313. *Oxidations of Organic Compounds with Quinquevalent Vanadium. Part X.*[1] *The Oxidations of Acetoin and 3-Hydroxy-3-methylbutan-2-one.*

By J. R. JONES and WILLIAM A. WATERS.

Acetoin is oxidised by C–H fission, but 3-hydroxy-3-methylbutan-2-one is oxidised by C–C fission. The acid-dependence of both oxidations can be related to the Hammett acidity function. Hence it is concluded that they involve cyclic complexes.

IN Part VII[2] it was shown that quinquevalent vanadium oxidised α-hydroxy-acids, R·CH(OH)·CO_2H, by the C–C fission of a ring complex. This is also the mechanism of oxidation by vanadium(V) of ditertiary 1,2-glycols, though secondary glycols are preferably oxidised by fission of the C–H bond of an alcohol group.[3] To extend knowledge of the structural features of organic molecules which favour C–C fission by 1-electron-abstracting agents we have now examined the oxidations of acetoin, Me·CH(OH)·COMe, and 3-hydroxy-3-methylbutan-2-one, $Me_2C(OH)$·COMe, both easily effected at 25°. The former evidently involves C–H fission and the latter C–C fission; also the two reactions differ slightly in kinetic features.

TABLE 1.

Order of the reaction with respect to the acyloin.

(Reactions in 1·0M-perchloric acid at 25°; ionic strength brought to 3·1M with sodium perchlorate.) Initial [V^V] = 0·05M.

[Acetoin] (10^{-2}M)	4·2	5·9	8·4	10·1	13·4	16·8
10^3k (sec.$^{-1}$)	1·25	1·68	2·58	3·00	4·22	5·83
10^3k/[Acetoin]	29·8	28·5	30·7	29·7	31·4	34·7

[HO·CMe_2·COMe] (10^{-2}M)	4·05	5·4	8·1	13·5
10^4k (sec.$^{-1}$)	2·59	3·61	5·27	9·27
10^3k/[HO·CMe_2·COMe]	6·4	6·7	6·5	6·8

TABLE 2.

Dependence of reaction velocity on acidity (at 25°).

[Acetoin] = 0·084M; ionic strength = 3·1M.

10^3k (sec.$^{-1}$)	[$HClO_4$] (M)	10^3k (sec.$^{-1}$)	[$HClO_4$] (M)
0·675	0·2	3·73	1·4
1·12	0·4	5·31	1·8
1·52	0·6	7·00	2·2
2·08	0·8	9·03	2·6
2·60	1·0	11·2	3·0

[HO·CMe_2·COMe] = 0·135M; ionic strength = 5·1M.

10^3k (sec.$^{-1}$)	(1·15)	1·25	1·38	1·50	1·78	2·10	2·65
[$HClO_4$] (M)	0·0	0·5	1·0	1·8	3·0	3·8	5·0

When the organic compound is in excess both oxidations follow strict first-order kinetics with respect to vanadium(V) for at least 85% of their course and, as Table 1 shows, the oxidations are also of first order with respect to the α-hydroxy-ketone. Table 2 shows

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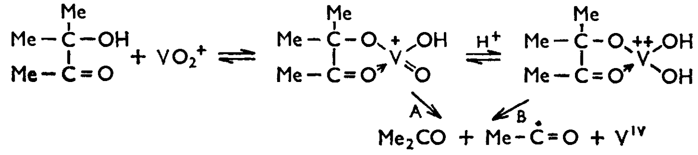
[1] Part IX, Julian and Waters, *J.*, 1962, 818.
[2] Jones, Waters, and Littler, *J.*, 1961, 630.
[3] Littler, Mallet, and Waters, *J.*, 1960, 2761.

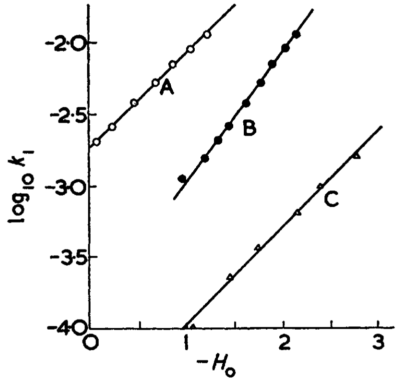
that in perchloric acid solutions of 3·1M-ionic strength oxidation of acetoin was entirely acid-catalysed whilst that of the *C*-methyl analogue was, in part, independent of the acid concentration. The Figure shows that the acid-catalysis of both substances is linearly proportional to Hammett's acidity function. Since H_0 values for perchloric acid solutions of 3·1M-ionic strength are not available, values of log *k* for the acetoin oxidation have been plotted against Paul and Long's values [4] for perchloric acid alone, and for perchloric acid–sodium perchlorate mixtures of 6·0M-ionic strength; they do not have exactly unit slope. The slope for the oxidation of the *C*-methyl compound in solutions of 5·1M-ionic strength is also low.

The *C*-methyl compound consumed only 2·0 equiv. of vanadium(V) per mole and yielded acetone: $Me_2C(OH)\cdot CO\cdot Me + 2V^V \longrightarrow Me_2CO + Me\cdot CO_2H + 2V^{IV}$. Since the kinetic features of its oxidation are identical with those observed for pinacol,[2] the annexed mechanism satisfactorily accounts for the process. Co-ordination of the vanadium atom with the oxygen of the carbonyl group can lead to a cyclic reaction complex from VO_2^+, and only a proton need be added to give the complex involved in the acid-catalysed reaction: hence the acidity dependence on the Hammett function.



A, Uncatalysed. B, Acid-catalyst.

Acetoin must be oxidised in a different manner, for it consumes 4·0 equivalents of vanadium(V) per mole and partly oxidised mixtures smell strongly of biacetyl. The reaction is thus: $Me\cdot CH(OH)\cdot COMe \longrightarrow Me\cdot CO\cdot COMe \longrightarrow 2Me\cdot CO_2H$. Tests showed that biacetyl was oxidised very much faster than is acetoin, whereas acetaldehyde, which would result from C–C fission, is oxidised more slowly than is acetoin and so cannot be an intermediate. The oxidation of acetoin to biacetyl by a 1-electron-abstracting reagent is not surprising, for this has proved to be the reaction course with alkaline cupric complexes [5] and with ferric perchlorate.[6] Neither of these reagents attacks 3-hydroxy-3-methylbutan-2-one and the two reaction mechanisms are evidently different from that indicated below. Though the oxidation of acetoin by vanadium(V) effects the change $>CH(OH) \longrightarrow >CO$ the reaction does not resemble the oxidation of cyclohexanol,[7] for which the velocity varied with the hydrogen-ion concentration and not the Hammett



Correlation of reaction velocity with the Hammett H_0 function.

A, Acetoin; H_0 for $HClO_4$; slope = 0·66.

B, Acetoin; H_0 for $[HClO_4]$–$[NaClO_4]$ of 6·0M-ionic trength; slope = 0·94.

C, $\log_{10}(k_1 - k_0)$ for $HO\cdot CMe_2\cdot COMe$; H_0 for $[HClO_4]$–$[NaClO_4]$; slope = 0·75.

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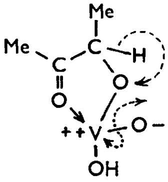
[4] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

[5] Marshall and Waters, *J.*, 1960, 2392.

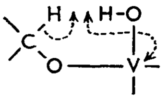
[6] Thomas, Trudel, and Bywater, *J. Phys. Chem.*, 1960, **64**, 51.

[7] Littler and Waters, *J.*, 1959, 4046.

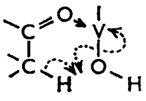
function. However, if one postulates that the reaction complex has structure (I), which is spatially similar to camphor and thus rational for quadricovalent vanadium, then all features of the oxidation are explicable, for (I) has both the cyclic structure (II) required for the oxidation of a secondary alcohol and the structure (III) which seems to be involved in the oxidation of ketones.[8] Co-ordination of the vanadium through the carbonyl group would facilitate the formation of the alcohol–vanadium complex (I) and so enhance the ease of oxidation of acetoin as an alcohol.



(I)



(II)



(III)

We have also measured the rate of oxidation of acetoin in deuterium oxide solution. In 0·38M-sulphuric acid the mean of several experiments gave $k_{D_2O}/k_{H_2O} = 1\cdot3$. This is smaller than the solvent isotope effect ($k_{D_2O}/k_{H_2O} = 2$—$2\cdot5$) expected for an acid-catalysed reaction[9] but is, correctly, >1. However acid-catalysed enolisation of acetoin could produce the molecule Me·CH(OH)·CO·CD_3 and the secondary isotope effect of the CD_3 group would decrease the reactivity of the latter molecule in comparison with that of normal acetoin.[10]

EXPERIMENTAL

Materials.—Commercial acetoin was washed with ether to remove biacetyl. The resulting dimer (Found: C, 54·7; H, 9·2. Calc. for $C_4H_8O_2$: C, 54·6; H, 9·2%) melted at 125° on rapid heating. It was dissolved in distilled water which had been boiled out and then saturated with nitrogen; solutions were stored under nitrogen (cf. ref. 5).

3-Hydroxy-3-methylbutane-2-one was prepared through 2-methylbut-3-yn-2-ol by condensation of acetone with acetylene in liquid ammonia.[11] The intermediate product, b. p. 101—102°, n_D^{20} 1·421 (yield 62%), was hydrated by means of dilute sulphuric acid and mercuric oxide;[12] the fractionated ketone had b. p. 136—138°, n_D^{20} 1·4150 (cf. lit.) and its semicarbazone had m. p. 164° (cf. lit.).

Vanadium(V) solutions in perchloric acid were prepared as described in Part VII[2] and the titrimetric procedure was that of previous Parts.[2,3,7] However, acetoin tended to be oxidised by the indicator, so for accuracy it was necessary to add one or two more drops of indicator solution just before the end-point. Initially the reactions were studied under nitrogen, but later it was found that the error due to atmospheric oxidation of acetoin during the reaction did not exceed 1—2%.

99·8% Deuterium oxide (Norske Hydro) was used to examine the solvent isotope effect and the vanadium(V) solution in this was prepared from solid ammonium metavanadate and concentrated sulphuric acid. Reaction mixtures were made up in a serum-cap-covered test-tube by use of an "Agla" micrometer syringe, the organic compound being added last. After thorough mixing the solution was transferred to a 2-mm. quartz cell, fitted into an Adkins thermostat cell holder at 25° ± 0·1°, and the increase of light absorption at 750 mμ due to the formation of vanadium(IV) was measured in a Unicam SP. 500 spectrophotometer.

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[8] Littler, *J.*, 1962, 832.

[9] Best, Littler, and Waters, *J.*, 1962, 822.

[10] Bell, "The Proton in Chemistry," Chap. XI, Methuen, London, 1959.

[11] Linstead, Elvidge, and Whalley, "Modern Techniques of Organic Chemistry," Butterworths Scientific Publns., London, 1955.

[12] Ansell, Hickinbottom, and Hyatt, *J.*, 1955, 1593.