the aldehyde by the cation VO_2^+. It is unlikely that $V(OH)_3^{2+}$ is the main oxidising agent since, in solutions of low acidity, it could hardly be present in sufficient concentration to react with all the enol as soon as it is formed.

The two normal aldehydes are evidently oxidised more slowly than they can be enolised, and the kinetics indicate that complex formation between the aldehyde and vanadium(v) precedes the reduction of the latter to vanadium(IV). Results in Table 2 show that about 25% of the vanadium is converted into the complex with propionaldehyde and 14% with butyraldehyde. Though the kinetic evidence does not show whether the complexes are being formed from the ketonic or the enolic form of the aldehydes it may be noted that, if the complexes were being formed from the enols, the initial rates of reaction would depend on the rates of build-up of enol concentration, and so the oxidations should have small initial induction periods.

Hence a plausible general structure for the complexes is (I). To account for the observed kinetics it must be postulated that this is stable, but that on protonation to (II) it decomposes. This scheme, however, does not account for the increase in rate in >3N-acid solution.



However, in view of recent evidence that ketones may be oxidised without enolisation direct reaction through a ketonic complex (III) cannot entirely be excluded.



(III)

EXPERIMENTAL

The aldehydes were treated with aqueous ferrous sulphate to remove peroxides, then washed with water, dried ($MgSO_4$), and fractionated under nitrogen. The kinetic studies of their oxidation were carried out by methods which have been described previously.[9]

Enolisation rates were investigated by using standardised solutions of " AnalaR " bromine in aqueous sodium bromine or of iodine in sodium iodide. At intervals aliquot parts of reacting mixtures were run into sodium hydrogen carbonate solution, and the residual free halogen was estimated with sodium thiosulphate.

One of us (J. R. J.) thanks the D.S.I.R. for a research studentship.

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[9] Littler and Waters, *J.*, 1959, 1299, 3014.