

Kinetics and Mechanisms of Oxidations by Metal Ions. V. Oxidation of 4-Oxopentanoic Acid by the Aquavanadium(V) Ion[†]

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The outer sphere oxidation of 4-oxopentanoic acid (4-OPA), studied at 50 °C by aquavanadium(V) ion, is H⁺-catalyzed reaction. The reaction has a first-order dependence on each of [V^V], [4-OPA], and [H⁺]. The H⁺ catalysis can not be ascribed to keto-enol equilibrium because of the knowledge that a γ -keto acid is the least enolized amongst keto acids. Hence V(OH)₃²⁺ (aq) ion is the active oxidant. The proposed mechanism, assumed to involve the initial decarboxylation, is supported by the spot test characterization of acetoin as the intermediate oxidation product. Acetoin is further oxidized to two moles of acetic acid which is the final oxidation product. The overall energy of activation ($\Delta H_1 = 26 \pm 3 \text{ kJ mol}^{-1}$) is lower than the normal value (84 kJ mol⁻¹) and therefore the highly negative value of the overall entropy of activation ($\Delta S_1 = -268 \pm 8 \text{ J K}^{-1} \text{ mol}^{-1}$) is considered to be responsible for the observed slow rate of oxidation.

Aquavanadium(V) ions in acid perchlorate solution are milder oxidants in comparison to the other aquametal ions such as Ce^{IV}, Mn^{III}, Co^{III}, Ag^{II} etc. However, the redox potential of V^V/V^{IV} couple in acidic solution¹⁾ is about 1 volt and is sufficient for the oxidation of a variety of organic compounds with ease. The subject matter has been reviewed.²⁻⁴⁾

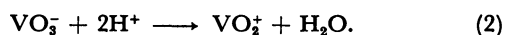
The equilibrium 1 is considered for explaining the acid catalysis having a first-order dependence in [H⁺] in the oxidations by vanadium(V). The protonation equilibrium constant K_1 has been not as yet estimated by physical methods though several studies^{5,6)} on redox kinetics have consistently suggested that $1 \gg K_1[\text{H}^+]$ in solutions of 1–5 mol dm⁻³ perchloric acid.⁶⁾



Recently, that $K_1 = 3.4 \text{ dm}^3 \text{ mol}^{-1}$ at 30 °C was estimated in the oxidation of pyruvic acid.⁷⁾ Since this value is of such a magnitude that would render the assumption^{5,6)} that $1 \gg K_1[\text{H}^+]$ erroneous even in dilute acid solutions $\geq 0.1 \text{ mol dm}^{-3}$. Hence a necessity was felt to have a recheck on this value of K_1 . It was only obvious to have a similar substrate and the choice of 4-oxopentanoic acid (here in after abbreviated as 4-OPA) was also motivated by the fact that γ -keto acid is least enolized in comparison to α - and β -keto acids.⁸⁾ The choice thus eliminated the complexity of the effect of enolization of the C=O group in the interpretation of the results.

Experimental

Reagents. Stock solution of vanadium(V) was prepared by dissolving ammonium metavanadate (Hopkin & Williams, G. R.) in twice distilled water. To the clear yellow solution was slowly added a calculated amount of standard perchloric acid to have a vanadium(V) solution having 2 mol dm⁻³ perchloric acid. In calculating the amount of perchloric acid, extra amount needed for the protonation reaction 2 was also considered.



[†]Reprints are not available.

The stock vanadium(V) solution was standardised titrimetrically⁹⁾ with a standard Fe(II) solution using *N,N*-diphenylsulfamate of barium as the indicator in presence of phosphoric acid.

Solutions of 4-oxopentanoic (E. Merck) and perchloric (E. Merck) acids were prepared by suitable dilutions and standardized against a standard alkali. Solutions of 4-oxopentanoic acid of long standing were discarded.

The stock solution of sodium perchlorate was prepared by neutralising sodium carbonate (BDH, AnalaR) with perchloric acid. The neutralized solution was later boiled to eliminate dissolved carbon dioxide. The solution was standardized gravimetrically.

All other reagents used were of analytical grade and distilled water was once again distilled from an all glass still.

Rate Measurements. The kinetics was studied at constant ionic strength (3 mol dm⁻³) maintained with sodium perchlorate. Reactant solutions of suitable strength were separately thermostatted in a water bath maintained at the desired temperature ($\pm 0.1^\circ\text{C}$). The reaction was generally initiated by the quick addition of 4-oxopentanoic acid. However, the rate was not affected when the reaction was initiated with vanadium(V). In all experiments, $[4\text{-OPA}] \gg [\text{V}^{\text{V}}]$ was used which ensured that k_{obsd} , the pseudo first-order rate constant with respect to vanadium(V), was not affected by any reactive intermediate produced during the course of the reaction.

The disappearance of vanadium(V) was followed with a Beckman DU 2 spectrophotometer at 350 nm.^{5,6,10)} Absorbance due to vanadium(IV) was negligible at this wavelength ($\epsilon_{350} = 1.0 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).¹¹⁾

The values of the pseudo first-order rate constant k_{obsd} were obtained by least square analysis of the slopes of the linear plots of $\ln(A_t - A_\infty)$ against time where A_t and A_∞ are the absorbance at any time t and at infinite time, respectively. The plots were linear ($r > 0.998$) beyond three half-lives. Few runs were repeated in presence of an inert nitrogen atmosphere and the k_{obsd} values so obtained were within the limits of experimental agreement ($\pm 3\%$) with those obtained in the presence of air, and the rate was not affected by the presence of vanadium(IV).

Stoichiometry. The stoichiometry of the complete oxidation reaction was determined under different acidity and atmospheric conditions as are detailed in Table 1. The [V^V] was present in excess and the reaction mixtures were left at 35 °C in a thermostatted water bath till $\Delta[\text{V}^{\text{V}}]/\Delta[4\text{-OPA}]$

TABLE 1. STOICHIOMETRIES AT 35 °C AND $I=3.0 \text{ mol dm}^{-3}$

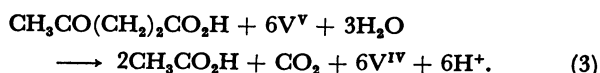
$[V^V]$ mol dm ⁻³	[4-OPA] mol dm ⁻³	$[H^+]$ mol dm ⁻³	Unreacted $[V^V]$ mol dm ⁻³	Atmosphere	$\Delta[V^V]$ $\Delta[4-OPA]$
0.08	0.010	3.0	0.019	Air	6.1
0.10	0.012	2.0	0.029	N ₂	5.9
0.10	0.015	2.0	0.011	Air	5.9
0.12	0.017	3.0	0.013	N ₂	6.0
0.14	0.020	1.0	0.021	Air	6.0
0.14	0.022	1.0	0.005	N ₂	6.1
					Means: 6.0 ± 0.1

TABLE 2. DEPENDENCE OF k_{obsd} ON [4-OXOPENTANOIC ACID] AT 50 °C.
[VANADIUM(V)]=0.02 mol dm⁻³, [HClO₄]=2.0 mol dm⁻³, AND $I=3.0 \text{ mol dm}^{-3}$

[4-OPA] mol dm ⁻³	$10^5 k_{\text{obsd}}/s^{-1}$	$10^5 k_{\text{obsd}}/[4-OPA]$ dm ³ mol ⁻¹ s ⁻¹	[4-OPA] mol dm ⁻³	$10^5 k_{\text{obsd}}/s^{-1}$	$10^5 k_{\text{obsd}}/[4-OPA]$ dm ³ mol ⁻¹ s ⁻¹
0.11	0.44	4.0	0.72	2.8	3.9
0.18	0.73	4.1	1.03	4.2	4.1
0.36	1.50	4.2	1.32	5.4	4.1
					Means: 4.1 ± 0.1

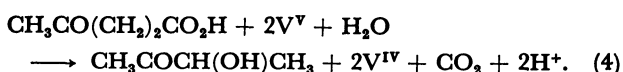
assumed a constant value (6.0 ± 0.1).

Product Analysis. The oxidation products were repeatedly extracted with ether from the reaction mixtures once $\Delta[V^V]/\Delta[4-OPA]$ was constant. The ether solution was slowly evaporated and the liquid left behind was found to smell like acetic acid. The presence of acetic acid was characterized by its usual test with neutral Fe(III) chloride and the spot test with lanthanum nitrate and iodine.¹² Hence the stoichiometry of the reaction is expressed by Eq. 3.



Reactive Intermediates. In another series of experiments the reaction mixtures were so prepared as to have large excess of 4-OPA over vanadium(V). The reaction products were repeatedly extracted from the partially oxidized reaction mixtures with ether. In this case acetoin was found to be the product and its presence was confirmed with the specific spot test.^{12b} Acetoin is reported to be oxidized to acetic acid *via* biacetyl as the reactive intermediate requiring four equivalents of vanadium(V) per mole of acetoin.¹³ The presence of biacetyl as the reactive intermediate could not be confirmed, perhaps, for the reason that it is oxidized at a much faster rate.

In view of the above it is clear that the keto acid is first oxidized to acetoin needing only two equivalents of vanadium(V) per mole. The formation of acetoin could be expressed by Eq. 4.



Test for Free Radical. Partially oxidized reaction mixtures which were previously flushed with nitrogen and maintained under nitrogen atmosphere produced polyacrylonitrile upon the addition of monomer acrylonitrile indicating the presence of free radical in the reaction mixtures. The blank experiments in which the monomer was separately added to the solutions of vanadium(V) and the keto acid did not show the formation of polyacrylonitrile. While these experiments are not helpful in identifying the actual free radical species, they did indicate the formation of free radicals during the progress of the reaction.

TABLE 3. DEPENDENCE OF k_{obsd} ON [HClO₄] AT DIFFERENT TEMPERATURES.
[VANADIUM(V)]=0.02 mol dm⁻³, [4-OPA]=0.36 mol dm⁻³, AND $I=3.0 \text{ mol dm}^{-3}$

[HClO ₄] mol dm ⁻³	$10^5 k_{\text{obsd}}/s^{-1}$				
	45 °	50 °	55 °	60 °	65 °C
0.5	0.30	0.36	0.43	0.50	0.58
1.0	0.61	0.74	0.84	1.02	1.15
1.5	0.91	1.10	1.27	1.51	1.75
2.0	1.22	1.47	1.67	2.02	2.30
2.5	1.53	1.85	2.11	2.54	2.92

Results

Dependence on [4-OPA]. A twelve fold variation in the initial [4-OPA] was effected to investigate its effect on the k_{obsd} ; the results are reported in Table 2. It was found that the plot of k_{obsd} against [4-OPA] was linear with zero intercept indicating that the order with respect to 4-oxopentanoic acid is unity.

Dependence on $[H^+]$. The effect of initial $[H^+]$ on k_{obsd} was investigated at five different temperatures in the range 0.5—2.5 mol dm⁻³ perchloric acid at a constant ionic strength adjusted with sodium perchlorate to 3.0 mol dm⁻³. The rate measurements in solutions with $[HClO_4] < 0.5 \text{ mol dm}^{-3}$ were not attempted because of the rate of reaction was found to be very slow. The results are reported in Table 3. The plot of k_{obsd} against $[H^+]$ was linear at all temperatures with zero intercept on the rate ordinate as is shown in Fig. 1. Similarly, the plot between k_{obsd} and $-\text{H}_0$, the Hammett acidity function,¹⁴ was linear at all the temperatures as is illustrated in Fig. 2. These plots, which are parallel to each other, indicated that slope of plot, 0.84, is independent of temperature. Thus the slope value is nearer to the ideal value of unity expected in this correlation.¹⁵ The H_0 values reported by Day and Wyatt¹⁶ were used.

Effect of Ionic Strength. The effect of ionic

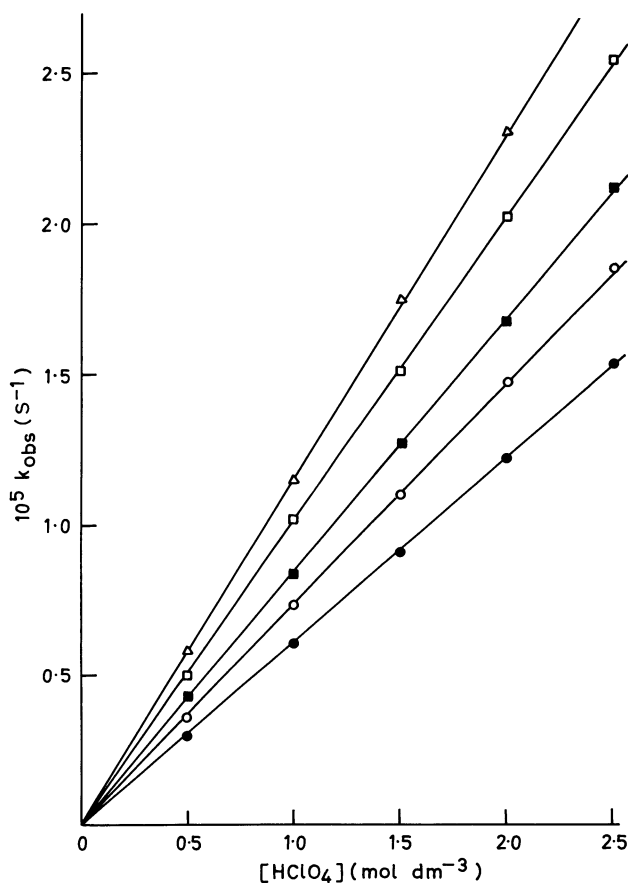


Fig. 1. The linear plots between k_{obsd} and $[\text{HClO}_4]$ with zero intercepts in solutions of constant ionic strength (3.0 mol dm^{-3}) at 45° (●), 50° (○), 55° (■), 60° (□), and 65° (△). $[\text{Vanadium(V)}]=0.02 \text{ mol dm}^{-3}$ and $[\text{4-Oxopentanoic acid}]=0.36 \text{ mol dm}^{-3}$.

strength on k_{obsd} was investigated by varying the $[\text{NaClO}_4]$ in the range $0.1\text{--}1.0 \text{ mol dm}^{-3}$ at a fixed $[\text{H}^+]$ (2.0 mol dm^{-3}) and $[\text{4-OPA}]$ (0.36 mol dm^{-3}) at 50°C . The k_{obsd} was almost independent of ionic strength ($10^5 k_{\text{obsd}}=1.5\pm 0.1 \text{ s}^{-1}$) indicating that one of the reactants is not charged. Since vanadium(V) species are positively charged¹⁷ in acid solutions $>0.1 \text{ mol dm}^{-3}$ it is obvious that 4-oxopentanoic acid reacted in the unionized state. A similar conclusion was also derived by considering its $\text{p}K_{\text{a}}$ value of 4.5 at 25°C .¹⁸ The $\text{p}K_{\text{a}}$ value indicated that the keto acid is a weak acid and therefore it would largely exist in its undissociated state under the $[\text{H}^+]$ used. Moreover, had the anion of the keto acid been reactive a retardation in the rate with increasing $[\text{H}^+]$ was expected and was not found.

Discussion

The spectrum of 4-oxopentanoic acid has indicated that any lactol contribution is very small and the keto-form predominates,¹⁹ a fact in conformity with the observation that γ -keto acids are least enolized.⁸ Although the formation of enol-lactones is more readily effected in the presence of acid catalysts yet these

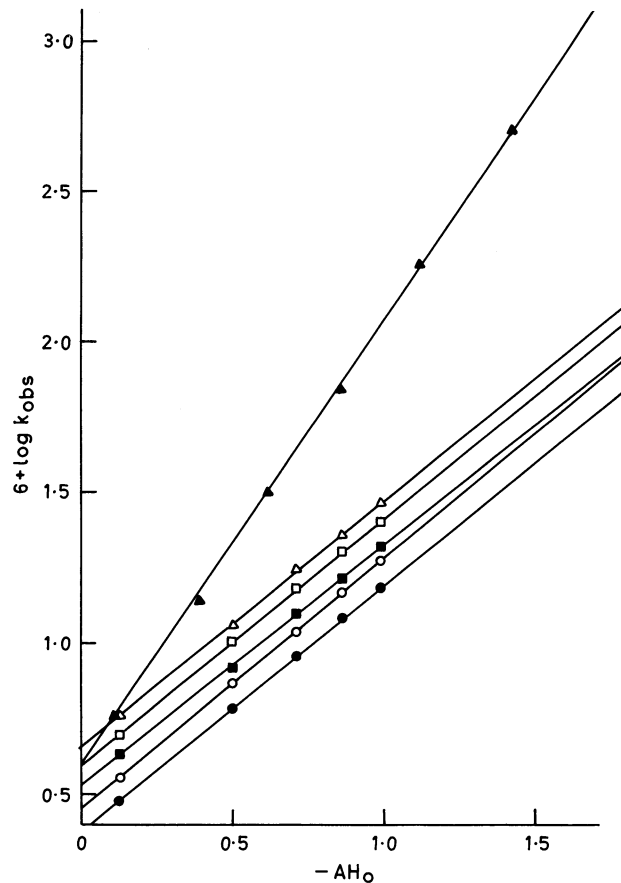


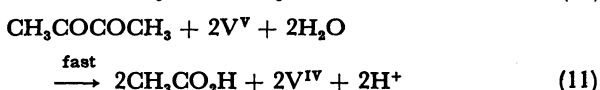
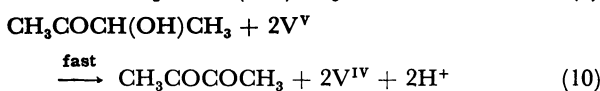
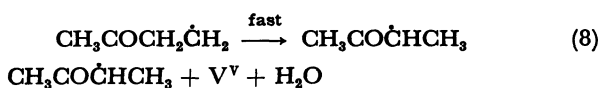
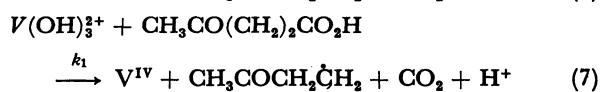
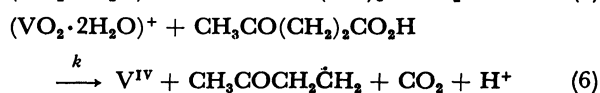
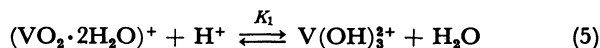
Fig. 2. The linear plots between $\log k_{\text{obsd}}$ and $-A_{\text{H}_0}$, the Hammett acidity function, for perchloric acid solutions of a constant ionic strength (3.0 mol dm^{-3}) at 45° (●), 50° (○), 55° (■), 60° (□), and 65° (△) with $A=1$, and for perchloric acid solution of varying ionic strength at 50° (▲) with $A=0.5$ $[\text{Vanadium(V)}]=0.02 \text{ mol dm}^{-3}$ and $[\text{4-Oxopentanoic acid}]=0.36 \text{ mol dm}^{-3}$.

are less stable,¹⁹ and therefore are not considered to be a major reactive entity. Similarly the keto \rightleftharpoons enol equilibrium has also been excluded from the proposed mechanism because (i) if the rate of keto \rightarrow enol transformation was rate controlling then the order of the reaction with respect to the oxidant was expected to be zero, and (ii) the very slow nature of the reaction ($10^5 k_{\text{obsd}}/[\text{4-OPA}]=4.1\pm 0.1 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 50°C and $[\text{HClO}_4]=2.0 \text{ mol dm}^{-3}$) did not indicate any possibility of the enol as being the reactive entity.

The cationic species of vanadium(V) in acidic aqueous solution are VO_2^+ (aq)^{20,21} and $\text{V}(\text{OH})_4^+$ (aq).^{22,23} The existence of $\text{V}(\text{OH})_4^+$ as $(\text{VO}_2 \cdot \text{H}_2\text{O})^+$ has been suggested.²⁴ The equilibrium between $(\text{VO}_2 \cdot 2\text{H}_2\text{O})^+$ and its protonated species $\text{V}(\text{OH})_3^{2+}$ is shown in equilibrium 5.

In view of the kinetics which has indicated a first-order dependence in each of $[\text{V}^{\text{V}}]$, $[\text{4-OPA}]$, and $[\text{H}^+]$, the following reactions are considered part of the mechanism which is based on the assumption that decarboxylation of the keto acid is the rate determining reaction. The exclusion of the possibility of

the oxidant attacking the >CO group is explained at a later stage of discussion.



where reactions 6 and 7 are rate determining, all other reactions are fast. The inclusion of reaction 9 is based on the belief that hydroxylation of free radicals in presence of an oxidant is always a fast process.

The oxidation of acetoin in reaction 10 as a fast one is based on the comparison of the rate constant k_1K_1 with $k_3(=k_{\text{obsd}}/4[\text{H}^+][\text{acetoin}])$. The value of k_3 is¹³⁾ $8.0 \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ compared to k_1K_1 which is $1.32 \times 10^{-6} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ in solutions of 1.5 mol dm^{-3} perchloric acid and 3 mol dm^{-3} ionic strength at 25°C . Hence it is seen that the oxidation of acetoin is somewhat 6×10^3 times faster than the rate of oxidation of the keto acid. The inclusion of reaction 10 as the fast one is thus justified. The value of k_1K_1 at 25°C was obtained by extrapolating the linear plot of $\ln k_1K_1$ and $1/T$. The values of k_1K_1 at different temperatures, Table 4, were obtained by the relation described latter. The actual rate measurements on the oxidation of biacetyl (2,3-butanedione) have as yet not been carried out but it is reported¹³⁾ to be much faster than that of acetoin.¹³⁾

The rate of disappearance of $[\text{V}^{\text{V}}]$ in terms of reactions 5—11 is given by Eq. 12 which could also be written as Eq. 13.

$$\frac{-d[\text{V}^{\text{V}}]}{dt} = \frac{6(k+k_1K_1[\text{H}^+])[\text{V}^{\text{V}}][4\text{-OPA}]}{1+K_1[\text{H}^+]} \quad (12)$$

$$k_{\text{obsd}}(1+K_1[\text{H}^+]) = 6(k+k_1K_1[\text{H}^+])[4\text{-OPA}] \quad (13)$$

Now if it is assumed that $K_1=3.4 \text{ dm}^3 \text{ mol}^{-1}$, reported by Sengupta and coworkers in the oxidation of

TABLE 4. VALUES OF k_1K_1 AT DIFFERENT TEMPERATURES AND THE VALUES OF THE ENTHALPY AND ENTROPY OF ACTIVATION

($^\circ\text{C}$)	45	50	55	60	65
$10^6 k_1K_1$	2.80	3.40	3.89	4.63	5.37
$\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$					
$\Delta H_1=26 \pm 3 \text{ kJ mol}^{-1}$					
$\Delta S_1=-268 \pm 8 \text{ J K}^{-1} \text{ mol}^{-1}$					

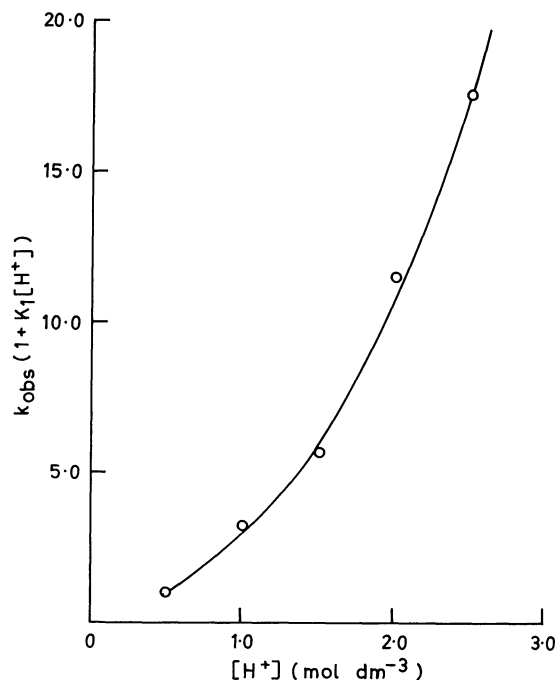


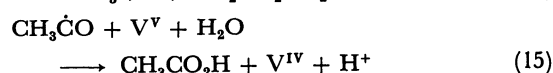
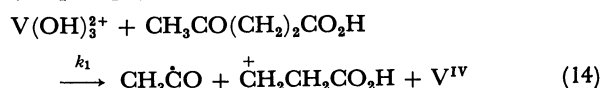
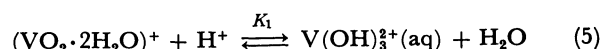
Fig. 3. The plot between $k_{\text{obsd}}(1+K_1[\text{H}^+])$ and $[\text{H}^+]$ at 50°C with $K_1=3.4 \text{ dm}^3 \text{ mol}^{-1}$ for perchloric acid solution of constant ionic strength (3.0 mol dm^{-3}). Similar plots were obtained at other temperatures too. $[\text{Vanadium(V)}]=0.02 \text{ mol dm}^{-3}$ and $[4\text{-Oxopentanoic acid}]=0.36 \text{ mol dm}^{-3}$.

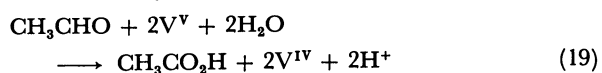
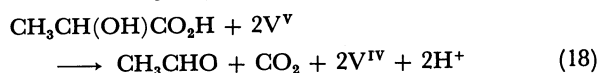
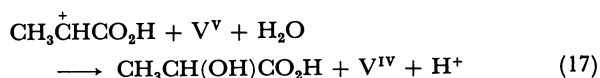
pyruvic acid,⁷⁾ then the plot of $k_{\text{obsd}}(1+K_1[\text{H}^+])$ against $[\text{H}^+]$ should be linear with a positive intercept on the rate ordinate. However, when this plot was constructed, Fig. 3, it was found that the plot is not linear indicating that the assumption of the high value of K_1 is at least not correct in the present case.

Next, the application of the assumption^{5,6)} that $1 \gg K_1[\text{H}^+]$ resulted in the linear correlation between k_{obsd} and $[\text{H}^+]$ as is shown in Fig. 1. The plot, however, has a zero intercept indicating that $k \ll k_1K_1[\text{H}^+]$ i.e. $\text{V}(\text{OH})_3^{2+}$ is more reactive than VO_2^+ which is rationalized by the assumption that an increase in the effective charge on metal ion increases its oxidizing capability.

The values of $k_1K_1(=k_{\text{obsd}}/6[\text{H}^+][4\text{-OPA}])$ at different temperatures were calculated from the data given in Table 3. The values so obtained are in Table 4 wherein are also reported the values of the thermodynamic parameters.

Alternate Mechanism. The following sequence of reactions are based on the probability of the initial electron transfer to vanadium(V) from the >CO group of the keto acid.





where reaction 14 is the rate determining and the corresponding reaction with $\text{VO}_2^+(\text{aq})$ is not included because of the knowledge that $\text{VO}_2^+(\text{aq})$ species are not effective oxidant species as had been discussed earlier. The reaction 19 may also not be very correct representation of the oxidation of acetaldehyde because it is just probable that its enol form might be undergoing oxidation as is the case with the oxidation of other aldehydes.²⁵⁾ Acetaldehyde is the first oxidation product of lactic acid in the oxidation by vanadium(V).²⁶⁾ The inclusion of fast oxidation of lactic acid in 18 is based on the comparison of k_1K_1 and k_4 ($=k_{\text{obsd}}/4[\text{H}^+][\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}]$). The value of k_4 is $2.95 \times 10^{-4} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ against a value of $1.41 \times 10^{-6} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ for k_1K_1 both at $[\text{HClO}_4]=1.0 \text{ mol dm}^{-3}$ at 25°C .

The rate of disappearance of $[\text{V}^{\text{V}}]$ in terms of reactions 5 and 14—19 of course will be given by Eq. 12 and as such the two mechanisms become indistinguishable. However, this alternate mechanism is not well supported by the initial oxidation product detected in the oxidation of the keto acid. Lactic acid, as required by the above mechanism was not the initial oxidation product which was acetoin. Moreover there is no similarity between the observed rate law in Eq. 12 and the one obtained in the oxidation of lactic acid²⁶⁾ and $\text{Me}_2\text{C}(\text{OH})\text{COMe}$ ¹³⁾ which involved C—C fission similar to reaction 14. Both lactic acid and $\text{Me}_2\text{C}(\text{OH})\text{COMe}$ were oxidized by a path independent of $[\text{H}^+]$.

Activation Parameters. The observed enthalpy (ΔH_1) and entropy (ΔS_1) of activation are in Table 4. The ΔH_1 value for the reaction is low compared with the value reported in the oxidation of other organic compounds.³⁾ Similarly ΔS_1 is highly negative compared to the values obtained in various redox reactions.³⁾ Since ΔH and ΔS are extensive properties, it is therefore clear that $\Delta H_1 = \Delta H^\circ + \Delta H^\ddagger$, and $\Delta S_1 = \Delta S^\circ + \Delta S^\ddagger$ where ΔH° , ΔS° , and ΔH^\ddagger , ΔS^\ddagger are the enthalpy and entropy of activation for reactions 5 and 7 respectively. A negative ΔS° for the reaction 5 is expected because there is a net increase in the charge on the reactive vanadium(V) species. Similarly a negative ΔS^\ddagger for the reaction 7 is expected because it involves the reaction between polyatomic molecules. Hence the high negative value of ΔS_1 for the combined reactions 5 and 7 is understandable.

The low value of ΔH_1 is probably due to the negative value of either ΔH° or ΔH^\ddagger . It is also clear that ΔH^\ddagger cannot be negative hence ΔH° must be negative which is consistent with the views available in the literature.²⁷⁾ The negative ΔH° means that there would

be less formation of $\text{V}(\text{OH})_3^{2+}$ with increasing temperature, a fact well supported by the report²⁸⁾ that a 0.2 mol dm^{-3} vanadium(V) solution in 4.4 mol dm^{-3} perchloric acid precipitated vanadium pentoxide when warmed above 60°C .

Conclusion. The keto acid is oxidized by the primary attack of the V^{V} on carboxylic group. That the keto acid is not oxidized at γCO group is concluded on the basis that k_{obsd} is at least one order less than the k_{obsd} value obtained in the oxidation of cyclohexanone under similar conditions of acidity and temperature and concentrations of the substrates. The carboxylic acids, except formic acid,⁹⁾ are resistant to the oxidation by vanadium(V) under conditions used in the present study. Thus the relatively easier yet slow oxidation of the keto acid could be ascribed to the presence of γCO group which is apparently not involved in the initial transfer of electron to the oxidant. Whether the γCO group remains in the keto form or is transformed to enol prior to the oxidation is not clear, yet certain conclusions can be derived from certain known facts.

Since the γ -keto acid is least enolised⁹⁾ it is suggested that 4-OPA is mainly oxidized in its keto form. The oxidation at γCO group site has been eliminated on the basis of magnitude of k_{obsd} value. A partial order with respect to 4-OPA was expected if the oxidation involved the enol form. However, this would be true only if the equilibrium constant K_e for keto=enol equilibrium has a significant value so that $1 \gg K_e[4\text{-OPA}]$. Since a strict first-order dependence in 4-OPA is observed, it is clear that K_e has no significant value and therefore the concentration of the enol form is considered to be kinetically insignificant. The emphasis that 4-OPA is oxidized in the keto form (where keto group remains unreactive) stems out from the fact that one equivalent oxidants generally oxidize a ketone by attacking the γCO group. That the γCO group is not attacked in the present case is another matter.

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