KINETICS AND MECHANISM OF OXIDATION OF D-GLUCOPYRANOSE 6-PHOSPHATE AND D-RIBOFURANOSE 5-PHOSPHATE BY VANADIUM(V) IN PERCHLORIC ACID MEDIA

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ABSTRACT

The second-order rate constants for the oxidations of D-glucopyranose 6-phosphate and D-ribofuranose 5-phosphate by vanadium(V) in perchloric acid media have been measured spectrophotometrically in the visible region. The order with respect to $[H^+]$ is less than unity for each reaction. The enthalpy and entropy of activations of the reactions are higher than those for the corresponding two-electron oxidations by chromium(VI). The oxidations involve free-radical intermediates.

INTRODUCTION

The kinetics of oxidation of some aldoses by $chromium(VI)^{1,2}$ and $vanadium(V)^{3,4}$ have been reported, but there are no systematic kinetic investigations of the oxidations of aldose phosphates by vanadium(V). Most of the vanadium(V) oxidations proceed *via* a free-radical mechanism^{5,6}, although an alternative sequence in which vanadium(V) undergoes a two-electron reduction⁷⁻⁹ followed by rapid oxidation of vanadium(III) to vanadium(V) has also been suggested. The present investigation was undertaken in order to compare the results obtained^{3,4} for the oxidations of the parent sugars by vanadium(V) as well as their phosphate derivatives⁵ by chromium(VI).

EXPERIMENTAL

General. — Details of the sugar phosphates have been reported⁵. A standard solution of vanadium(V) was prepared by dissolving ammonium metavanadate in standard perchloric acid. The strength of vanadium(V) was determined by mixing

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a known volume of the solution with an excess of standard Mohr's salt solution. The excess of Mohr's salt was titrated against standard dichromate solution using diphenylamine sulfonate as indicator.

Absorption spectra of vanadium(IV) and vanadium(V). — The standard solution of vanadium(V) was reduced to vanadium(IV) by excess of each substrate. Spectra of vanadium(IV) solutions in the range 2–20mM were recorded at 500–950 nm with λ_{max} 765 nm (ε_{max} 16.8 ±0.2). Beer's law was valid at 765 nm in the concentration ranges of vanadium(IV) studied. Vanadium(V) has¹⁰ λ_{max} 350 nm and at this wavelength it is the only absorbing species.

Kinetic measurements. — The rate of formation of vanadium(IV) was followed spectrophotometrically¹¹. The second-order rate constants (k_2) were calculated from plots of $1/(A_{\alpha} - A_t)$ against "t". Some experiments where [substrate]₀ \geq [vanadium(V)]₀ were also carried out, and the decrease of [vanadium(V)] was noted at 350 nm. Pseudo-first-order rate constants were determined graphically from plots of log A_{350} vs. time and were linear.

Rate law. — The reactions appeared to take place according to equations *1* and *2*.

$$C_6H_{13}PO_9 + 2 V(V) \rightarrow C_6H_{11}PO_9 + 2V(IV) + 2 H^+$$
 (1)

$$C_{5}H_{11}PO_{8} + 2 V(V) \rightarrow C_{5}H_{9}PO_{8} + 2 V(IV) + 2 H^{+}$$

$$(2)$$

Since the rate-determining step involves the decomposition of the transition state formed by the fast reaction between one mole each of substrate and oxidant, the rate equation may be expressed as

$$rate = k_2[substrate][oxidant].$$
(3)

If at any time "t", x mol of vanadium(IV) are formed, then the V(V) reacted will also be x mol. Since half of this amount reacts with the substrate in the rate-determining step, the amount of substrate reacted is 0.5x mol and the differential form of the rate equation would be given by equation 4.

$$\frac{dx}{dt} = k_2(a - x/2)(b - x),$$
(4)

where a and b are the initial molar concentrations of the substrate and the oxidant respectively. When b = 2a, integration of equation 4 gives equation 5.

$$\frac{1}{b-x} = \frac{1}{2}k_2t + \frac{1}{b}$$
(5)

Since $x \propto A_t$ and $b \propto A_{\infty}$, $1/(b - x) \propto 1/(A_{\infty} - A_t)$. Hence, a plot of $1/(A_{\infty} - A_t)$

against t gives a straight line. The slope of the straight line gives the value of $k'_2/2$, where k'_2 is the second-order rate constant in terms of absorbance (A). Multiplication of k'_2 by the molar extinction coefficient gives the actual value of the rate constants k_2 in terms of molarity. Typical second-order plots at different temperatures have been shown in Figs. 1 and 2.

Test for unstable intermediates. — Polymerisation tests were carried out for mixtures containing aldose phosphates and vanadium(V) in the presence of 8% of acrylamide. The reactions were done at concentrations of D-glucose 6-phosphate and D-ribose 5-phosphate of 5.0mM and 1.0mM, respectively, whereas the concentrations of vanadium(V) and HClO₄ were 10mM and 2.42M, respectively. Gel formation occurred after several hours, hence free radicals were formed.

RESULTS

Effect of reactant concentration. — The reactions were studied at various $[substrate]_0$, but the initial concentrations of vanadium(V) and acid were fixed for each run. The pseudo-first-order rate constant increased with increase in $[substrate]_0$ (Table I). The plots of k_{obs} against $[substrate]_0$ were linear and passed through the origin in each reaction. This finding indicated that each reaction was first order with respect to $[substrate]_0$. The average values of $k_{obs}/[substrate]_0$ at 42° were 3.11×10^{-3} and 9.40×10^{-2} $1.mol^{-1}.s^{-1}$ for D-glucose 6-phosphate and D-ribose 5-phosphate, respectively. Since the total order of the reactions is two, the order with respect to each substrate and vanadium(V) is unity.

Effect of perchloric acid. — The effect of $[H^+]_0$ was studied at various $[HClO_4]_0$, but at constant [reactants]_0 and temperature. The ionic strength could not be maintained constant. The plots of log k_2 against log $[HClO_4]_0$ were linear for each reaction. The slopes of the plots of log k_2 against log $[HClO_4]_0$ were 0.73 and

TABLE I

EFFECT OF SUBSTRATE	CONCENTRATIONS ON	PSEUDO-FIRST-ORDER	RATE CONSTANTS
BITEOT OF BUBBINAILE	Concentration of on	TOLODO LINGT ORDER	Mile constraints

[D-Glucose 6-phosphate] $_0^a \times 10^3$ (M)	2.5	5	10	15	20	
$k_{\rm obs} imes 10^4 ({ m s}^{-1})$	0.080	0.156	0.310	0.461	0.634	
$\frac{k_{\rm obs}}{[{\rm D-Glucose 6-phosphate}]_0} \times 10^3$	3.20	3.12	3.10	3.07	3.17	
[D-Ribose 5-phosphate] $_0^b \times 10^3$ (M)	2.5	5	7.5	10	15	
$k_{\rm obs} imes 10^4 ({ m s}^{-1})$	2.40	4.60	6.99	9.41	14.20	
$\frac{k_{\rm obs}}{[\text{D-Ribose 5-phosphate}]_0} \times 10^2$	9.60	9.20	9.32	9.41	9.47	

^a[V(V)]₀ 1.0mм, [HClO₄]₀ 4.84м, 42°. *^b*[V(V)]₀ 1.0mм, [HClO₄]₀ 1.21м, 45°.



Fig. 1. Second-order plots of $1/(A_{\perp} - A_{t})$ against time for the oxidation of D-glucopyranose 6-phosphate by vanadium(V): $-\Delta - 420^{\circ}$; $-\Phi - 500^{\circ}$, $-\Box - 550^{\circ}$; $-\Box - 550^{\circ}$; $-\Box - 650^{\circ}$; [D-glucose 6-phosphate]₀ = 12.5mM, [Vanadium(V)]₀ = 25mM, (HClO₄]₀ = 6.05M.

0.80 for the respective reactions at $[HClO_4]_0 \le 3.0M$.

Effect of salt concentration. — The concentration of $NaClO_4$ was varied in different sets, but the concentrations of oxidant, substrate, and acid were kept the same. The rates increased to the extent of 100% and 30% in M $NaClO_4$ in the respective oxidation-reduction reactions.

Influence of temperature. — The second-order rate constants (k_2) were calculated for various temperatures from the Figs. 1 and 2. The plots of log (k_2/T) against 1/T were linear (Fig. 3). The enthalpies of activation (ΔH^{\pm}) were calculated from the slopes of plots of log (k_2/T) against 1/T followed by the calculation⁵ of the entropies of activation (ΔS^{\pm}) . The values are recorded in Table II. The enthalpy and entropy of activations of the present reactions followed an order similar to that for the oxidation of the corresponding substrates with chromic acid⁵.

DISCUSSION

The kinetics of oxidation of D-glucopyranose 6-phosphate and D-ribofuranose 5-phosphate by vanadium(V) were similar in all respects, indicating that similar mechanisms are operative. Each reaction was first order with respect to oxidant as well as organic reductant. The order with respect to acid was <1 in each raction.

Monosodium D-glucose 6-phosphate in highly acidic (4.84M) medium is



Fig. 2. Second-order plots of $1/(A_{\infty} - A_i)$ against time for the oxidation of D-ribofuranose 5-phosphate by vanadium(V): $-\bigcirc$, 37.0°; $-\boxdot$, 48.0°; $-\bigtriangleup$, 52.0°; $-\bigoplus$, 57.0°; [D-ribose 5-phosphate]₀ = 12.5mM, [Vanadium(V)]₀ = 25mM, (HClO₄]₀ = 6.05M.



Fig. 3. Plots of log (k_2/T) against 1/T: [Vanadium(V)]₀ and [HClO₄]₀ = 25mM and 6.05M, respectively; [D-glucose 6-phosphate]₀ (-- \bigcirc -) = 12.5mM; [D-ribose 5-phosphate]₀ (-- \bigcirc -) = 12.5mM.

rapidly protonated to give D-glucose 6-phosphoric acid which exists mainly as the β -pyranoid chair form⁵. Moreover, the second hydrogen atom of the phosphate group is bonded to the ring oxygen of the sugar moiety. Although the medium is strongly acidic, protonation of the ring oxygen atom is not feasible owing to intramolecular hydrogen-bonding. This is reflected in the relatively lower value (0.73) with respect to acid in comparison to that (1.2) for the oxidation of D-glucose.

TABLE II

Substrate	$\Delta \mathrm{H}^{\ddagger}(kJ.mol^{-1})$	$\Delta S^{\ddagger} (J.deg^{-1}.mol^{-1})$
D-Glucose	97 $\pm 5 (56 \pm 4)$	+3.6 $\pm 5 (-89.7 \pm 14)$
D-Glucopyranose 6-phosphate	89.5 $\pm 4 (50 \pm 5)$	-3.38 $\pm 12 (-105.2 \pm 16)$
D-Ribose	81 $\pm 4 (49 \pm 3)$	-29.9 $\pm 12 (-108 \pm 10)$
D-Ribofuranose 5-phosphate	56.8 $\pm 3 (34.6 \pm 3.4)$	-82.2 $\pm 10 (-139.7 \pm 11)$

ACTIVATION PARAMETERS FOR THE OXIDATIONS OF D-GLUCOPYRANOSE 6-PHOSPHATE AND D-RIBOFURANOSE 5-PHOSPHATE AND THE PARENT ALDOSES BY VANADIUM(V) AND CHROMIUM(VI)^{α}

^aFigures in parentheses are the values for chromium(VI) oxidations⁵.

Hence, the molecular species is believed to be the reactive reductant. Disodium D-ribose 5-phosphate also undergoes fast protonation in strongly acid medium (1.21M) to give D-ribose 5-phosphoric acid which exists mainly as the α -furanose form¹². Here also protonation of the ring oxygen atom is not feasible because of intramolecular hydrogen-bonding between the ring oxygen of the sugar moiety and the acid hydrogen of the phosphate group. Hence, the molecular species is considered to be the effective reductant.

Acidification of vanadate yields the pervanadyl ion (VO_2^+) which is protonated^{13,14} in stronger acid medium. The fractional order (<1.0) in acid may be explained by the fact that $VO(OH)^{2+}$, which is formed by the reversible protonation of the pervanadyl ion, reacts with the unprotonated substrate. The observed kinetic salt effect is in keeping with the suggested ion-dipole mechanism.

The observed stoichiometry as well as the order with respect to substrate and oxidant may be explained by the steps shown in Schemes 1 and 2. The electron transfer from organic substrate to $VO(OH)^{2+}$ occurs *via* an intermediate which



p-Glucono-1,4-lactone 6-phosphate

D-Gluconic acid 6-phosphate

P-Glucono-1,5-lactore 6-phosphate

Scheme 1. Oxidation of D-glucopyranose 6-phosphate by vanadium(V).



Scheme 2. Oxidation of D-ribofuranose 5-phosphate by vanadium(V).

decomposes to give a free radical and VO^{2+} . The free radical is then oxidised by $VO(OH)^{2+}$ in a fast step to give lactones which remain in equilibrium with the free acids. The rate of disappearance of vanadium(V) may be expressed as equation 6.

$$\frac{-d[V(V)]}{dt} = \frac{kK[V(V)][S]}{1+K[S]}$$
(6)

Since kinetic evidence for intermediate complex formation is insignificant and $K[S] \ll 1$, the rate expression 6 changes to 7.

$$\frac{-d[\mathbf{V}(\mathbf{V})]}{dt} = k_2[\mathbf{V}(\mathbf{V})][\mathbf{S}]$$
⁽⁷⁾

The enthalpy and entropy of activations for one-electron transfer processes, in general are higher than those for the two-electron transfer processes⁷. The present reactions are characterised by higher activation parameters, unlike chromium(VI) which is predominantly a two-electron transfer oxidant. The formation of gel in the presence of acrylamide and the higher activation data suggested a free-radical mechanism. The mechanism of the oxidations of the sugar phosphates by vanadium(V) are different from those suggested for the oxidations of the parent sugars³ by this oxidant in perchloric acid media. It may be concluded that the presence of a phosphate group in the parent sugars not only changes the mechanism of the reactions but also increases the reactivity of the respective parent sugars towards metal ion oxidants. ACKNOWLEDGMENTS

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