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KINETICS AND MECHANISM OF OXIDATION OF SOME ALDOSES BY VANADIUM(V) IN PERCHLORIC ACID MEDIUM

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ABSTRACT

The kinetics of oxidation of some aldoses by vanadium(V) in perchloric acid media have been investigated. Each reaction is first order with respect to both [Vanadium(V)] and [Aldose]. The reactions are catalysed by acid. The addition of sodium perchlorate accelerates the rate of reaction. Kinetic evidence for the formation of an intermediate compound between vanadium(V) and aldoses is insignificant, and a mechanism is suggested in which vanadium(V) reacts with the aldoses by a fast step to form a transition state, followed by the decomposition of the latter to give the products of reaction in a slow step. The formation of free-radical intermediates has been demonstrated, and one-electron reduction of vanadium(V) by aldoses seems to be the most plausible mechanism. The oxidation rates follow the order: xylose > arabinose > galactose > mannose. The activation parameters are reported.

INTRODUCTION

Aldoses are important for the understanding of carbohydrate metabolism because they can undergo a wide variety of reactions and give rise to different products[1]. Vanadium is present as vanadium(III) in the blood cells of certain marine invertebrates[2a], and is formed by the reduction of vanadium(V). There is increasing evidence that vanadium has a significant biological role[2b,c].

Much work has been done on the kinetics of oxidation of organic[3] and inorganic compounds[4] by vanadium(V), but no systematic kinetic study of the oxidation of aldoses by vanadium(V) appears to have been made. We have investigated[5] the oxidation of some aldoses by chromic acid in perchloric acid medium. Vanadium, in its highest oxidation state (+5) has close similarities with its successor in the first transition series, *i.e.*, chromium in the highest oxidation state (+6). Thus, the standard redox potential[6a] of $HCrO_4^-/Cr^{3+}$ is 1.195 volts, whereas that of V^{5+}/V^{4+} is 1.00 volt at 25°. This prompted us to select vanadium(V) as an oxidant for the aldoses. As expected from the lower E^0 value, the rates of oxidation by vanadium(V) were considerably lower than that by chromium(VI). Since $E^\circ_{V^{5+}-V^{4+}}$ increases[6b] from 1.00 volt in 1.0M $HClO_4$ to 1.18 volts in 5.0M $HClO_4$, the oxidation of aldoses by vanadium(V) was investigated at higher acidities as well as at higher temperatures. Some

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work has been done[7] on the kinetics of oxidation of aldoses by transition metal ions, but most of the studies involved sulphuric acid media. Since perchlorate ion is a weak ligand (unlike bisulphate and sulphate ions), it was thought worthwhile to investigate the present reactions in perchloric acid medium.

EXPERIMENTAL

Reagents. — D-Galactose and L-arabinose (E. Merck), and D-mannose and D-xylose (BDH) were used. Aqueous solutions of the aldoses were freshly prepared in doubly distilled water. Standard solutions of vanadium(V) were prepared by dissolving ammonium metavanadate (Merck) in a standard solution of perchloric acid (Merck, proanalysi sample). Sodium perchlorate was prepared by neutralization of perchloric acid with sodium hydroxide.

Kinetic measurements. — Solutions of vanadium(V) and the reaction mixture containing predetermined quantities of the organic substrate, perchloric acid, and other reagents (whenever necessary) were separately thermostated (variation, ±0.1 °). The reaction was initiated by adding the requisite amount of the oxidant, and followed by withdrawing aliquot portions at intervals and quenching them in a cold mixture of phosphoric acid and a known excess of standard Mohr's salt solution. The unreacted iron(II) was then immediately determined by titrating against standard vanadium(V) solution, using sodium diphenylamine sulphonate as the redox indicator. Iron(III) was found to have no effect on the organic substrate and vanadium(IV), since the $E^\circ_{Fe^{3+}-Fe^{2+}}$ was considerably lowered[6a] (from 0.77 volt to 0.438 volt in 1F H_3PO_4) in the presence of a sufficient excess of phosphoric acid.

The experiments were carried out in the presence of a large excess of organic substrate for at least 90, 75, 70, and 60% conversion of the initial concentration of vanadium(V) for the oxidations of galactose, mannose, arabinose, and xylose, respectively. The conversion was much higher at higher substrate concentrations, as well as at higher temperature. Generally, 6–8 experimental points were obtained in each experiment. Good first-order plots with respect to vanadium(V) were obtained. The pseudo-first-order rate constants (k_{obs} in sec^{-1}) were calculated from the slopes of plots of log [Vanadium(V)] against time. Duplicate experiments gave results that were reproducible to within ±5%.

Stoichiometry. — The reaction mixture containing organic substrate and perchloric acid was kept mixed with a large excess of vanadium(V) for several days at 45°. The unreacted oxidant was then determined. The results, as recorded in Table I, indicate the stoichiometry, *i.e.*, the ratio of the number of moles of vanadium(V) consumed to those of aldose consumed, with the assumption that no aldose was left. Thus, vanadium(V) ultimately effects the oxidation of aldoses to formic acid in the presence of excess of oxidant. This finding also supports the observation by Kemp and Waters[8] that formic acid is not oxidized by vanadium(V) in perchloric acid medium. However, the organic substrates have been used in sufficient excess throughout the kinetic investigations to ensure that the rate of reduction of the vanadium(V) is

TABLE I

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

Aldose	*Consumption ratio*	
	Experimentally observed	*On the basis of formation of only formic acid*
D-Galactose	11.8	12.0
D-Mannose	11.9	12.0
L-Arabinose	9.80	10.0
D-Xylose	9.85	10.0

proportional to the rate of oxidation of the organic substrates themselves, but not to the rate of destruction of any reactive organic intermediates[9]. Moreover, since the initial rate of consumption of vanadium(V) under these conditions was always first order, the rate of oxidation of the intermediate products cannot be kinetically significant[9].

Product analysis. — Since all of the kinetic investigations were carried out in presence of an excess of aldose, the reaction product was identified in reaction mixtures where an excess of aldose was oxidised separately by vanadium(V) in perchloric acid medium. The details have been described elsewhere[5]. Paper chromatography indicated the presence of aldonic acids along with the corresponding δ- and γ-lactones. This is in agreement with the observation[5,10] that the aldonic acid invariably remains in equilibrium with the corresponding δ- and γ-lactones in acid medium.

Polymerisation test. — A series of reactions between vanadium(V) and each of the aldoses was carried out under kinetic conditions in the presence of 10%(w/v) of acrylamide. When the reaction mixture was allowed to stand for 24 h, a viscous solution was obtained at lower acidities ($[HClO_4] \sim 0.1$M); at higher acidities ($[HClO_4] \sim 3.0$M), the whole of the reaction mixture turned to a thick gel. Control experiments, from which either vanadium(V) or aldose was excluded, indicated no polymerisation. These experiments indicate that the reaction between vanadium(V) and aldoses produces species that are capable of initiating acrylamide polymerisation.

RESULTS

Effect of oxidant concentration. — The pseudo-first-order rate constants were calculated at different initial concentrations of vanadium(V), but at a constant $[\text{Aldose}]_0$ and $[HClO_4]_0$ at 45°. The average values of k_{obs} are given in Table II. The results indicate that the pseudo-first-order rate constant is independent of initial analytical [Vanadium(V)], suggesting thereby that the reaction is first order with respect to [Vanadium(V)].

TABLE II

EFFECT OF INITIAL VANADIUM(V) CONCENTRATION ON PSEUDO-FIRST-ORDER RATE CONSTANT[a]

Aldose	*[V(V)] × 10²M*	k_{obs} × *10⁴ (sec⁻¹)*
D-Galactose	0.2–1.0	4.9 ± 0.2
D-Mannose	0.2–1.0	4.1 ± 0.1
L-Arabinose	0.2–1.0	15.0 ± 0.6
D-Xylose	0.2–1.0	25.1 ± 1.0

[a][Aldose] = 100mM. [HClO$_4$] = 5.75M. Temperature = 45°.

TABLE III

EFFECT OF SUBSTRATE CONCENTRATIONS ON PSEUDO-FIRST-ORDER RATE CONSTANTS[a]

[Substrate] × 10M	0.4	0.7	1.0	2.0	3.0	4.0
D-*Galactose*						
$k_{obs} \times 10^4$ (sec^{-1})	2.00	3.50	5.066	9.98	14.95	19.95
$\frac{k_{obs}}{[\text{Substrate}]} \times 10^2$ (M^{-1}.sec^{-1})	0.500	0.500	0.507	0.499	0.498	0.499
D-*Mannose*						
$k_{obs} \times 10^4$ (sec^{-1})	1.60	2.89	4.126	8.06	11.95	16.20
$\frac{k_{obs}}{[\text{Substrate}]} \times 10^2$ (M^{-1}.sec^{-1})	0.400	0.413	0.413	0.403	0.398	0.405
L-*Arabinose*						
$k_{obs} \times 10^4$ (sec^{-1})	6.00	10.20	15.55	31.09	43.40	58.27
$\frac{k_{obs}}{[\text{Substrate}]} \times 10^2$ (M^{-1}.sec^{-1})	1.500	1.600	1.555	1.555	1.447	1.457
D-*Xylose*						
$k_{obs} \times 10^4$ (sec^{-1})	10.40	18.42	26.10	51.82	79.07	98.96
$\frac{k_{obs}}{[\text{Substrate}]} \times 10^2$ (M^{-1}.sec^{-1})	2.600	2.632	2.610	2.591	2.636	2.474

[a][V(V)] = 10mM. [HClO$_4$] = 5.75M. Temperature = 45°.

Effect of aldose concentration. — The pseudo-first-order rate constants were measured at different initial concentrations of aldoses, but at constant [Vanadium(V)]$_0$ and [HClO$_4$]$_0$ at 45°. The results show that the reactions are first order with respect to both [Aldohexose] and [Aldopentose] (Table III). The average values of the second-order rate constants ($k_2 = k_{obs}/[\text{Aldose}]_0$) have been computed to be (0.50 ±0.01) × 10^{-2}, (0.40 ±0.01) × 10^{-2}, (1.52 ±0.1) × 10^{-2}, and (2.59 ±0.1) ×

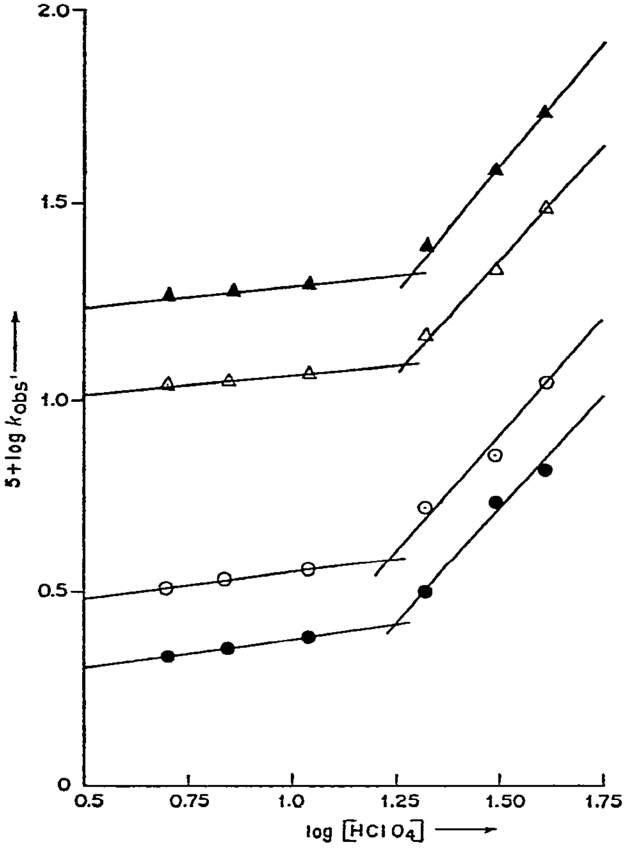


Fig. 1. Dependence of pseudo-first-order rate constant on perchloric acid concentration. [V(V)] = 10mM, [Aldose] = 100mM, μ = 4.1M, and temperature = 45°. —○—, D-Gal; —●—, D-Man; —△—, L-Ara; —▲—, D-Xyl.

TABLE IV

SLOPES OF THE ZUCKER–HAMMETT PLOTS

[HClO$_4$] (M)	*Slope of Zucker–Hammett plot*[a]			
	D-*Gal*	D-*Man*	L-*Ara*	D-*Xyl*
<2.0	0.14	0.16	0.12	0.12
>2.0	1.3	1.2	1.2	1.3

[a] log k_{obs} *vs.* log [HClO$_4$].

10^{-2} $M^{-1}.sec^{-1}$ for the oxidations of galactose, mannose, arabinose, and xylose respectively. The oxidation rates, which follow the order: xylose > arabinose > galactose > mannose, agree with previous observations[5,11].

Effect of perchloric acid concentration. — The effects of variation of acidity at

TABLE V

EFFECT OF SODIUM PERCHLORATE CONCENTRATIONS ON PSEUDO-FIRST-ORDER RATE CONSTANTS[a]

$[NaClO_4]$ (M)	$k_{obs} \times 10^4$ (sec^{-1})			
	D-*Gal*	D-*Man*	L-*Ara*	D-*Xyl*
0.0	1.13	0.67	3.20	5.60
0.5	1.49	1.08	3.99	6.53
1.0	1.79	1.41	5.06	8.64
1.5	2.03	1.82	7.38	11.71
2.0	2.78	2.50	9.21	14.78

[a] [V(V)] = 10mM. [Aldose] = 100mM. $[HClO_4]$ = 4.1M. Temperature = 45°.

TABLE VI

ACTIVATION PARAMETERS FOR THE OXIDATION OF ALDOSES BY VANADIUM(V) IN PERCHLORIC ACID MEDIUM

Aldose	Ea ($kJ.mol^{-1}$)	$\Delta H^{\ddagger}$ ($kJ.mol^{-1}$) *at 318 K*	$\Delta S^{\ddagger}$ ($J.deg^{-1}.mol^{-1}$) *at 318 K*	$\Delta G^{\ddagger}$ ($kJ.mol^{-1}$) *at 318 K*
D-Galactose	109 ± 6	106 ± 6	36.2 ± 19.8	94 ± 0.7
D-Mannose	101 ± 4	98.5 ± 4.2	10.4 ± 13.1	95 ± 0.2
L-Arabinose	82.8 ± 6.3	80 ± 6.5	−36.2 ± 19.8	92 ± 0.3
D-Xylose	84.8 ± 2	82 ± 2	−25.7 ± 6.6	90 ± 0.3

constant $[\text{Vanadium(V)}]_0$, $[\text{Aldose}]_0$, and ionic strength (maintained by addition of $NaClO_4$) at 45° on the pseudo-first-order rate constants were measured. The rate of oxidation of aldoses increases with increase in acid concentration. The plots of log k_{obs} against log $[HClO_4]$ shown in Fig. 1 are not linear over the entire acid range studied. The values of the slopes, as reported in Table IV, suggest that the acid dependence is complex.

Effect of sodium perchlorate concentration. — The effect of different initial concentrations (0–2.0M) of sodium perchlorate on the pseudo-first-order rate constants was measured. In all of the cases, the rate of oxidation increased with the increase in salt concentration (Table V). This indicates that the reaction takes place between ions of similar charge or that the reactions are of the ion–dipole type[12].

Effect of temperature and activation parameters. — The second-order rate constants ($k_2 = k_{obs}/[\text{Aldose}]_0$) for the oxidation of each of the aldoses at various temperatures from 35° to 50° were determined. The plots of log k_2 against 1/T were linear. The Arrhenius activation energies (*Ea*, calculated from the slopes of such plots) are of the order: *Ea* (aldohexose) > *Ea* (aldopentose), in accord with previous results[5,13]. The other activation parameters, calculated as described elsewhere[5], are recorded in Table VI.

DISCUSSION

The oxidations of aldohexoses and aldopentoses are all similar in character, indicating that similar mechanisms may be operative in all these cases of oxidations. It has already been mentioned that each of the oxidation reactions is first order with respect to [Vanadium(V)] as well as [Aldose]. The order with respect to $[H^+]$ is not constant and is much less than unity (0.12–0.16) at lower acidities ($[H^+] < 2.0$M), whereas it is slightly greater than unity (1.2–1.3) at higher acidities ($[H^+] > 2.0$M). Vanadium(V), although amphoteric in character, exists only as a cationic species[14] in solutions having acidity >0.05M. Thus, when vanadate is acidified by (non-complexing) perchloric acid, the yellow pervanadyl ion VO_2^+ is formed as the initial species[15].

$$VO_3^- + 2H^+ \rightleftharpoons VO_2^+ + H_2O \tag{1}$$

This may exist in the hydrated form[16], namely $V(OH)_4^+$. In stronger perchloric acid, this species becomes protonated[17], to form $VO(OH)^{2+}$ and VO^{3+} (which may also exist as $V(OH)_3^{2+}$ and $V(OH)_2^{3+}$, respectively), according to equations *2* and *3*.

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

$$VO(OH)^{2+} + H^+ \overset{K_2}{\rightleftharpoons} V(OH)_2^{3+} \tag{3}$$

The reactive oxidant species is any one or more of the cationic species in equations *2* and *3*. Since only a very small amount of the diprotonated vanadium(V) exists in solution, its reaction with unprotonated as well as protonated aldose is believed to be insignificant. Aldohexoses and aldopentoses exist mainly as cyclic hemiacetals, and a rapid and reversible transfer of H^+ to the ring oxygen atom may occur in strongly acidic medium. Thus, the existence of equilibrium *4* cannot be ruled out in strongly acidic medium.

$$S + H^+ \overset{K_3}{\rightleftharpoons} SH^+, \tag{4}$$

where S and SH^+ are the substrate and its protonated form, respectively.

Since the acid-dependence of rate of reaction was remarkably different at lower (<2.0M) and higher (>2.0M) acidities, it is possible that the mechanisms of oxidation are also different at lower and higher acidities.

At lower acidities (<2.0M), the order with respect to $[H^+]$ is 0.12–0.16, and the reaction is believed to follow simultaneously both acid-independent and acid-dependent pathways. Thus, unprotonated vanadium(V), namely VO_2^+, reacts with the aldose as well as the protonated aldose (formed according to equation *4*), according to equations *5* and *6*.

$$S + VO_2^+ \xrightarrow{k_a} \text{Products} + VO^{2+} \tag{5}$$

$$SH^+ + VO_2^+ \xrightarrow{k_b} \text{Products} + VO^{2+} \tag{6}$$

The corresponding rate expression is

$$-\frac{d[V(V)]}{dt} = k_a[S][VO_2^+] + k_b[SH^+][VO_2^+]. \tag{7}$$

From equations *4* and *7*, we get

$$-\frac{d[V(V)]}{dt} = k_a[S][VO_2^+] + k_bK_3[S][H^+][VO_2^+] \tag{8}$$

or

$$k_{obs} = k_a[S]\{1 + f[H^+]\}, \tag{9}$$

where $f = (k_bK_3)/k_a$.

At higher acidities (>2.0M), the order with respect to $[H^+]$ is 1.2–1.3, and the reaction is believed to follow simultaneously two acid-dependent pathways, one being proportional to $[H^+]$ and the other to $[H^+]^2$. Thus, monoprotonated vanadium(V) [namely, $VO(OH)^{2+}$, as shown in equation *2*] reacts with the aldose as well as the protonated aldose, according to equations *10* and *11*.

$$S + VO(OH)^{2+} \xrightarrow{k'_a} \text{Products} + VO^{2+} \tag{10}$$

$$SH^+ + VO(OH)^{2+} \xrightarrow{k'_b} \text{Products} + VO^{2+} \tag{11}$$

The corresponding rate expression is

$$-\frac{d[V(V)]}{dt} = k'_a[S][VO(OH)^{2+}] + k'_b[SH^+][VO(OH)^{2+}]. \tag{12}$$

From equations *2*, *4*, and *12*, we get

$$-\frac{d[V(V)]}{dt} = k'_aK_1[S][VO_2^+][H^+] + k'_bK_1K_3[S][VO_2^+][H^+]^2 \tag{13}$$

or

$$k_{obs} = k'[S][H^+]\{1 + f'[H^+]\}, \tag{14}$$

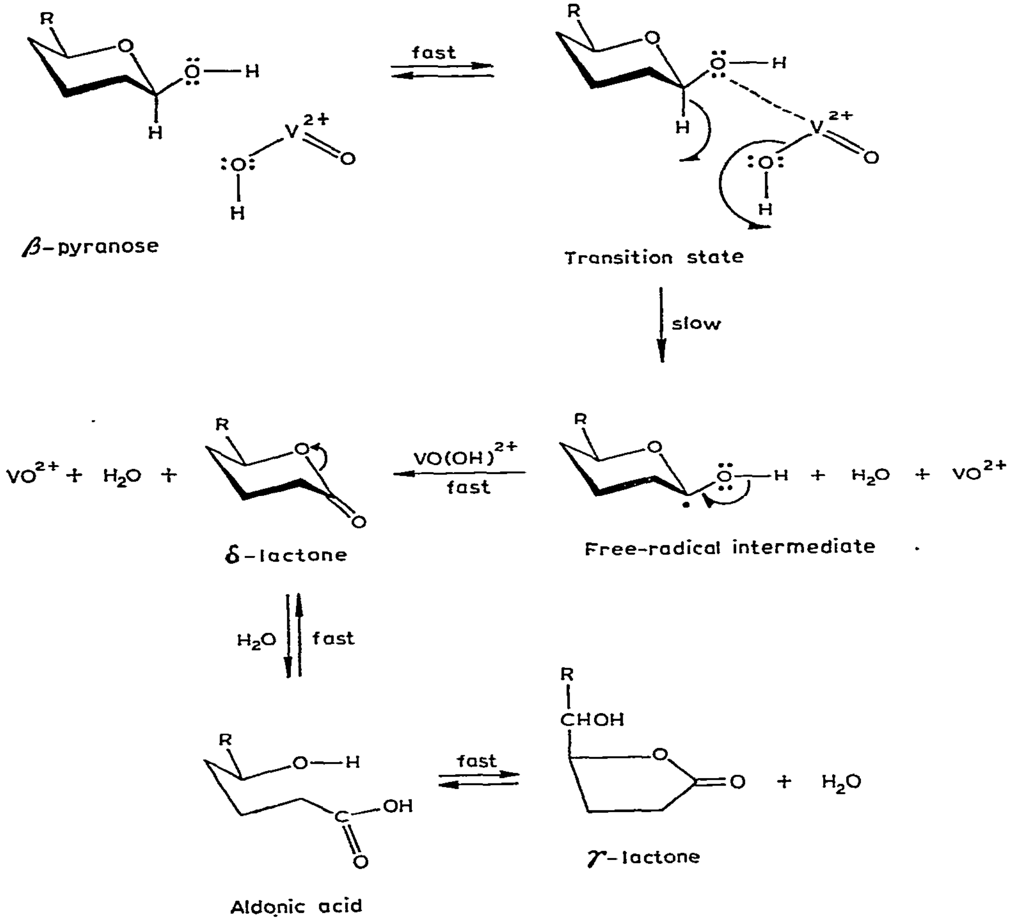
where $k' = k'_aK_1$ and $f' = (k'_bK_3)/k'_a$.

Equations *9* and *14* thus explain the observed orders obtained in the oxidations of aldohexoses and aldopentoses in the lower and higher acid regions, respectively. The observed, positive salt effect can thus be explained with the help of the reactions

5, *6*, *10*, and *11*, which may be due to cation–cation and cation–dipole interactions. Since unprotonated aldose is more nucleophilic than protonated aldose, reactions *5* and *10* are believed to be predominant.

Aldohexoses and aldopentoses exist mainly as pyranoid and furanoid forms, the former being more stable. The pyranoid form exists mainly in a chair conformation. The most reactive centre in these compounds is C-1. The interaction energies for the chair conformers of the aldohexoses and aldopentoses show that usually the conformer having the bulky HO-1 group equatorial is the most stable variety[10]. This preponderant conformer can form the "transition state" faster than the corresponding anomer having HO-1 axial. This situation is true for D-galactose, L-arabinose, and D-xylose[18a]. For D-mannose, the α anomer is preponderant[18b], and its axial HO-1 group is less exposed and is consequently less accessible to the oxidant. Hence, for D-mannose also, the β anomer is believed to react more rapidly[18b].

Since most of the kinetic experiments were carried out at higher acidities, the oxidation of aldoses at higher acidities may be explained by the reactions in Scheme 1.



Scheme 1 R = CH_2OH or H

The reactive monoprotonated species of vanadium(V) combines with the more-reactive unprotonated anomer of the aldoses by a fast step, to form a "transition state". The latter decomposes slowly, in the rate-determining step, by homolytic fission of the C-1–H-1 bond to give an organic free-radical and a vanadium(IV) species. The free-radical then reacts rapidly with another vanadium(V) to yield the δ-lactone, which undergoes fast and reversible hydrolysis to yield the corresponding aldonic acid which, in turn, equilibrates with the γ-lactone. Vanadium(V) is ultimately reduced to the blue vanadium(IV), which is known[19] to exist as vanadyl ion VO^{2+}.

Thus, a mechanism that fits all of the evidence is a one-electron decomposition of the "transition state", where bond formation occurs between the axially oriented H-1 of the aldoses and the OH group of the reactive oxidant species. Vanadium(V), therefore, behaves as a one-equivalent oxidant towards the aldohexoses and aldopentoses in perchloric acid medium.

It has earlier been shown[20] that chromium(VI) behaves as a two-equivalent oxidant, and chromic acid oxidations of some inorganic and organic compounds are characterized by lower activation energies. The activation energies obtained in the present investigation are much higher than those obtained for chromic acid oxidation of the respective aldoses[5]. This further supports the foregoing interpretation.

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