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

By Abdul Fattah M. Nazer and Cecil F. Wells,* Department of Chemistry, University of Birmingham, Edgbaston, P.O. Box 363, Birmingham B15 2TT

Measurements on the rate of oxidation of 2-hydroxy-2-methylpropanoic acid (hmpa) by V_{aq}^v in aqueous perchloric acid at high initial ratios [hmpa] : $[V_{aq}^v]$ show that the order in $[V_{aq}^v]$ 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_{aq}^v and those for the oxidation of hmpa by other aqua-cations.

In a few measurements on the rate of oxidation of 2hydroxy-2-methylpropanoic acid (a-hydroxyisobutyric acid), hereafter referred to as hmpa, by VV, Kemp and Waters¹ found the reaction to be first order in both [VV] and [hmpa] in 1 mol dm⁻³ HClO₄ 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}_{ao}] remains at unity, that in [hmpa] becomes fractional between zero and one. In these latter conditions, plots of the reciprocal of the pseudofirst-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 [Mn³⁺{(CH₃)₂COH-COO⁻}] (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 $[Ce^{4+}{(CH_{3})_{2}COHCOOH}]$ (aq) plays a negligible part compared with that involving [Ce4+{(CH3)2COH-COO⁻}](aq).

We now report the results of a kinetic investigation of the oxidation of hmpa by V_{aq}^v under conditions of high initial [hmpa]: $[V_{ap}]$ 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 cm³) with 1 mol dm⁻³ Na[OH] to remove the phenolic stabilizer and subsequently washed four times with distilled water: after drying over anhydrous Na₂[SO₄], 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 $[V_{aq}^{\nabla}]$ were determined by sampling into a solution of iron(II) perchlorate with spectrophotometric estimation of Fe^{III} at 260 nm ($\varepsilon = 2.88 \times 10^3$ dm³ mol⁻¹ cm⁻¹): ⁹ the absorption of light derived from VIV_{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 $[V_{aq}]$ were followed spectrophotometrically at 350 nm as described earlier.⁷

RESULTS AND DISCUSSION

Stoicheiometry.—Values for the consumption ratio $|\Delta[V_{aq}]| : |\Delta[hmpa]|$ were determined at two temperatures by using an excess of V_{aq}^v . Either all the hmpa was allowed to be oxidized or the reaction was stopped by sampling into a solution containing Fe^{II}. Values for $|\Delta[acetone]| : |\Delta[V_{aq}]|$ were also measured by determining the [acetone] produced as the anion of the 2,4dinitrophenylhydrazone after first distilling it off from

TABLE 1

Consumpti	on ratios in	5.00 mol dm ⁻³ H	ICIO4
10 ³ Initial [V ^v]/		Δ [acetone]	$ \Delta[V^{v}] $
mol dm ⁻³	θ _c /°C	$\Delta[V^{r}]$	$\Delta[hmpa]$
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
* Re	action perfo	rmed under nitrog	en.

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.

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

Rate Measurements.—Plots of log (optical density) against time were always linear using initial $[Vv_{aq}] = 1.00 \times 10^{-3}$ 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 [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 HClO₄ 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,

TABLE 2

Values for the pseudo-first-order rate constant k_0 (10³ s⁻¹) for varying [hmpa], [HClO₄], and temperature at constant ionic strength = 5.00 mol dm⁻³

Disease and I			[HClO ₄]/	mol dm ⁻³		
mol dm ^{-;}	³ 1.00	2.00	3.00	4.00	4.50	5.00
(a) Te	emperatu	1111 = 30.6	°C			
0.200	r	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) Te	mperatu	re = 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) Te	mperatu	re = 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) Te	emperatu	ure = 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) Te	mperatu	are = 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

38.0, 49.0, 55.6, and 74.5 °C. Values for the slopes and intercepts of the plots of k_0^{-1} against [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.

Mechanism of the Oxidation.—The curves obtained for the plots of k_0 against [hmpa] together with the



FIGURE 1 Plots of k_0^{-1} against [hmpa]⁻¹ at 49.0 °C and a constant ionic strength of 5.00 mol dm⁻³ with [HClO₄] (mol dm⁻³) as follows: 1.00 (\bigcirc); 2.00 (\square); 3.00 (\triangle); 4.00 (\times); and 5.00 (\bigtriangledown)

linear plots of k_0^{-1} against [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_{aq}^{v}

$$\operatorname{VO}_{2^{+}aq}^{+} + \operatorname{H}_{aq}^{+} \stackrel{K_{1}}{\overset{\leftarrow}{\overset{\leftarrow}{\overset{\leftarrow}{\overset{\leftarrow}}}}} \operatorname{VO}(\operatorname{OH})^{2^{+}}aq \tag{2}$$

$$hmpa_{aq} + H^{+}_{aq} \stackrel{\Lambda_{c}}{\Longrightarrow} Hhmpa^{+}_{aq}$$
(3)

$$\operatorname{VO}_{2^{+}aq}^{+} + \operatorname{hmpa}_{aq} \xrightarrow{\beta_{1}} \operatorname{VO}_{2^{+}} \operatorname{hmpa}_{aq}$$
(4)

$$\operatorname{VO}_2^+\operatorname{hmpa}_{\operatorname{aq}} + n \operatorname{H}^+ \stackrel{K_n'}{\longrightarrow} \operatorname{VO}_2(\operatorname{H})_n^{(1+n)+}\operatorname{hmpa}_{\operatorname{aq}} (5)$$

$$O_2^{+hmpa} \xrightarrow{k_1} V^{IV}_{aq} + (CH_3)_2 COH + CO_2 + H^{+}_{aq}$$
(6)

V

$$\frac{\operatorname{VO}_{2}(\mathrm{H})_{n}^{(1+n)}+\operatorname{hmpa}_{\mathrm{aq}}}{\operatorname{VIv}_{\mathrm{aq}}} + (\mathrm{CH}_{3})_{2}\mathrm{COH} + \mathrm{CO}_{2} + (n+1)\mathrm{H}^{+}_{\mathrm{aq}} \quad (7)$$

$$V^{v}_{aq} + (CH_3)_2 \dot{C}OH \xrightarrow{k} V^{v}_{aq} + (CH_3)_2 CO + H^+_{aq} \quad (8)$$

and (3) allows for the probable protonation of the substrate ligand in these high acidities.¹⁰ The preequilibrium 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 [hmpa]⁻¹ for varying [HClO₄] and temperature at a constant ionic strength = 5.00 mol dm⁻³

	Slope or	$\theta_{c}/^{\circ}C$				
mol dm^{-3}	intercept	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

^{*} In (6) and (7) very rapid interactions of V_{aq}^{v} and V_{aq}^{1v} with protons are also involved in the change $VO_{a}^{+}{}_{aq} \rightarrow VO^{2+}{}_{aq}$ to achieve a stoicheiometric balance in H⁺ and O.

by the observation that the redox system 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

$$-\mathrm{d}[\mathrm{V}^{\nabla}]_{\mathrm{T}}/\mathrm{d}t = \frac{2(k_{1} + \sum_{n} k_{n}' K_{n}' h^{n}) \beta_{1}[\mathrm{V}^{\nabla}]_{\mathrm{T}}[\mathrm{hmpa}]_{\mathrm{T}}}{(1 + K_{\mathrm{c}}h)(1 + K_{1}h) + \beta_{1}[\mathrm{hmpa}]_{\mathrm{T}}(1 + \sum_{n} K_{n}' h^{n})} \quad (9)$$

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}

$$1/k_{0} = \frac{(1 + K_{c}h)(1 + K_{1}h)}{2(k_{1} + \sum_{n} k_{n}'K_{n}'h^{n})\beta_{1}[\text{hmpa}]_{T}} + \frac{1 + \sum_{n} K_{n}'h^{n}}{(k_{1} + \sum_{n} k_{n}'K_{n}'h^{n})} \quad (10)$$

against $[\text{hmpa}]_{\text{T}}^{-1}$ 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

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

 $K_c = 0.1 \text{ dm}^3 \text{ mol}^{-1,3}$ (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



FIGURE 2 Plots of $(1 + K_c h)$ (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 (\bigcirc); 38.0, A = 0.500 (\bigcirc); 49.0, A = 0.100 (\triangle); 55.6, A = 0.100 (\bigtriangledown); and 74.5, A = 0.010 (\times) (A is a numerical adjustment parameter for the ordinate)

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 $\beta_1 k_1$ and $\beta_1 k_2' K_2'$ are given in Table 4. Plots of log $\beta_1 k_1$ and log $\beta_1 k_2' K_2'$ against the reciprocal of absolute temperature give linear plots and from the slopes and intercepts of these plots determined by least squares, the enthalpies ΔH^{\ddagger} and entropies of activation ΔS^{\ddagger} are as follows: for $\beta_1 k_1$, $\Delta H^{\ddagger} = 78 \pm 5$ kJ mol⁻¹ and $\Delta S^{\ddagger} = -41 \pm 15$ J K⁻¹ mol⁻¹ and for

Values of $\beta_1 k_1$ and $\beta_1 k_2' K_2'$ calculated from the slope and intercepts of Figure 2

	$10^{5} \beta_{1} k_{1} /$	$10^3 \beta_1 k_2' K_2' /$
θ _c /°C	dm³ mol ⁻¹ s ⁻¹	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

 $\beta_1 k_2' K_2'$, $\Delta H^{\ddagger} = 82 \pm 7$ kJ mol⁻¹ and $\Delta S^{\ddagger} = -52 \pm 20$ J K⁻¹ mol⁻¹.

For n = 2, the pseudo-first-order rate constant is given by (12). This can be rearranged to give (13). $k_0 =$

$$\frac{2(k_{1} + k_{2}'K_{2}'h^{2})\beta_{1}[\text{hmpa}]_{T}}{(1 + K_{c}h)(1 + K_{1}h) + \beta_{1}[\text{hmpa}]_{T}(1 + K_{2}'h^{2})} (12)$$

$$\frac{2(k_{1} + k_{2}'K_{2}'h^{2})\beta_{1}[\text{hmpa}]_{T}}{k_{0}(1 + K_{c}h)} = 1 + K_{1}h + \left\{ \frac{\beta_{1}[\text{hmpa}]_{T}}{(1 + K_{c}h)} \right\} (1 + K_{2}'h^{2}) (13)$$

If $K_1h \ll 1$, as found previously ⁶⁻⁸ and assumed here, plots of the left-hand side of equation (13) against [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



FIGURE 3 Plots of the left-hand side of equation (13) against $[hmpa]_T$ at 55.6 °C and a constant ionic strength of 5.00 mol dm⁻³ with [HClO₄] (mol dm⁻³) as follows: 1.00 (\bigcirc); 2.00 (\square); 3.00 (\triangle); 4.00 (\times); and 5.00 (\heartsuit)

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

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

against h^2 should be linear with an intercept = β_1 and a slope = $\beta_1 K_2'$. 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 $(1 + K_c h)$ (slope) against h^2 can be regarded as remotely acceptable; these are shown in Figure 4. From the intercepts on the ordinate,



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 follow-ing temperatures (°C): 49.0, A = 1.00 (\bigcirc); 55.6, A = 0.100(\Box); and 74.5, A = 0.100 (\triangle)

very approximate values for $\beta_1~(\text{dm}^3~\text{mol}^{-1})$ are 7 at 49.0 °C, 10 at 55.6 °C, and 16 at 74.5 °C: values for $\beta_1 K_2'$ from the slopes cannot be assessed.

The overall entropies of activation for the oxidation pathways are both negative, comparable with the overall values for ΔS^{\ddagger} for the oxidation of benzohydroquinone,⁶ PrⁱOH,⁷ and hydroxylamine⁸ by Vv_{aq}. As J.C.S. Dalton

remarked in the comparison⁷ of the oxidations of $Pr^{i}OH$ by various aqua-cations, that by V_{aq}^{v} is the only one where ΔS^{\ddagger} is negative (-43 J K⁻¹ mol⁻¹). Likewise, for the oxidation of hmpa, the overall ΔS^{\ddagger} $(J K^{-1} mol^{-1})$ for V_{aq}^v is again negative (-41) compared with the overall positive values for Mn^{III} (81)³ and for Ce^{IV} (25).⁴ As with PrⁱOH, 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 H₂O molecules and a positive ΔS^{\ddagger} ; whereas, for VO₂⁺_{aq} changing to VO²⁺_{aq}, the charge increases, restricting the movement of more H₂O molecules and leading to a negative ΔS^{\ddagger} . This result, obtained with both PriOH and hmpa as oxidizable ligands, supports the view that the entropy of activation is largely controlled by the movement of solvent water molecules.

[0/030 Received, 7th January, 1980]

REFERENCES

¹ T. J. Kemp and W. A. Waters, *J. Chem. Soc.*, 1964, 1192. ² G. V. Bakore, R. Shanker, and S. S. Dua, *Z. phys. Chem.* (Leipzig), 1967, 236, 129.

C. F. Wells and C. Barnes, Trans. Faraday Soc., 1971, 67, 3297.

⁴ Z. Amjad, A. McAuley, and U. Gomwalk, J.C.S. Dalton, 1977, 82.

 ⁶ C. F. Wells, *Tetrahedron*, 1966, 22, 2685.
 ⁶ C. F. Wells and L. V. Kuritsyn, *J. Chem. Soc.* (A), 1970, 1372.

C. F. Wells and A. F. M. Nazer, J.C.S. Faraday I, 1976, 910.

A. F. M. Nazer and C. F. Wells, J.C.S. Dalton, 1980, 1532.

⁹ R. Bastian, R. Weberling, and F. Palilla, Analyt. Chem., 1956, 28, 459

¹⁰ C. F. Wells, Trans. Faraday Soc., 1965, 61, 2194; 1966, 62, 2815; 1967, 63, 147; in 'Hydrogen-bonded Solvent Systems, eds. A. K. Covington and P. Jones, Taylor and Francis, London, 1968, pp. 323-334; C. F. Wells, C. Barnes, and G. Davies, Trans. Faraday Soc., 1968, 64, 3069; C. F. Wells and C. Barnes, *ibid.*, 1970, 66, 1154; C. F. Wells, *J.C.S. Faraday I*, 1972, 993; *J.* Phys. Chem., 1973, 77, 1994, 1997.