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KINETICS AND MECHANISM OF OXIDATION OF D-ERYTHROSE AND DL-GLYCERALDEHYDE BY CHROMIUM(VI) AND VANADIUM(V) IN PERCHLORIC ACID MEDIUM

KALYAN KALI SEN GUPTA* AND SAMARENDRA NATH BASU
Department of Chemistry, Jadavpur University, Calcutta-700032 (India)
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ABSTRACT

The kinetics of oxidation of D-erythrose and DL-glyceraldehyde by chromium (VI) and vanadium(V) in perchloric acid medium have been investigated spectrophotometrically. Each reaction was first-order with respect to [oxidant] and [substrate]. The reactions were catalysed by acid, but their dependence on acidity was complex. Sodium perchlorate accelerated the rate of each reaction. The oxidation rates follow the order glyceraldehyde > erythrose. The activation parameters were calculated and mechanisms consistent with the experimental observations are proposed.

INTRODUCTION

Erythrose and its oxidation–reduction products are of interest, particularly with reference to their use as intermediates in the synthesis of sugars and their conversion into various phosphate esters[1a]. Glyceraldehyde is also an important compound because of its interesting physiological actions[1b]. Only limited data are available[2] on the mechanisms of the oxidation reactions of this aldotetrose and aldotriose.

The kinetics and mechanism of oxidations of some aldohexoses and aldopentoses by chromium(VI) and vanadium(V) in perchloric acid medium have been reported[3–5]. Unlike aldohexoses and aldopentoses, the aldotetrose and aldotriose exist mainly in acyclic forms[6]. So it is conceivable that the kinetics and mechanism of their oxidations could be different from those of higher aldoses. We have therefore studied the kinetics of the oxidations of D-erythrose and DL-glyceraldehyde by chromium(VI) and vanadium(V) in perchloric acid medium.

EXPERIMENTAL

Reagents. — D-Erythrose and DL-glyceraldehyde were commercial materials.

*To whom correspondence should be directed.

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Their aqueous solutions were freshly prepared in doubly distilled water. Details of the oxidants and other chemicals were given in earlier communications[3-5].

Kinetic measurements. — Solutions of the oxidants and the reaction mixture containing known quantities of the organic substrate, perchloric acid, and salts (where necessary) were separately thermostated (±0.1 °). The reaction was initiated by mixing requisite amounts of the oxidant with the reaction mixture as described earlier[3-5]. The rates of oxidation were determined spectrophotometrically by using a Perkin–Elmer Spectrophotometer (digital) equipped with a thermospacer cell compartment. Chromium(VI) oxidations were followed[3] by recording the decrease in Cr(VI) absorbance at 350 nm. The vanadium(V) oxidation of D-erythrose was studied by following the increase of the absorbance at 765 nm (λ_{max}[7]) for V(IV); whereas that of DL-glyceraldehyde was followed by observing the decrease of absorbance for vanadium(V) at 313 nm[8,9]. Neither the substrates nor their oxidised products absorb at the above wavelengths. All reactions were performed in the presence of a large excess of substrate. Pseudo-first-order rate constants (k_{obs}) were calculated[3] for the Cr(VI) oxidations. The values of k_{obs} for the V(V) oxidation of D-erythrose were calculated from the slopes of the plots of $\log(A_\infty - A_t)$ against time, where A_∞ and A_t are the absorbances of V(IV) at infinity and time t, respectively. The values of k_{obs} for the other reaction were calculated from the slopes of the plots of log A_t' *vs.* time, where A_t' is the absorbancy of V(V) at time t. Second-order rate constants (k_2) were obtained from the relationship $k_2 = k_{obs}/[\text{Aldose}]_0$. Duplicate measurements were reproducible within ±5%. The reactions were followed for up to ~2 half-lives.

Stoichiometry. — The stoichiometry of these oxidations was determined by using a large excess of oxidants. For the Cr(VI) oxidations, unreacted Cr(VI) was determined whereas for V(V) oxidations, the product V(IV) was determined spectrophotometrically. The results (Table I) indicate that D-erythrose and DL-glyceraldehyde were oxidised to carbon dioxide by Cr(VI), whereas formic acid was formed in the

TABLE I

STOICHIOMETRY OF THE OXIDATION OF ALDOSES BY CHROMIUM(VI) AND VANADIUM(V) IN THE PRESENCE OF A LARGE EXCESS OF OXIDANT

Aldose	*Consumption ratio*		
	Experimentally observed	*On the basis of formation of*	
		Formic acid	*Carbon dioxide*
D-Erythrose[a]	2.60	1.33	2.67
DL-Glyceraldehyde[a]	1.95	1.0	2.0
D-Erythrose[b]	7.4	8.0	16.0
DL-Glyceraldehyde[b]	5.6	6.0	12.0

[a]Cr(VI). [b]V(V).

V(V) oxidations when the reaction mixtures were kept for several days. The reactions accord with Equations *1* and *2*.

$$3\,C_nH_{2n}O_n + 4n\,HCrO_4^- + 16n\,H^+ \rightarrow 3n\,CO_2 + 4n\,Cr^{3+} + 13n\,H_2O \qquad (1)$$

$$C_nH_{2n}O_n + 2n\,V(V) + n\,H_2O \rightarrow n\,HCOOH + 2n\,V(IV) + 2n\,H^+ \qquad (2)$$

The rate of oxidation of the intermediates cannot be kinetically significant[10], since the rate of reduction of [oxidant] was first order under the kinetic conditions.

Product analysis. — The reaction products, under kinetic conditions, were identified by paper chromatography[3,4]. This indicated the presence of erythronic and glyceric acids as the main products, which were identical with those obtained by bromine[11] oxidation of the respective aldoses.

Polymerisation test. — A solution of Cr(VI) or V(V) was added to a mixture containing aldose, perchloric acid, and acrylamide (10% w/v). In media of low and high acidity, polymers were formed in the Cr(VI) and V(V) oxidations of both D-erythrose and DL-glyceraldehyde. However, no polymerisation occurred when either the oxidant or the substrate was excluded. These results indicated that the reactions between chromium(VI) or vanadium(V) and the aldoses produced free-radical intermediates.

RESULTS

Effect of variation of concentration of reactants. — For each oxidation, the values of k_{obs} were ascertained at various $[oxidant]_0$, but at constant $[aldose]_0$, $[HClO_4]_0$, and temperature. The average values of k_{obs} (Table II) were independent of $[oxidant]_0$, thereby establishing that these reactions were first order with respect to [oxidant]. The reactions were also studied at constant $[oxidant]_0$, $[HClO_4]_0$, and temperature, but at different $[aldose]_0$. The values of k_{obs} increased with increase in $[aldose]_0$ (Table III). The plots of k_{obs} against $[aldose]_0$ were linear and

TABLE II

EFFECT OF INITIAL CONCENTRATION OF OXIDANT ON PSEUDO-FIRST-ORDER RATE CONSTANT AT $[HClO_4]_0$ = 2.4M

Aldose	*Temperature (degrees)*	$k_{obs} \times 10^4$ *(sec^{-1})*
D-Erythrose[a]	30	11.75 ±0.3
DL-Glyceraldehyde[a]	20	33.7 ±0.8
D-Erythrose[b]	25	1.22 ±0.04
DL-Glyceraldehyde[b]	28	3.19 ±0.09

[a] $[Cr(VI)]_0 = (0.55–3.33) \times 10^{-4}$M and $[aldose]_0 = 1.0 \times 10^{-3}$M. [b] $[V(V)]_0 = (1.0–2.5) \times 10^{-3}$M and $[aldose]_0 = 1.0 \times 10^{-2}$M.

TABLE III

EFFECT OF SUBSTRATE CONCENTRATION ON PSEUDO-FIRST-ORDER RATE CONSTANTS AT $[HClO_4]_0 = 2.4M$

[Erythrose] × 10^3M[a]	0.5	0.8	1.0	1.5	2.0		
k_{obs} × 10^4 (sec^{-1})	5.70	9.56	11.75	18.00	23.6		
$\frac{k_{obs}}{[Erythrose]}$ ($M^{-1}.sec^{-1}$)	1.14	1.195	1.175	1.20	1.18		
[Glyceraldehyde] × 10^3M[b]	0.5	0.8	1.0	1.3	1.5	2.0	3.0
k_{obs} × 10^4 (sec^{-1})	16.6	26.2	33.7	45.7	53.1	70.0	107.5
$\frac{k_{obs}}{[Glyceraldehyde]}$ ($M^{-1}.sec^{-1}$)	3.32	3.28	3.37	3.51	3.54	3.50	3.58
[Erythrose] × 10^2M[c]	0.5	0.7	0.8	0.9	1.0		
k_{obs} × 10^4 (sec^{-1})	0.60	0.82	0.98	1.12	1.22		
$\frac{k_{obs}}{[Erythrose]}$ × 10^2 ($M^{-1}.sec^{-1}$)	1.20	1.17	1.20	1.24	1.22		
[Glyceraldehyde] × 10^2M[d]	0.5	1.0	2.0	3.0	4.0	5.0	
k_{obs} × 10^4 (sec^{-1})	1.59	3.19	6.02	9.30	12.2	15.4	
$\frac{k_{obs}}{[Glyceraldehyde]}$ × 10^2 ($M^{-1}.sec^{-1}$)	3.18	3.19	3.01	3.10	3.05	3.08	

[a] $[Cr(VI)]_0 = 1.67 \times 10^{-4}$M; temperature, 30°. [b] $[Cr(VI)]_0 = 1.67 \times 10^{-4}$M; 20°. [c] $[V(V)]_0 = 2.0 \times 10^{-3}$M; 25°. [d] $[V(V)]_0 = 1.0 \times 10^{-3}$M; 28°.

TABLE IV

SLOPES OF THE ZUCKER–HAMMETT PLOTS (log k_{obs} *vs.* log $[HClO_4]_0$) AT $\mu = 2.4M$

Aldose	$[HClO_4]$(M)	*Slope*
D-Erythrose[a]	<1.0	0.5
	>1.0	1.0
DL-Glyceraldehyde[b]	<0.7	1.0
	>0.7	1.5
D-Erythrose[c]	<1.0	0.1
	>1.0	0.5
DL-Glyceraldehyde[d]	<1.0	0.1
	>1.0	0.55

[a] $[Cr(VI)]_0 = 1.67 \times 10^{-4}$M, $[Aldose]_0 = 1.0 \times 10^{-3}$M, and temperature = 30°. [b] $[Cr(VI)]_0 = 1.67 \times 10^{-4}$M, $[Aldose]_0 = 1.0 \times 10^{-3}$M, 20°. [c] $[V(V)]_0 = 2.0 \times 10^{-3}$M, $[Aldose]_0 = 1.0 \times 10^{-2}$M, 25°. [d] $[V(V)]_0 = 1.0 \times 10^{-3}$M, $[Aldose]_0 = 1.0 \times 10^{-2}$M, 28°.

passed through the origin for each reaction, indicating that these oxidations were essentially first order with respect to each [aldose]. The average values of k_2 for Cr(VI) oxidations of erythrose and glyceraldehyde are 1.18 $\pm$0.04 and 3.44 $\pm$0.16 $M^{-1}.sec^{-1}$ at 30° and 20°, respectively. The corresponding values for the V(V) oxidations are (1.21 $\pm$0.04) $\times$ 10^{-2} and (3.10 $\pm$0.09) $\times$ 10^{-2} $M^{-1}.sec^{-1}$ at 25° and 28°, respectively. Thus, the oxidation rates with both these oxidants follow the order glyceraldehyde > erythrose.

Effect of variation of concentration of perchloric acid. — The effect of variation of $[H^+]$ on the rate of oxidation was studied at different $[HClO_4]_0$, but at constant $[oxidant]_0$, $[substrate]_0$, ionic strength (maintained by adding the requisite amounts of $NaClO_4$), and temperature. These oxidations were found to be acid-catalysed. The slopes of the plots of log k_{obs} *vs* log $[HClO_4]_0$ are presented in Table IV.

Effect of variation of concentration of sodium perchlorate. — The effect of variation of $[NaClO_4]_0$ on the rate of oxidation was measured at fixed $[oxidant]_0$, $[substrate]_0$, $[HClO_4]_0$, and temperature. The rates increased with increase of $[salt]_0$. In 2.0M $NaClO_4$, the increases in rate were 86 and 141%, respectively, for the Cr(VI) oxidations of erythrose and glyceraldehyde, and 50 and 98%, respectively, for the V(V) oxidations. The results are similar to those obtained[3-5] for the oxidations of higher aldoses by these oxidants.

Effect of variation of temperature and activation parameters. — The values of the second-order rate constants (k_2) for the oxidations of the aldoses were measured at various temperatures, but at fixed $[oxidant]_0$, $[substrate]_0$, and $[HClO_4]_0$. The activation parameters, calculated as described previously[3-5], are $\Delta H^{\ddagger}$ = 40 $\pm$3 (erythrose) and 35.5 $\pm$1 (glyceraldehyde) kJ.mol^{-1} and $\Delta S^{\ddagger}$ = $-$119 $\pm$10 (erythrose) and $-$121 $\pm$4 (glyceraldehyde) J.deg^{-1}.mol^{-1} for chromium(VI) oxidations; and $\Delta H^{\ddagger}$ = 70 $\pm$4 (erythrose) and 67 $\pm$3 (glyceraldehyde) kJ.mol^{-1} and $\Delta S^{\ddagger}$ = $-$54 $\pm$13 (erythrose) and $-$61 $\pm$7 (glyceraldehyde) J.deg^{-1}.mol^{-1} for vanadium(V) oxidations at 35°.

DISCUSSION

D-Erythrose, in aqueous solution, exists[12] as an equilibrium mixture of solvated forms. A dimeric form is believed to be present besides the solvated and the unsolvated monomers. Similarly, although the crystalline form of DL-glyceraldehyde is dimeric with a 1,4-dioxane structure, in aqueous solution, monomeric forms are present[12] in an equilibrium of hydrated and non-hydrated forms. Thus, a very rapid equilibrium is established between the three forms for both aldoses:

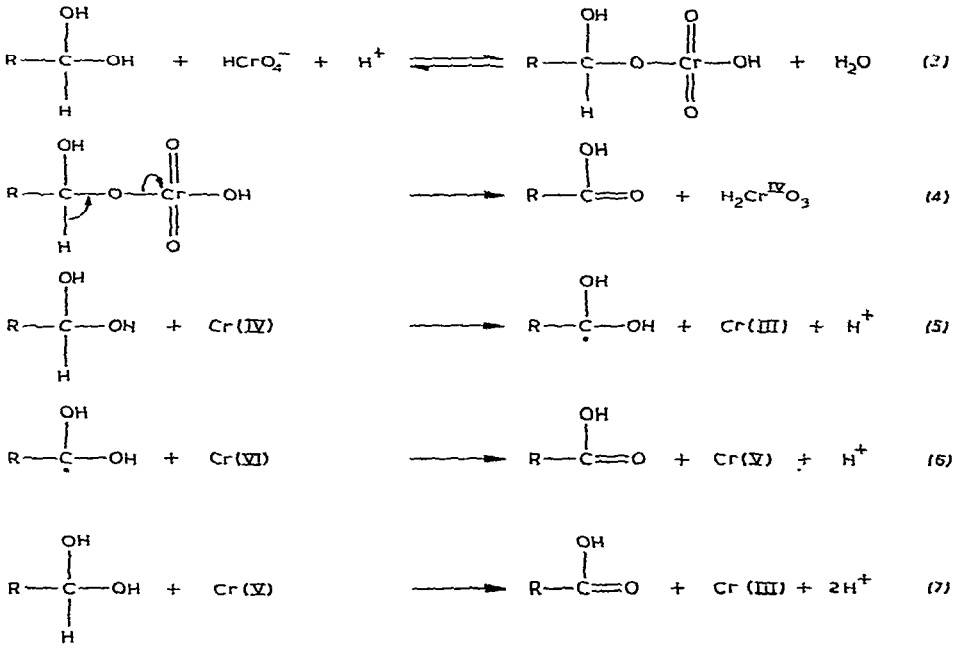
Dimer $\rightleftharpoons$ Monomer $\rightleftharpoons$ Hydrated monomer.

Since the experiments were performed with low concentrations ($\leqslant 5.0 \times 10^{-2}$M) of substrates, it is expected that the hydrated monomeric forms should be preponderant. Moreover, sugars that exist mainly in aldehydo-forms, like some aliphatic aldehydes[13a], are known to be hydrated[13b]. Since the kinetic data as well as the activation parameters are not widely different from those obtained for the oxidations

of alcohols[14] by Cr(VI) and V(V), it is suggested that it is the hydrated monomeric forms of these aldoses which are mainly oxidised by these oxidants.

The oxidation of erythrose and glyceraldehyde by chromium(VI) was first order in [Cr(VI)] and in [aldose], but the order with respect to $[H^+]$ was complex. For erythrose, the order with respect to $[HClO_4]$ was 0.5 when $[H^+]$ was <1.0M, and 1.0 when $[H^+]$ was >1.0M. The order with respect to $[HClO_4]$ in the oxidation of glyceraldehyde was 1.0 in the acid range 0.24–0.70M, whereas at higher acidities (up to 2.4M), this value was 1.5. Again, as most of these oxidations were carried out at [Cr(VI)] of 1.67×10^{-4}M and the values of k_{obs} were independent of [Cr(VI)], the monomeric species[18a] of Cr(VI), namely $HCrO_4^-$, is considered to be the reactive oxidant.

The formation of erythronic acid in the oxidation of erythrose by Cr(VI) under kinetic conditions is believed to proceed *via* a chromic ester of the hydrated form of the aldose, $HCrO_4^-$, and H^+ ions, followed by decomposition of the intermediate ester. Since there is no direct kinetic evidence for the existence of such an intermediate chromic ester, the equilibrium constant for reaction *3* would be very small. The mechanism of oxidation of erythrose by Cr(VI) in perchloric acid media ($[H^+] > 1.0$M) may therefore be explained by each of the following Schemes (I–III), where $R = CH_2OH.(CHOH)_2$. Of the different steps suggested, only step *4* is slow.



Scheme I

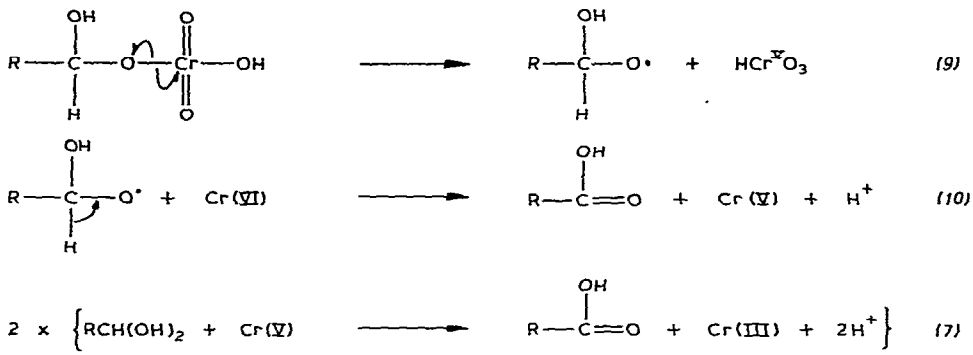
Reactions 3 and 4

$$Cr(IV) + Cr(VI) \longrightarrow 2\,Cr(V) \quad (8)$$

$$2 \times \{RCH(OH)_2 + Cr(V) \longrightarrow RCOOH + Cr(III) + 2H^+\} \quad (7)$$

Scheme II

Reaction 3



Scheme III

The addition of $[Mn^{2+}]$ of 5.0×10^{-2}M decreased the rate of oxidation of the aldoses considerably, *i.e.*, by 50 and 35% in the respective reactions. The retardation was not due to the change in ionic strength, since addition of $NaClO_4$ of the same ionic strength as that of the Mn^{2+} compounds did not seem to have any effect on the rate of oxidation. Regardless of which scheme is correct, the participation of intermediate valence states of chromium[15–18] cannot, therefore, be ruled out.

The formation of free-radical intermediates, as evidenced by the initiation of polymerisation of acrylamide, is not in keeping with Scheme II. On the other hand, both RCH(OH)O· and Cr(V) are highly reactive, with the result that one would not expect them to be formed in step *9* of Scheme III. Consequently, the reaction cannot proceed by the steps shown in Schemes II and III. This further indicates that Cr(IV), which is formed in step *4* of Scheme I, may react further with substrate to yield the free radical[19a] and the stable Cr(III) species, according to step *5*. Thus, Scheme I seems to be the preferred mechanism, where the rate-determining step is a two-electron carbon–hydrogen bond cleavage of a chromic ester. The free radicals that are formed by subsequent fast reaction[19a] between the reactive species of aldose and Cr(IV) probably initiate the polymerisation of acrylamide. The free radical R-$\dot{C}(OH)_2$, with trivalent carbon, is known to be in tautomeric equilibrium with R-CH(OH)O·, but the former is likely to preponderate[19b], as the C–H bond is weaker than the O–H bond.

The oxidation of glyceraldehyde by Cr(VI) at lower acidities (where $[H^+] < 0.7$M) may also be explained by Scheme I (where R = $CH_2OH.CHOH$). However, at higher acidities (up to 2.4M), the order with respect to $[HClO_4]$ was higher (1.5)

than 1. This may be due to the fact that the 1 : 1 ester reacts further with a proton, to yield a protonated ester that subsequently decomposes to give the products of the reaction.

The kinetics of oxidation of erythrose and glyceraldehyde by V(V) were similar in all respects, indicating that identical mechanisms may occur in these cases. Thus, the total order of these oxidations at constant acidity was 2, being 1 with respect to [oxidant] and [substrate]; the order with respect to $[HClO_4]$ was not constant, but ~0.1 at lower acidities (when $[H^+] < 1.0$M) and ~0.5 at higher acidities (when $[H^+] > 1.0$M).

It has been reported earlier[20] that, in acidified vanadate solution, pervanadyl ion (VO_2^+) and its protonated species[21] (which may exist in the hydrated form) are present. Since most of the experiments were performed at a $[HClO_4]$ of 2.4M, it is likely that protonated vanadium(V) is the reactive oxidant species. The observed hydrogen-ion dependence on rate constant suggests that these oxidations are effected by the monoprotonated V(V) species $VO(OH)^{2+}$ [or its hydrated form $V(OH)_3^{2+}$], which remains in equilibrium with the non-protonated species VO_2^+ (or its hydrated form, $V(OH)_4^+$]. The reactions are believed to occur according to steps *11* and *12*.

$$VO_2^+ + H^+ \overset{K}{\rightleftharpoons} VO(OH)^{2+} \tag{11}$$

$$\text{Aldose} + VO(OH)^{2+} \overset{k}{\rightarrow} \text{Products} \tag{12}$$

The corresponding rate equation would be

$$-\frac{d[V(V)]}{dt} = k[\text{Aldose}][VO(OH]^{2+}] \tag{13}$$

$$= \frac{kK[\text{Aldose}]\,[V(V)]\,[H^+]}{1 + K[H^+]} \tag{14}$$

Since total $[V(V)] = [VO_2^+] + [VO(OH)^{2+}]$,

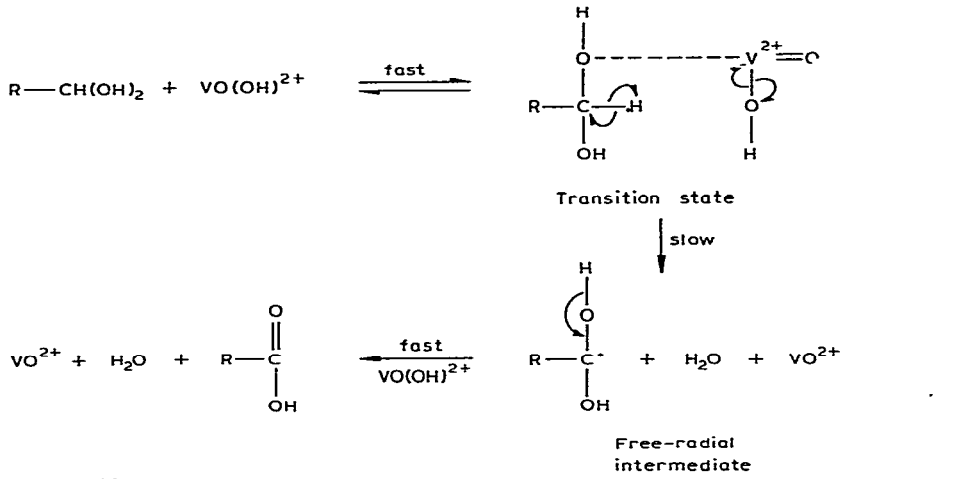
$$[VO(OH)^{2+}] = V(V)\left\{\frac{K[H^+]}{1 + K[H^+]}\right\},$$

or,

$$k_{obs} = -\frac{d[V(V)]}{dt} \times \frac{1}{[V(V)]} = \frac{kK[\text{Aldose}][H^+]}{1 + K[H^+]} \tag{15}$$

The rate expression *15* is in keeping with the observed orders with respect to each reactant. Moreover, the linear plots of $\log k_{obs}$ against μ (where μ is the ionic strength) further supports the view that the reaction takes place between a neutral molecule and an ion[22]. It is therefore suggested that vanadium(V) reacts with the hydrated

aldoses in the slow step, to yield free-radical intermediates and VO^{2+}. The free radical is further oxidised by another $VO(OH)^{2+}$ in a fast step, to yield the products (Scheme IV).



Scheme IV

The formation of a polymeric suspension when acrylamide was added to the reaction mixture indicates that the decomposition of the "transition state" into species like $R\text{-}\dot{C}(OH)_2$, and V (III),followed by their reactions with water and V(V), respectively, to yield the stable R.COOH and V(IV), are unlikely. On the other hand, unlike Cr(V) or Cr(IV), V(IV) is stable towards reduction and hence further reaction of the free radical with V(IV) would not take place. Vanadium(V) therefore behaves as a 1-equivalent oxidant in the rate-determining step, and the two-electron reduction mechanism of the type shown by Cr(VI) can be ruled out in the present study. The enthalpy of activation data further corroborate the above contention and are in keeping with earlier observations[5].

It is well known that aldohexoses and aldopentoses exist mainly in cyclic

TABLE V

VALUES OF MEASURED SECOND-ORDER RATE CONSTANTS AND ENTHALPY OF ACTIVATION AT 308 K FOR THE OXIDATIONS OF DIFFERENT TYPES OF ALDOSE

	Chromium(VI)		*Vanadium(V)*	
	$k_2 \times 10$ $(M^{-1}.sec^{-1})$	$\Delta H^{\ddagger}$ $(kJ.mol^{-1})$	$k_2 \times 10^3$ $(M^{-1}.sec^{-1})$	$\Delta H^{\ddagger}$ $(kJ.mol^{-1})$
Aldohexoses[3-5]	1.78–3.40	56–72	0.95–1.26	97–106
Aldopentoses[3-5]	3.70–7.55	46–54	5.94–9.29	80–82
Aldotetrose[a]	14.9	40	31.4	70
Aldotriose[a]	84.0	35.5	56.8	67

[a]Present study.

forms[23], whereas aldotetroses and the aldotriose exist mainly in acyclic forms[6]. It is suggested that the higher as well as the lower aldoses react in their preponderant forms with both Cr(VI) and V(V). Moreover, the dependence of the rate of oxidation on acidity with both oxidants is different for the higher and the lower aldoses. This behaviour seems to be due to the protonation of the cyclic forms of the higher aldoses, followed by their reaction with the oxidants, unlike the present studies, where the non-protonated, acylic forms of the lower aldoses are oxidised. However, in an attempt to correlate the pseudo-second-order rate constants (k_2) for the oxidations of the higher as well as the lower aldoses (Table V), it was found that the oxidation rates follow the order: triose> tetrose > pentose > hexose. This observation is also in agreement with the values of enthalpy of activation (Table V). Thus, with both Cr(VI) and V(V), the rates of oxidation of aldoses existing mainly in the acyclic form are higher than for aldoses existing mainly in cyclic forms.

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REFERENCES

1 (*a*) R. Barker and D. L. MacDonald, *J. Am. Chem. Soc.*, 82 (1960) 2301–2303; (*b*) E. Baer and H. O. L. Fischer, *ibid.*, 61 (1939) 761–765.
2 K. M. Holdorsen, *Carbohydr. Res.*, 63 (1978) 61–68.
3 K. K. Sen Gupta, S. Sen Gupta, and S. N. Basu, *Carbohydr. Res.*, 71 (1979) 75–84.
4 K. K. Sen Gupta and S. N. Basu, *Carbohydr. Res.*, 72 (1979) 139–149.
5 K. K. Sen Gupta and S. N. Basu, *Carbohydr. Res.*, 80 (1980) 223–232.
6 R. T. Morrison and R. N. Boyd, *Organic Chemistry*, Prentice-Hall, New Delhi, 2nd edition, 1973, pp. 998–1001.
7 K. K. Sen Gupta and H. R. Chatterjee, *Inorg. Chem.*, 17 (1978) 2429–2431.
8 Y. Sulfab and A. I. Abu-Shady, *Inorg. Chim. Acta*, 21 (1977) 115–118.
9 R. C. Thompson, *Inorg. Chem.*, 10 (1971) 1892–1895.
10 P. A. Best, J. S. Littler, and W. A. Waters, *J. Chem. Soc.*, (1962) 822–827.
11 W. G. Overend, M. Stacey, and L. F. Wiggins, *J. Chem. Soc.*, (1949) 1358–1363.
12 T. M. Feeley, M. K. Hargreaves, and D. L. Marshall, *Tetrahedron Lett.*, (1968) 4831–4834.
13 (*a*) R. P. Bell, *Adv. Phys. Org. Chem.*, 4 (1967) 1; (*b*) W. G. Overend, A. R. Peacocke, and J. B. Smith, *J. Chem. Soc.*, (1961) 3487–3497.
14 T. J. Kemp and W. A. Waters, *Proc. R. Soc. London, Ser. A*, 274 (1963) 480–499.
15 F. H. Westheimer, *Chem. Rev.*, 45 (1949) 419–451.
16 K. B. Wiberg and T. Mill, *J. Am. Chem. Soc.*, 80 (1958) 3022–3029.
17 Y. W. Chang and F. H. Westheimer, *J. Am. Chem. Soc.*, 82 (1960) 1401–1405.
18 (*a*) K. K. Sen Gupta and J. K. Chakladar, *J. Chem. Soc., Perkin Trans. 2*, (1973) 929–932; (*b*) *J. Chem. Soc., Dalton Trans.*, (1974) 222–225.
19 (*a*) J. Rocek and A. E. Radkowsky, *J. Am. Chem. Soc.*, 95 (1973) 7123–7132; (*b*) J. H. Merz and W. A. Waters, *Discuss. Faraday Soc.*, 2 (1947) 179–188.
20 T. A. Turney, *Oxidation Mechanisms*, Butterworths, London, 1965, pp. 35–66.
21 (*a*) R. N. Mehrotra, *J. Chem. Soc., B*, (1968) 642–644; (*b*) C. F. Wells and L. V. Kuritsyn, *J. Chem. Soc., A*, (1970) 1372–1376; (*c*) P. V. Subba Rao, N. Venkateswara Rao, R. V. S. Murthy, and K. S. Murthy, *Indian J. Chem.*, 15A (1977) 16–18.
22 A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, Wiley, New York, 1970, pp. 123–159.
23 W. Pigman and H. S. Isbell, *Adv. Carbohydr. Chem.*, 23 (1968) 11–57.