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

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ABSTRACT

The kinetics of oxidation of D-glucopyranose 6-phosphate and D-ribofuranose 5-phosphate by chromium(VI) in perchloric acid media have been studied by u.v. spectroscopy. Each reaction is first order with respect to [chromium(VI)] and [substrate]. The reactions are acid-catalysed and accelerated by the addition of sodium perchlorate. The mechanism of the reactions is discussed.

INTRODUCTION

The oxidation of D-glucopyranose 6-phosphate and D-ribofuranose 5-phosphate by metal ion oxidants in highly acidic media has not been reported, although the kinetics of the oxidations of some aldoses in perchloric acid media have been studied[1–4]. We have investigated the oxidation of D-glucopyranose 6-phosphate and D-ribofuranose 5-phosphate by chromium(VI) in perchloric acid media in order to determine the effect of the phosphate group on the rate and mechanism of reaction.

MATERIALS AND METHODS

All the materials employed were of the highest purity available commercially. Aqueous solutions of the sugar phosphates were freshly made in doubly distilled water.

Kinetics measurements. — The rate of disappearance of chromium(VI) was measured by u.v. spectrophotometry (1-cm path length). The reactions were initiated by mixing the requisite quantity of the substrate with the solution of chromium(VI) and perchloric acid and were followed for at least 60% consumption of the initial [chromium(VI)]. Generally, 15–20 experimental points were noted in

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each run. The pseudo-first-order rate constants (k_{obs}) were calculated from the plots of log A (absorbance) *vs*. time, which were reproducible to within ±5%. Sodium perchlorate was added, whenever necessary, to maintain a constant ionic strength.

Product analysis. — The aldose phosphates were oxidised separately by chromium(VI) under the kinetic conditions. The oxidation products were analysed as described previously[5-8].

RESULTS

Effect of reactant concentration. — The pseudo-first-order rate constants were calculated at different initial concentrations of chromium(VI), but at constant [substrate]$_0$, $[HClO_4]_0$, and temperature of 2.5 × 10^{-3}M, 2.5M, and 26.5°, respectively, for the oxidation of D-glucose 6-phosphate, and 10^{-3}M, 2.5M, and 45°, respectively, for D-ribose 5-phosphate. The pseudo-first-order rate constants (k_{obs}) were independent of the initial [chromium(VI)] and indicated $HCrO_4^-$, or its protonated species, H_2CrO_4 or $HCrO_3^+$, to be the reactive species. The values of k_{obs} were (1.0 ±0.03) × 10^{-4} s^{-1} and (6.56 ±0.9) × 10^{-4} s^{-1} when [chromium(VI)]$_0$ was varied in the region (0.83–8.3) × 10^{-4}M. The pseudo-first-order rate constants were also measured at different [substrate]$_0$ but at constant [chromium(VI)]$_0$, $[HClO_4]_0$, and temperature. The results recorded in Table I indicate that the reactions are first order with respect to [D-glucose 6-phosphate] and [D-ribose 5-phosphate]. The average second-order rate constants (k_2) were 6.45 × 10^{-2} and 4.41 × 10^{-1} $l.mol^{-1}.s^{-1}$ at 35° for the oxidations of D-glucose 6-phosphate and D-ribose 5-phosphate, respectively.

Effect of perchloric acid concentration. — At constant $[Cr(VI)]_0$, [substrate]$_0$, temperature, and ionic strength (μ = 2.5M), the rates of oxidation of D-glucose 6-phosphate and D-ribose 5-phosphate increased with increase of $[H^+]_0$ (Fig. 1), and the slopes of the plots of log k_{obs} against log $[HClO_4]_0$ were 1.5 and 1.2, respectively.

Effect of salt concentration. — At constant $[Cr(VI)]_0$, [substrate]$_0$, $[HClO_4]_0$, and temperature, the rate constants for the oxidations of D-glucose 6-phosphate and D-ribose 5-phosphate increased by 60% and 30%, respectively, in 0.2M $NaClO_4$.

TABLE I

EFFECT OF SUBSTRATE CONCENTRATIONS ON PSEUDO-FIRST-ORDER RATE CONSTANTS

[D-Glucose 6-phosphate]$_0^a$ × 10^3 (M)	2.5	5 0	10.0	15.0	20.0
k_{obs} × 10^4 (s^{-1})	1.00	2.03	4.03	6.02	7 75
k_{obs}/[D-Glucose 6-phosphate]$_0$ × 10^2	4.00	4.06	4.03	4.01	3.87
[D-Ribose 5-phosphate]$_0^b$ × 10^3 (M)	0.5	1.0	2.0	3.0	4.0
k_{obs} × 10^4 (s^{-1})	3.22	6 56	12.3	19.0	26.1
k_{obs}/[D-Ribose 5-phosphate]$_0$ × 10	6.44	6.56	6.15	6 33	6 52

[a] $[Cr(VI)]_0$ 166μM, $[HClO_4]_0$ 2.5M, 26.5°. [b] $[Cr(VI)]_0$ 166μM, $[HClO_4]_0$ 2.5M, 45°.

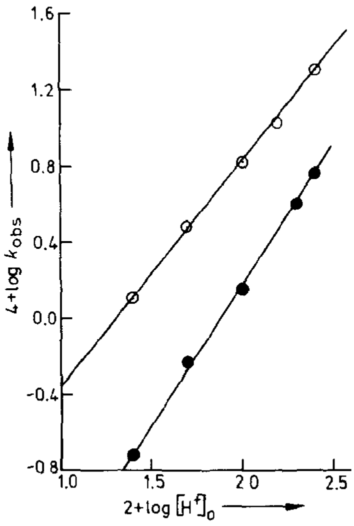


Fig. 1. Dependence of pseudo-first-order rate constant on $[HClO_4]_0$ at $[Cr(VI)]_0$ 166 μM: [D-Glucose 6-phosphate]$_0$ (—●—) 10mM, μ 2.5M, 26.7°; [D-Ribose 5-phosphate]$_0$ (—○—) mM, μ 2.5M, 42°.

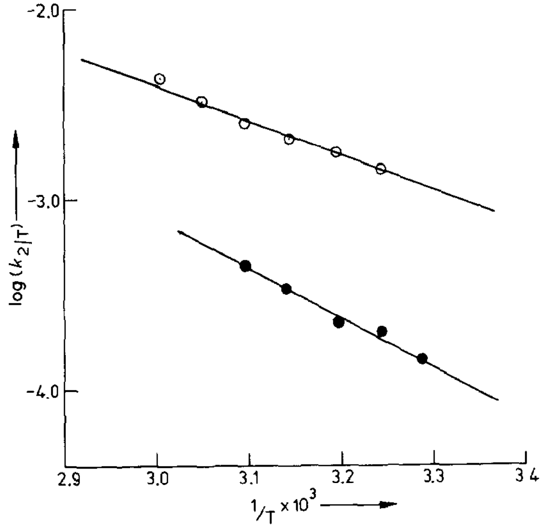


Fig. 2. Variation of second-order rate constant with temperature at $[Cr(VI)]_0$ and $[HClO_4]_0$ of 166 μM and 2.5M, respectively: [D-Glucose 6-phosphate]$_0$ (—●—) 10mM; [D-Ribose 5-phosphate]$_0$ (—○—) mM.

Activation parameters. — The second-order rate constants (k_2) were calculated at different temperatures. The plots of log(k_2/T) against 1/T were linear (Fig. 2). The enthalpies of activation ($\Delta H^\ddagger$) were calculated from the slopes of plots of log(k_2/T) against 1/T. The following equation[9] was used to calculate the entropy of activation ($\Delta S^\ddagger$):

TABLE II

ACTIVATION PARAMETERS OF THE OXIDATIONS OF D-GLUCOPYRANOSE 6-PHOSPHATE AND D-RIBOFURANOSE 5-PHOSPHATE AND THE PARENT ALDOSES BY CHROMIC ACID

Substrate	$\Delta H^{\ddagger}$ *(kJ.mol⁻¹)*	$\Delta S^{\ddagger}$ *(J.deg⁻¹.mol⁻¹)*
D-Glucose[3]	56 ±4	−89.7 ±14
D-Glucopyranose 6-phosphate	50.1 ±5	−105.2 ±16
D-Ribose[3]	49 ±3	−108 ±10
D-Ribofuranose 5-phosphate	34.6 ±3.4	−139.7 ±11

$$\log(k_2/\mathrm{T}) = \left\{ \log \frac{\mathrm{k}}{\mathrm{h}} + \frac{\Delta S^{\ddagger}}{2.303\,\mathrm{R}} \right\} - \frac{\Delta H^{\ddagger}}{2.303\,\mathrm{RT}},$$

where k is the Boltzmann constant and h is Planck's constant. The activation parameters of the present reactions along with the values obtained[3] for the oxidations of D-glucose and D-ribose are recorded in Table II. The enthalpy of activations follow the order, D-glucose > D-glucose 6-phosphate > D-ribose > D-ribose 5-phosphate.

DISCUSSION

Monosodium D-glucose 6-phosphate exists as a mononegative anion in aqueous solution, but, under conditions of high acidity (2.5M), it is rapidly protonated to yield D-glucose 6-phosphate (Robinson's ester) which exists mainly as the cyclic hemiacetal form. The apparent ionisation constants of D-glucose 6-phosphate are known[10]. The pK_a values (pK_{a_1} 0.94, pK_{a_2} 6.11) indicate that it exists preponderantly in the β-pyranose form, and the unusually strong ionisation of the first acid hydrogen has been attributed[10] to the formation of a hydrogen bond[11] between the ring oxygen of the sugar moiety and the second acid hydrogen of the phosphate group. The ring oxygen atom of D-glucose can undergo[3] rapid and reversible protonation in strongly acidic media, but this is not feasible for the 6-phosphate because of intramolecular hydrogen-bonding. Hence, unlike D-glucose, the reactive reductant is believed to be the molecular species. The relatively lower order of reaction (1.5) in acid in comparison to that (2.1) for D-glucose is also in keeping with this fact.

Disodium D-ribose 5-phosphate exists as a dinegative anion in aqueous solution, but, under highly acid conditions (2.5M), fast diprotonation to yield D-ribose 5-phosphate is believed to occur, which also exists[12] mainly as the furanose form where intramolecular hydrogen-bonding involving the ring oxygen atom and the phosphate group can occur. Because of intramolecular hydrogen-bonding between HO-2 and O-1, the α anomer is expected to be the preponderant form. Unlike D-ribose, the reactive form of D-ribose 5-phosphate cannot be protonated and this is reflected in the orders of reaction with respect to acid (2.15 and 1.20, respectively) for the oxidation of D-ribose and its 5-phosphate.

The oxidations of D-glucopyranose 6-phosphate and D-ribofuranose 5-phosphate by chromium(VI) are kinetically similar, indicating that similar mechanisms are operative. Each reaction is first order with respect to oxidant as well as organic reductant, whereas the order with respect to acid is 1.5 and 1.2, respectively. This complex order in acid is believed to be due to the fast reaction of uncharged organic substrate (S) with chromic acid (H_2CrO_4) as well as with protonated chromic acid ($HCrO_3^+$) yielding an intermediate ester.

$$S + H_2CrO_4 \rightarrow \text{Products} + \text{Cr(IV)} \qquad (1)$$

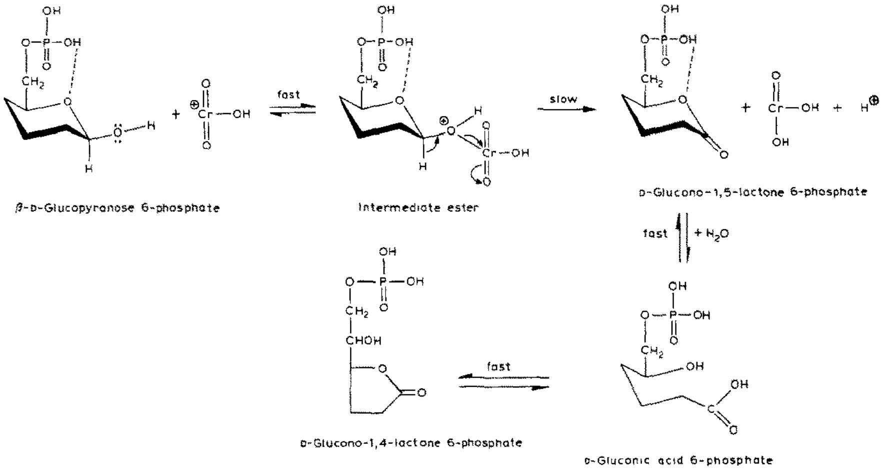
$$S + HCrO_3^+ \rightarrow \text{Products} + \text{Cr(IV)} \qquad (2)$$

The increase in pseudo-first-order rate constant with increase in salt concentrations indicates that the path involving ion–dipole[13] reaction predominates.

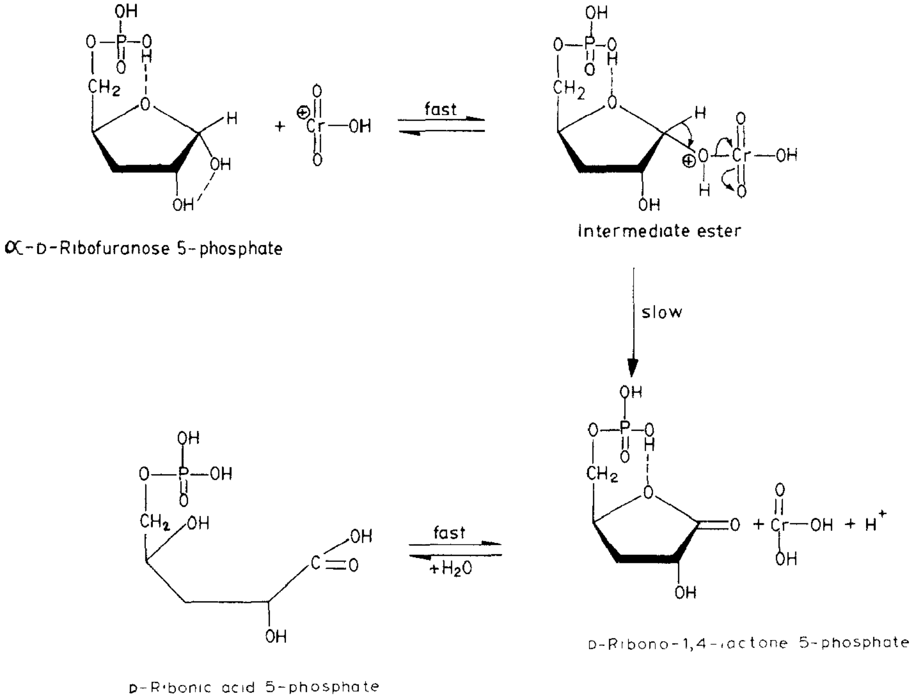
The intermediate ester slowly disproportionates to give chromium(IV) and lactone (1,5 from D-glucose 6-phosphate and 1,4 from D-ribose 5-phosphate) which rapidly equilibrates with the free acids and, for the glucose derivative, also with the 1,4-lactone. The oxidations of D-glucopyranose 6-phosphate and D-ribofuranose 5-phosphate are shown in Schemes 1 and 2, respectively.

Chromium(IV), formed in the slow step, is unstable, disproportionates, and reacts with chromium(VI) to form chromium(V). The latter, being a stronger oxidant than chromium(VI), rapidly oxidises another reactive species of the organic substrate to yield products as before together with stable Cr(III).

As with D-glucose and D-ribose, D-ribose 5-phosphate is oxidised much more rapidly than D-glucose 6-phosphate, and the phosphates react more rapidly than the corresponding parent sugar in conformity with the enthalpy of activation ($\Delta H^\ddagger$)



Scheme 1. Oxidation of D-glucopyranose 6-phosphate by chromium(VI).



Scheme 2. Oxidation of D-ribofuranose 5-phosphate by chromium (VI)

data. Thus, the presence of the phosphate increases the rate of oxidation, as found[5] for the oxidations of D-glucose and D-glucose 6-phosphate by iridium(IV).

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