Kinetics of the Oxidation of 2-Hydroxy-2-methylpropanoic Acid by Aquavanadium(V) Ions in Aqueous Perchlorate Media

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Measurements on the rate of oxidation of 2-hydroxy-2-methylpropanoic acid (hmpa) by V^V_{aq} in aqueous perchloric acid at high initial ratios [hmpa] : $[V^V_{aq}]$ show that the order in $[V^V_{aq}]$ is unity but that in [hmpa] lies between zero and unity. The variation of rate with acidity shows that two pathways operate, each involving a 1 : 1 complex of V^V and hmpa; one complex differs from the other by the addition of two protons. Overall values of the enthalpies and entropies of activation are determined; these are compared with values obtained for the oxidation of other substrates by V^V_{aq} and those for the oxidation of hmpa by other aqua-cations.

IN a few measurements on the rate of oxidation of 2-hydroxy-2-methylpropanoic acid (α-hydroxyisobutyric acid), hereafter referred to as hmpa, by V^V, Kemp and Waters[1] found the reaction to be first order in both $[V^V]$ and [hmpa] in 1 mol dm^{-3} $HClO_4$ at 25 °C and at an ionic strength of 3.10 mol dm^{-3}. These orders were confirmed[2] by a few measurements in aqueous sulphuric acid at 29 °C and in aqueous perchloric acid at 25 °C with an ionic strength of 5.00 mol dm^{-3}; the reaction was accelerated by increasing the acid concentration. With Mn^{III}_{aq} as oxidant in aqueous perchlorate media,[3] the rate is again first order in both $[Mn^{III}_{aq}]$ and [hmpa], provided the initial ratio of [hmpa] : $[Mn^{III}_{aq}]$ is low enough: at higher values of the initial ratio, whilst the order in $[Mn^{III}_{aq}]$ remains at unity, that in [hmpa] becomes fractional between zero and one. In these latter conditions, plots of the reciprocal of the pseudo-first-order rate constant against [hmpa]$^{-1}$ are linear and an intermediate complex $[Mn^{3+}\{(CH_3)_2COHCOOH\}]$(aq) is involved; the variation of the rate with acidity shows that a pathway involving $[Mn^{3+}\{(CH_3)_2COHCOO^-\}]$ (aq) plays a negligible part compared with that involving $[Mn^{3+}\{(CH_3)_2COHCOOH\}]$ (aq). With Ce^{IV}_{aq} as the oxidant,[4] the reaction again proceeds through an intermediate complex, but now the pathway involving $[Ce^{4+}\{(CH_3)_2COHCOOH\}]$ (aq) plays a negligible part compared with that involving $[Ce^{4+}\{(CH_3)_2COHCOO^-\}]$(aq).

We now report the results of a kinetic investigation of the oxidation of hmpa by V^V_{aq} under conditions of high initial [hmpa] : $[V^V_{ap}]$ in aqueous perchloric acid over a range of acidities and temperatures.

EXPERIMENTAL

Materials.—The purification of 2-hydroxy-2-methylpropanoic acid was as described for the oxidation by Mn^{III}_{aq}.[3] Carbonyl-free methanol and other materials for the determination of acetone were prepared as before.[5] Acrylonitrile was washed (3 × 25 cm^3) with 1 mol dm^{-3} Na[OH] to remove the phenolic stabilizer and subsequently washed four times with distilled water: after drying over anhydrous $Na_2[SO_4]$, the acrylonitrile was distilled under nitrogen at reduced pressure. All other materials were prepared and purified as described for other oxidations involving V^V_{aq}.[6-8]

Procedure.—The values of $[V^V_{aq}]$ were determined by sampling into a solution of iron(II) perchlorate with spectrophotometric estimation of Fe^{III} at 260 nm ($\varepsilon = 2.88 \times 10^3$ dm^3 mol^{-1} cm^{-1}):[9] the absorption of light derived from V^{IV}_{aq} at 260 nm was allowed for as described before.[7] The organic product, acetone, was first removed from the inorganic material by distillation under high vacuum in a closed system and then determined spectrophotometrically as the anion of the 2,4-dinitrophenylhydrazone.[5]

Rates of decay of $[V^V_{aq}]$ were followed spectrophotometrically at 350 nm as described earlier.[7]

RESULTS AND DISCUSSION

Stoicheiometry.—Values for the consumption ratio $|\Delta[V^V_{aq}]| : |\Delta[\text{hmpa}]|$ were determined at two temperatures by using an excess of V^V_{aq}. Either all the hmpa was allowed to be oxidized or the reaction was stopped by sampling into a solution containing Fe^{II}. Values for $|\Delta[\text{acetone}]| : |\Delta[V^V_{aq}]|$ were also measured by determining the [acetone] produced as the anion of the 2,4-dinitrophenylhydrazone after first distilling it off from the reaction mixture as described above. Values for these two ratios in Table 1 show that the reaction conforms to (1). Table 1 also shows that this is unaffected by the presence, or otherwise, of oxygen.

TABLE 1

Consumption ratios in 5.00 mol dm^{-3} $HClO_4$

10^3 Initial $[V^v]$/ mol dm^{-3}	θ_c/°C	$\frac{|\Delta[\text{acetone}]|}{|\Delta[V^v]|}$	$\frac{|\Delta[V^v]|}{|\Delta[\text{hmpa}]|}$
2.00	40	0.50	1.79
2.00	40		1.99
5.00	40	0.50	
10.00	40		2.07
2.00	60		1.99
2.00	60		2.09
10.00	60		2.07
5.00 *	40	0.52	
6.50 *	40		2.09
6.50 *	60		2.09

* Reaction performed under nitrogen.

$$2V^V_{aq} + (CH_3)_2COHCOOH \longrightarrow 2V^{IV}_{aq} + (CH_3)_2CO + CO_2 + H_2O \quad (1)$$

Rate Measurements.—Plots of log (optical density) against time were always linear using initial $[V^V_{aq}] = 1.00 \times 10^{-3}$ mol dm^{-3} with an excess of hmpa. It was found that the pseudo-first-order rate constant k_0 taken from the slopes of these plots was unaffected by the addition of V^{IV} or by doing the reaction under nitrogen. All the detailed results were therefore produced under aerobic conditions. Plots of k_0 against [hmpa] at constant temperature and acidity all proved to be curves, but plots of k_0^{-1} against $[\text{hmpa}]^{-1}$ at constant temperature and acidity were linear with a positive intercept on the k_0^{-1} axis; examples of these plots for 49 °C are shown in Figure 1. Values of k_0 for [hmpa] varying between 0.01 and 0.2 mol dm^{-3} and acidities varying between 1 and 5 mol dm^{-3} $HClO_4$ at a constant ionic strength of 5.00 mol dm^{-3}, achieved by the addition of sodium perchlorate, are all given in Table 2 for the temperatures 30.6, 38.0, 49.0, 55.6, and 74.5 °C. Values for the slopes and intercepts of the plots of k_0^{-1} against $[\text{hmpa}]^{-1}$ determined by the least-squares procedure are given in Table 3. It can be seen that at constant temperature both slopes and intercepts vary with acidity.

TABLE 2

Values for the pseudo-first-order rate constant k_0 (10^3 s^{-1}) for varying [hmpa], [$HClO_4$], and temperature at constant ionic strength = 5.00 mol dm^{-3}

[hmpa]/mol dm^{-3}	[$HClO_4$]/mol dm^{-3} 1.00	2.00	3.00	4.00	4.50	5.00
(*a*) Temperature = 30.6 °C						
0.200		0.360	0.492	0.61	0.67	0.76
0.100		0.240	0.320	0.380	0.380	0.473
0.080		0.200	0.250	0.300	0.330	0.376
0.060		0.170	0.190	0.240	0.250	0.305
0.040		0.130	0.152	0.170	0.180	0.196
(*b*) Temperature = 38.0 °C						
0.200	1.04		1.54	1.75		2.24
0.150	0.81		1.13	1.38		1.68
0.100	0.490			0.85		1.14
0.080	0.396		0.57	0.75		0.90
0.060	0.314		0.445	0.54		0.69
0.040	0.220		0.330	0.376		0.50
(*c*) Temperature = 49.0 °C						
0.200	2.79					
0.150				3.10		
0.100	1.45	1.59	2.00	2.60		3.25
0.080	1.19	1.31	1.92	2.05		2.90
0.060	1.01	1.13	1.41	1.74		2.35
0.040	0.74	0.81	1.06	1.26		1.71
0.020				0.68		0.90
(*d*) Temperature = 55.6 °C						
0.100	1.71	2.02				2.80
0.080	1.53	1.77	1.81	1.98		
0.060	1.24	1.38	1.49	1.75		2.05
0.040	0.89	1.06	1.22	1.28		1.55
0.020	0.54		0.71	0.78		0.95
0.010	0.309	0.317	0.377	0.436		0.55
(*e*) Temperature = 74.5 °C						
0.100	8.0	9.7	8.5	12.4		16.7
0.080	6.5	9.0		10.6		14.5
0.060		7.8		8.6		12.8
0.040	4.24	6.4	7.1			11.6
0.020	2.91	3.98	3.79	4.52		5.9
0.010	1.66	2.06	2.01	2.45		3.04

Mechanism of the Oxidation.—The curves obtained for the plots of k_0 against [hmpa] together with the linear plots of k_0^{-1} against $[\text{hmpa}]^{-1}$ suggest that the oxidation proceeds through intermediate complexes. The steps (2)—(8) are proposed. It is well established [6-8] that equilibrium (2) is involved in oxidations by V^{V}_{aq}

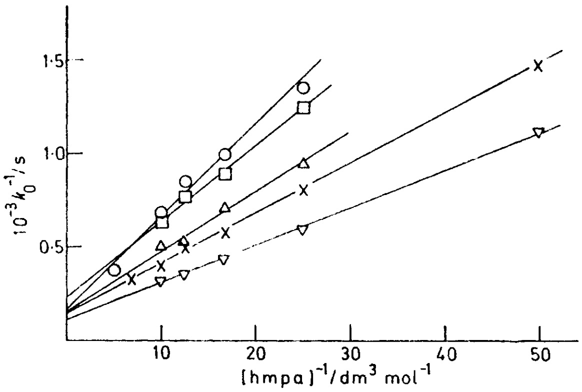

FIGURE 1 Plots of k_0^{-1} against $[\text{hmpa}]^{-1}$ at 49.0 °C and a constant ionic strength of 5.00 mol dm^{-3} with [$HClO_4$] (mol dm^{-3}) as follows: 1.00 (○); 2.00 (□); 3.00 (△); 4.00 (×); and 5.00 (▽)

$$VO_2{}^+{}_{aq} + H^+{}_{aq} \overset{K_1}{\rightleftharpoons} VO(OH)^{2+}{}_{aq} \qquad (2)$$

$$\text{hmpa}_{aq} + H^+{}_{aq} \overset{K_0}{\rightleftharpoons} \text{Hhmpa}^+{}_{aq} \qquad (3)$$

$$VO_2{}^+{}_{aq} + \text{hmpa}_{aq} \overset{\beta_1}{\rightleftharpoons} VO_2{}^+\text{hmpa}_{aq} \qquad (4)$$

$$VO_2{}^+\text{hmpa}_{aq} + nH^+ \overset{K_n'}{\rightleftharpoons} VO_2(H)_n{}^{(1+n)+}\text{hmpa}_{aq} \qquad (5)$$

$$VO_2{}^+\text{hmpa} \xrightarrow{k_1} V^{IV}{}_{aq} + (CH_3)_2\dot{C}OH + CO_2 + H^+{}_{aq} \qquad (6)$$

$$VO_2(H)_n{}^{(1+n)+}\text{hmpa}_{aq} \xrightarrow{k_n'} V^{IV}{}_{aq} + (CH_3)_2\dot{C}OH + CO_2 + (n+1)H^+{}_{aq} \qquad (7)$$

$$V^{V}{}_{aq} + (CH_3)_2\dot{C}OH \xrightarrow{k} V^{IV}{}_{aq} + (CH_3)_2CO + H^+{}_{aq} \qquad (8)$$

and (3) allows for the probable protonation of the substrate ligand in these high acidities.[10] The pre-equilibrium equations (2)—(5) are all established much faster than the rate-determining steps (6) and (7).* It is assumed that $k \gg k_1$ and $k \gg k_n'$; this is supported

TABLE 3

Values for the slopes and intercepts for the plots of k_0^{-1} against $[\text{hmpa}]^{-1}$ for varying [$HClO_4$] and temperature at a constant ionic strength = 5.00 mol dm^{-3}

[$HClO_4$]/mol dm^{-3}	Slope or intercept	θ$_c$/°C 30.6	38.0	49.0	55.6	74.5
1.00	slope		180	48.5	29.4	5.16
1.00	intercept		144	170	326	88
2.00	slope	244		39.8	29.4	4.23
2.00	intercept	1 740		241	210	55
3.00	slope	234	124	31.0	23.9	4.39
3.00	intercept	970	63	170	244	52
4.00	slope	213	105	26.6	20.5	3.56
4.00	intercept	580	59	136	250	49
4.50	slope	203				
4.50	intercept	530				
5.00	slope	189	78.4	20.2	16.1	3.06
5.00	intercept	279	89	135	223	25

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* In (6) and (7) very rapid interactions of $V^{V}{}_{aq}$ and $V^{IV}{}_{aq}$ with protons are also involved in the change $VO_2{}^+{}_{aq} \rightarrow VO^{2+}{}_{aq}$ to achieve a stoicheiometric balance in H^+ and O.

by the observation that the redox system V^V + hmpa will not initiate the polymerization of acrylonitrile in anaerobic conditions. From equations (2)—(8), the following expression can be derived for the rate of disappearance of the total added vanadium(v), where

$$-\mathrm{d}[V^V]_T/\mathrm{d}t = \frac{2(k_1 + \sum_n k_n'K_n'h^n)\beta_1[V^V]_T[\mathrm{hmpa}]_T}{(1 + K_ch)(1 + K_1h) + \beta_1[\mathrm{hmpa}]_T(1 + \sum_n K_n'h^n)} \quad (9)$$

the subscript T indicates a total added concentration and $h = [H^+{}_{aq}]$. The pseudo-first-order rate constant k_0 is given by (10), and the slopes of the linear plots of k_0^{-1}

$$1/k_0 = \frac{(1 + K_ch)(1 + K_1h)}{2(k_1 + \sum_n k_n'K_n'h^n)\beta_1[\mathrm{hmpa}]_T} + \frac{1 + \sum_n K_n'h^n}{(k_1 + \sum_n k_n'K_n'h^n)} \quad (10)$$

against $[\mathrm{hmpa}]_T^{-1}$ should be given by (11), assuming that $K_1h \ll 1$.[6-8] The most likely values for n in (5) are 1 or 2 and, using the values of the slopes in Table 3 and

$$(1 + K_ch)(\mathrm{slope})^{-1} = 2\beta_1(k_1 + \sum_n k_n'K_n'h^n) \quad (11)$$

$K_c = 0.1$ dm^3 mol^{-1},[3] (11) can be tested graphically for the dominance of equilibrium (5) with $n = 1$ or with $n = 2$. The plots of the left-hand side of equation (11) against h all give curves, whereas, in Figure 2, the plots of the left-hand side against h^2 give good straight lines with positive intercepts on the ordinate for all five temperatures. It seems reasonable to assume, therefore, that reactions (2)—(8) operate with a dominance of (5) with $n = 2$ and only $h = 2$ operating in (9). From equation (11) with $n = 2$, the intercepts in Figure 2 are equal to $2\beta_1k_1$ and the slopes equal to $2\beta_1k_2'K_2'$. The slopes and intercepts of the plots in Figure 2 have been determined from a least-squares analysis and the resulting values for β_1k_1 and $\beta_1k_2'K_2'$ are given in Table 4. Plots of log β_1k_1 and log $\beta_1k_2'K_2'$ against the reciprocal of absolute temperature give linear plots and from the slopes and intercepts of these plots determined by least squares, the enthalpies $\Delta H^\ddagger$ and entropies of activation $\Delta S^\ddagger$ are as follows: for β_1k_1, $\Delta H^\ddagger = 78 \pm 5$ kJ mol^{-1} and $\Delta S^\ddagger = -41 \pm 15$ J K^{-1} mol^{-1} and for $\beta_1k_2'K_2'$, $\Delta H^\ddagger = 82 \pm 7$ kJ mol^{-1} and $\Delta S^\ddagger = -52 \pm 20$ J K^{-1} mol^{-1}.

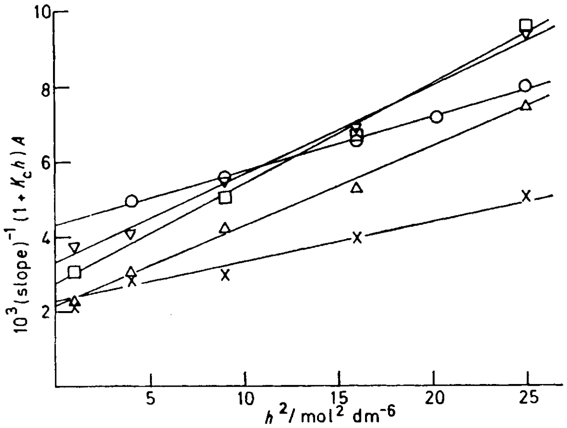

FIGURE 2 Plots of (1 + K_ch) (slope)$^{-1}$ against h^2 at a constant ionic strength of 5.00 mol dm^{-3} and temperatures (°C) as follows: 30.6, A = 1.00 (○); 38.0, A = 0.500 (□); 49.0, A = 0.100 (△); 55.6, A = 0.100 (▽); and 74.5, A = 0.010 (×) (A is a numerical adjustment parameter for the ordinate)

TABLE 4

Values of β_1k_1 and $\beta_1k_2'K_2'$ calculated from the slope and intercepts of Figure 2

θ_c/°C	10^5 β_1k_1/ dm^3 mol^{-1} s^{-1}	10^3 $\beta_1k_2'K_2'$/ dm^9 mol^{-3} s^{-1}
30.6	7.2	2.15
38.0	2.65	2.75
49.0	104	10.7
55.6	117	16.5
74.5	570	106

For $n = 2$, the pseudo-first-order rate constant is given by (12). This can be rearranged to give (13).

$$k_0 = \frac{2(k_1 + k_2'K_2'h^2)\beta_1[\mathrm{hmpa}]_T}{(1 + K_ch)(1 + K_1h) + \beta_1[\mathrm{hmpa}]_T(1 + K_2'h^2)} \quad (12)$$

$$\frac{2(k_1 + k_2'K_2'h^2)\beta_1[\mathrm{hmpa}]_T}{k_0(1 + K_ch)} = 1 + K_1h + \left\{\frac{\beta_1[\mathrm{hmpa}]_T}{(1 + K_ch)}\right\}(1 + K_2'h^2) \quad (13)$$

If $K_1h \ll 1$, as found previously[6-8] and assumed here, plots of the left-hand side of equation (13) against $[\mathrm{hmpa}]_T$ should give linear plots at constant acidity and temperature with an intercept of unity. This is found to be the case at all five temperatures; typical plots for 55.6 °C are shown in Figure 3. A least-squares analysis confirms for all temperatures that the intercept is unity: the assumption that $K_1h \ll 1$ is again confirmed.[6-8] The slopes of these plots should be given by equation

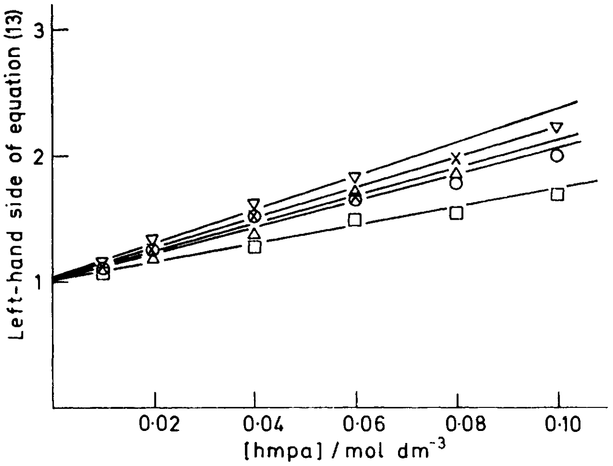

FIGURE 3 Plots of the left-hand side of equation (13) against $[\mathrm{hmpa}]_T$ at 55.6 °C and a constant ionic strength of 5.00 mol dm^{-3} with [$HClO_4$] (mol dm^{-3}) as follows: 1.00 (○); 2.00 (□); 3.00 (△); 4.00 (×); and 5.00 (▽)

(14), and plots of the left-hand side of equation (14)

$$(1 + K_ch)(\text{slope}) = \beta_1(1 + K_2'h^2) \qquad (14)$$

against h^2 should be linear with an intercept $= \beta_1$ and a slope $= \beta_1K_2'$. At this stage, the errors are becoming quite large and the spread of the points prevents a real test of equation (14) being made. Only the plots at 49.0, 55.6, and 74.5 °C for $(1 + K_ch)$(slope) against h^2 can be regarded as remotely acceptable; these are shown in Figure 4. From the intercepts on the ordinate, very approximate values for β_1 (dm^3 mol^{-1}) are 7 at 49.0 °C, 10 at 55.6 °C, and 16 at 74.5 °C: values for β_1K_2' from the slopes cannot be assessed.

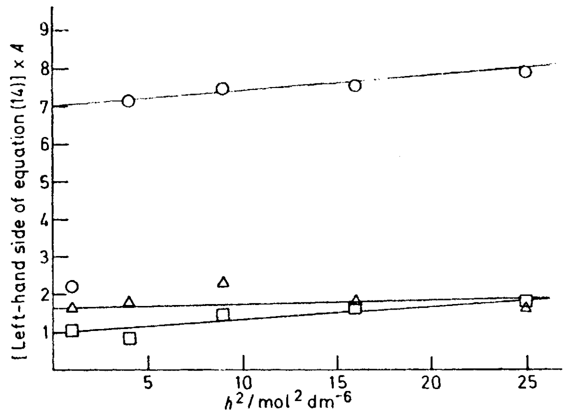

FIGURE 4 Plots of the left-hand side of equation (14) against h^2 at a constant ionic strength of 5.00 mol dm^{-3} for the following temperatures (°C): 49.0, A = 1.00 (○); 55.6, A = 0.100 (□); and 74.5, A = 0.100 (△)

The overall entropies of activation for the oxidation pathways are both negative, comparable with the overall values for $\Delta S^\ddagger$ for the oxidation of benzohydroquinone,[6] Pr^{i}OH,[7] and hydroxylamine[8] by V^V_{aq}. As remarked in the comparison[7] of the oxidations of Pr^{i}OH by various aqua-cations, that by V^V_{aq} is the only one where $\Delta S^\ddagger$ is negative (−43 J K^{-1} mol^{-1}). Likewise, for the oxidation of hmpa, the overall $\Delta S^\ddagger$ (J K^{-1} mol^{-1}) for V^V_{aq} is again negative (−41) compared with the overall positive values for Mn^{III} (81)[3] and for Ce^{IV} (25).[4] As with Pr^{i}OH, this seems to be a reflection of the different ways in which the charge changes in going from the initial to the transition states. For the latter two cations, the charge decreases, resulting in the freeing of restricted H_2O molecules and a positive $\Delta S^\ddagger$; whereas, for $VO_2{}^+{}_{aq}$ changing to $VO^{2+}{}_{aq}$, the charge increases, restricting the movement of more H_2O molecules and leading to a negative $\Delta S^\ddagger$. This result, obtained with both Pr^{i}OH and hmpa as oxidizable ligands, supports the view that the entropy of activation is largely controlled by the movement of solvent water molecules.

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