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KINETICS AND MECHANISM OF OXIDATION OF D-GLUCOSE AND D-RIBOSE BY CHROMIUM(VI) AND VANADIUM(V) IN PERCHLORIC ACID MEDIUM

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ABSTRACT

The kinetics of oxidations of D-glucose and D-ribose by chromium(VI) and vanadium(V) in perchloric acid medium have been studied. 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 reaction. The rate of oxidation of ribose was greater than that of glucose. Mechanisms for these oxidations are suggested. An attempt has also been made to correlate rate constants and activation parameters for the oxidations of different aldoses by these two oxidants.

INTRODUCTION

The kinetics of oxidations of some aldoses by chromium(VI) and vanadium(V) have been reported[1,2] and, of the very few reports on the kinetics of oxidations of glucose and ribose by metal-ion oxidants[3,4], most have been concerned with oxidants other than chromium(VI) and vanadium(V). Moreover, there has been no systematic, kinetic study of the oxidations of these sugars by these two oxidants in perchloric acid medium. We now report on the kinetics of oxidations of D-glucose and D-ribose by chromium(VI) and vanadium(V) in perchloric acid medium.

EXPERIMENTAL

D-Glucose and D-ribose were commercial products, and their aqueous solutions were freshly prepared in doubly distilled water. Oxidants and other chemicals were the same as described earlier[1,2].

Kinetic measurements. — Solutions of the oxidant and reaction mixtures containing known quantities of the organic substrate, perchloric acid, and other chemicals (where necessary) were separately thermostated (±0.1 °). The reaction was initiated by mixing requisite amounts of the oxidant with the reaction mixture. Chromium(VI)

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oxidations were followed spectrophotometrically[1] at 30° and those with vanadium(V) were followed titrimetrically[2] at 45°, unless otherwise mentioned.

The reactions were carried out in the presence of a large excess of aldose for at least 70 and 75% conversion of initial [Cr(VI)], and 80 and 90% conversion of initial [V(V)], for the oxidations of D-glucose and D-ribose, respectively.

Stoichiometry. — The stoichiometries of the reactions using excess of oxidants were determined titrimetrically[1,2]. The results are recorded in Table I and indicate that these aldoses are oxidised to formic acid and subsequently to carbon dioxide by chromium(VI), whereas with vanadium(V), only formic acid was obtained. The reactions may be represented by Eqs. *1* and *2*.

$$3\,C_nH_{2n}O_n + (4n-2)\,Cr^{6+} + 3n\,H_2O \rightarrow 3\,H.COOH + 3(n-1)\,CO_2 + (4n-2)\,Cr^{3+} + 6(2n-1)\,H^+ \qquad (1)$$

$$C_nH_{2n}O_n + 2n\,V^{5+} + n\,H_2O \rightarrow n\,HCOOH + 2n\,V^{4+} + 2n\,H^+ \qquad (2)$$

However, under the kinetic conditions, the rate of reduction of the oxidants is controlled by the rate of oxidation of the substrates only, and not by that of the intermediate products[5].

TABLE I

STOICHIOMETRY OF THE OXIDATIONS[a,b] OF ALDOSES IN THE PRESENCE OF A LARGE EXCESS OF OXIDANT

Aldose	*Consumption ratio*		
	Experimentally observed	*On the basis of formation of*	
		Formic acid only	*Carbon dioxide only*
D-Glucose[a]	3.95	2.0	4.0
D-Ribose[a]	3.2	1.65	3.3
D-Glucose[b]	11.6	12.0	24.0
D-Ribose[b]	9.9	10.0	20.0

[a]Chromium (VI). [b]Vanadium (V).

Polymerisation test. — Tests for polymerisation were conducted for mixtures containing aldoses, oxidant, and perchloric acid in the presence of 10% of acrylamide. Gel formation was observed when vanadium(V) was used as oxidant, but neither glucose nor ribose initiated visible polymerisation with chromium(VI). Blank experiments, from which vanadium(V) or the aldose was excluded, indicated no polymerisation.

RESULTS

Effect of variation of reactant concentration. — The reactions were studied at various $[\text{oxidant}]_0$, maintaining constant $[\text{aldose}]_0$, $[HClO_4]_0$, and temperature.

The results indicated that the pseudo-first-order rate constant (k_{obs}) was independent of initial [oxidant], suggesting that the reactions are first order with respect to [oxidant] (Table II). Also, k_{obs} was determined at different $[\text{aldose}]_0$, but at constant $[\text{oxidant}]_0$, $[HClO_4]_0$, and temperature. The results (Table III) indicated that the reactions were first order with respect to both [glucose] and [ribose]. The average values of the second-order rate constants, k_2 (where $k_2 = k_{obs}/[\text{aldose}]_0$), were $(0.97 \pm 0.05) \times 10^{-1}$ and $(5.46 \pm 0.06) \times 10^{-1}$ $\text{M}^{-1}.\text{s}^{-1}$ for the oxidations of D-glucose and D-ribose by chromium(VI), and $(0.34 \pm 0.015) \times 10^{-2}$ and $(2.39 \pm 0.06) \times 10^{-2}$ $\text{M}^{-1}.\text{s}^{-1}$ for those by vanadium(V), respectively. The oxidation rates, therefore, follow the order ribose > glucose for each oxidant.

TABLE II

EFFECT OF INITIAL CONCENTRATION OF OXIDANT ON PSEUDO-FIRST-ORDER RATE CONSTANTS

Aldose	$k_{obs} \times 10^4$ (s^{-1})
D-Glucose[a]	1.00±0.2
D-Ribose[a]	5.3 ±0.1
D-Glucose[b]	3.3 ±0.01
D-Ribose[b]	22.6 ±1.0

[a][Cr(VI)] = (0.55–2.75) × 10^{-4}M, [aldose] = 1.0 × 10^{-3}M, and [$HClO_4$] = 2.4M. [b][V(V)] = (0.2–1.0) × 10^{-2}M, [aldose] = 1.0 × 10^{-1}M, and [$HClO_4$] = 5.75M.

TABLE III

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

[Glucose] × 10^3 (M)[a]	0.5	1.0	2.0	3.0	4.0	5.0	6.0
$k_{obs} \times 10^4$ (s^{-1})	0.485	1.00	1.88	2.84	3.80	4.91	5.87
$\frac{k_{obs}}{[\text{Glucose}]} \times 10$ ($\text{M}^{-1}.\text{s}^{-1}$)	0.97	1.00	0.94	0.95	0.95	0.98	0.98
[Ribose] × 10^3 (M)[a]	0.5	1.0	2.0	3.0	4.0	5.0	6.0
$k_{obs} \times 10^4$ (s^{-1})	2.71	5.29	10.6	16.1	22.2	27.3	33.9
$\frac{k_{obs}}{[\text{Ribose}]} \times 10$ ($\text{M}^{-1}.\text{s}^{-1}$)	5.42	5.29	5.3	5.37	5.55	5.46	5.65
[Glucose] × 10 (M)[b]	0.4	0.7	1.0	2.0	3.0	4.0	—
$k_{obs} \times 10^4$ (s^{-1})	1.37	2.45	3.39	6.6	10.2	13.0	—
$\frac{k_{obs}}{[\text{Glucose}]} \times 10^2$ ($\text{M}^{-1}.\text{s}^{-1}$)	0.343	0.350	0.339	0.330	0.340	0.325	—
[Ribose] × 10 (M)[b]	0.4	0.7	1.0	2.0	3.0	4.0	—
$k_{obs} \times 10^4$ (s^{-1})	9.6	17.0	23.6	47.5	71.0	96.0	—
$\frac{k_{obs}}{[\text{Ribose}]} \times 10^2$ ($\text{M}^{-1}.\text{s}^{-1}$)	2.40	2.43	2.36	2.38	2.37	2.40	—

[a][Cr(VI)] = 1.67 × 10^{-4}M and [$HClO_4$] = 2.4M. [b][V(V)] = 1.0 × 10^{-2}M and [$HClO_4$] = 5.75M.

Effect of variation of perchloric acid concentration. — The effect of variation of acidity at constant $[\text{oxidant}]_0$, $[\text{aldose}]_0$, ionic strength (maintained by addition of $NaClO_4$), and temperature, on k_{obs} was measured. The rate of oxidation of aldoses increased with the increase in acid concentration. The plots of log k_{obs} against log $[HClO_4]$ (Fig. 1) were linear for chromium(VI) oxidations, but non-linear for vanadium(V) oxidations, over the acid range studied. These results indicate that these reactions are acid-catalysed. The slopes of the above plots are recorded in Table IV.

TABLE IV

SLOPES OF THE PLOTS OF log k_{obs} *vs.* log $[HClO_4]$ FOR THE OXIDATIONS OF ALDOSES BY (*a*) CHROMIUM(VI) AND (*b*) VANADIUM(V)

[HClO₄] (M)	D-*Glucose*	D-*Ribose*
(*a*)[a] Up to 2.4	2.1	2.15
(*b*)[a] <2.0	0.26	0.17
>2.0	1.2	1.2

[a] (*a*) [Cr(VI)] = 1.67 × 10^{-4}M, [aldose] = 1.0 × 10^{-3}M, and μ = 2.4M. (*b*) [V(V)] = 1.0 × 10^{-2}M, [aldose] = 1.0 × 10^{-1}M, and μ = 4.1M.

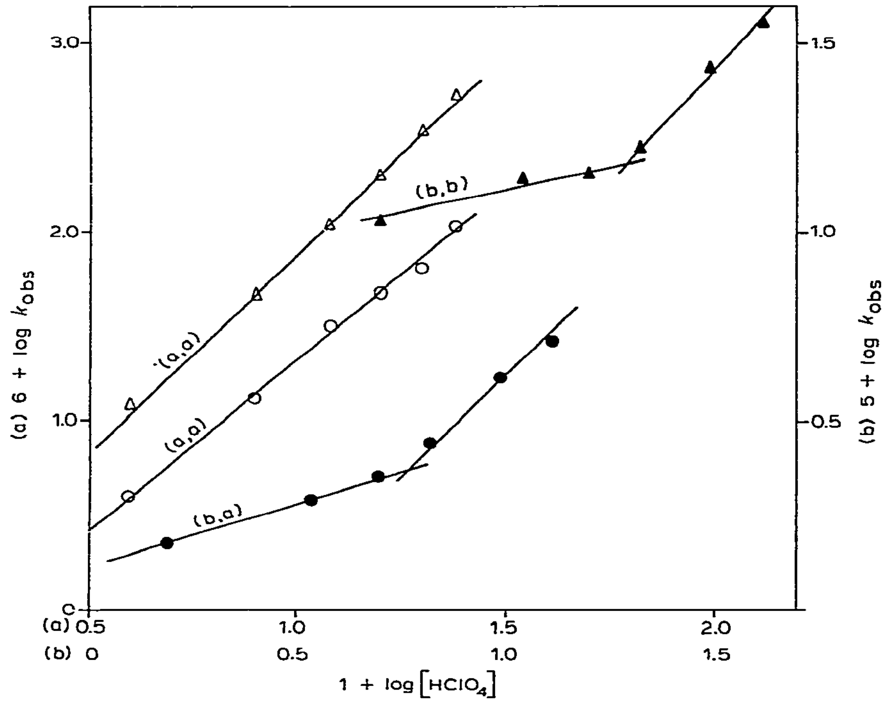

Fig. 1. Dependence of pseudo-first-order rate constant on perchloric acid concentration: (a) [Cr(VI)], 1.67 × 10^{-4}M; [aldose], 10^{-3}M; μ, 2.4M; 30° (—○—, D-glucose; —△—, D-ribose). (b) [V(V)], 10^{-2}M; [aldose], 10^{-1}M; μ, 4.1M; 45° (—●—, D-glucose; —▲—, D-ribose).

TABLE V

EFFECT OF VARIATION OF SODIUM PERCHLORATE CONCENTRATION ON PSEUDO-FIRST-ORDER RATE CONSTANTS

$[NaClO_4]$ (M)	$k_{obs} \times 10^4$ (s^{-1})		$[NaClO_4]$ (M)	$k_{obs} \times 10^4$ (s^{-1})	
	D-*Glucose*[a]	D-*Ribose*[a]		D-*Glucose*[b]	D-*Ribose*[b]
0.0	1.00	5.29	0.0	0.52	3.54
0.4	1.27	5.56	0.5	0.90	5.12
0.8	1.61	7.48	1.0	1.09	6.03
1.2	2.16	9.21	1.5	1.31	7.73
1.6	2.53	12.5	2.0	1.68	9.60
2.0	3.41	16.0			

[a] [Cr(VI)] = 1.67 × 10^{-4}M, [aldose] = 1.0 × 10^{-3}M, and [$HClO_4$] = 2.4M. [b] [V(V)] = 1.0 × 10^{-2}M, [aldose] = 1.0 × 10^{-1}M, and [$HClO_4$] = 4.1M.

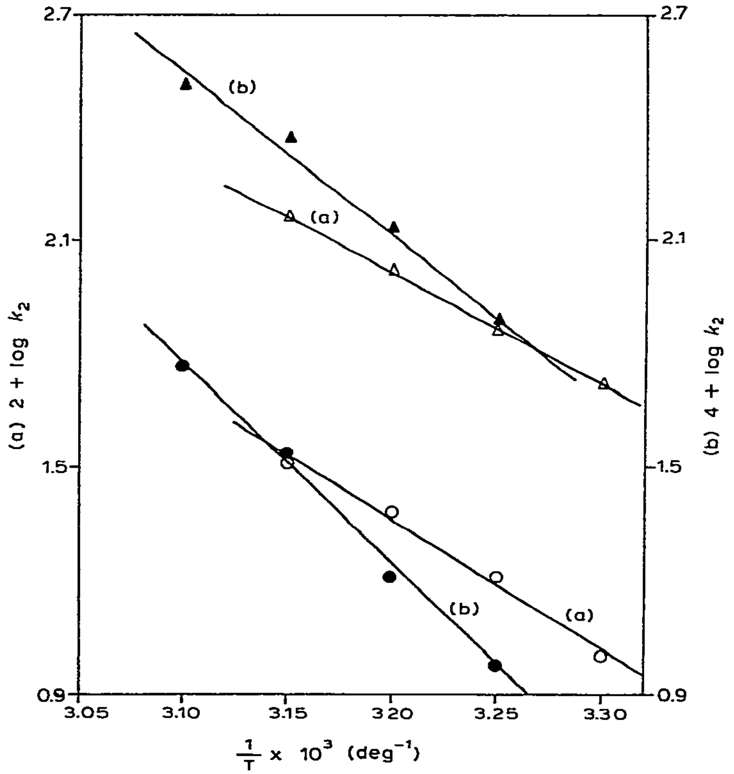

Fig. 2. Variation of second-order rate constant with temperature: (a) [Cr(VI)], 1.67 × 10^{-4}M; [aldose], 10^{-3}M; [$HClO_4$], 2.4M (—○—, D-glucose; —△—, D-ribose). (b) [V(V)], 10^{-2}M; [aldose], 10^{-1}M; [$HClO_4$], 5.75M (—●—, D-glucose; —▲—, D-ribose).

Effect of variation of sodium perchlorate concentration. — The pseudo-first-order rate constants (k_{obs}) increased with the increase of sodium perchlorate concentration (Table V). The results are in agreement with earlier observations[1,2] for the oxidations of other aldoses by these oxidants.

Effect of variation of temperature and activation parameters. — The values of k_2 for the oxidation of glucose and ribose at different temperatures, but at constant $[\text{oxidant}]_0$, $[\text{aldose}]_0$, and $[HClO_4]_0$, were determined. The plots of log k_2 against 1/T were linear (Fig. 2), and the Arrhenius activation energies (E_a) were evaluated from the slopes. The values of E_a ($kJ.mol^{-1}$) for the oxidations of glucose and ribose by Cr(VI) are 58.4 ± 4 and 51.6 ± 3, respectively, whereas those for V(V) oxidation are 99.6 ± 5 and 83.8 ± 4 for the respective reactions. The values of E_a are of the order E_a(aldohexose) > E_a(aldopentose), which is in conformity with the results obtained earlier[1,2].

DISCUSSION

The rates of oxidation of glucose and ribose with Cr(VI) or V(V) are of the same order, indicating a common mechanism. Thus, for Cr(VI) oxidations, each reaction was first order with respect to [chromium(VI)] as well as [aldose], whereas the order with respect to $[HClO_4]$ was 2.1 and 2.15 for the respective reactions. The formation of diprotonated aldoses is unlikely, but the formation of the protonated chromic acid molecule[6], *i.e.*, $H_3{}^+CrO_4$, or the corresponding anhydride, *e.g.* HCr^+O_3, is known to occur. Consequently, the protonated chromic acid (HCr^+O_3) molecule is believed to react with the protonated substrate (SH^+) molecule according[1] to Eq. *3*. The addition of sodium perchlorate increases the rate of this reaction, which supports the view that the reaction involves ions of similar charge[7].

$$SH^+ + HCr^+O_3 \rightarrow \text{Products} + H_2CrO_3 \qquad (3)$$

For V(V) oxidation of these aldoses, the order with respect to [vanadium(V)] and [aldose] is one. The order with respect to $[HClO_4]$ is not constant, but much less than unity ($\sim$0.2) at lower acidities (<2M) and slightly greater than unity (1.2) at higher acidities (>2M). Since most of the experiments were carried out at a $[HClO_4]$ of 5.75M, it is likely[8] that monoprotonated vanadium(V), *i.e.*, $VO(OH)^{2+}$, reacts with both unprotonated (S) as well as protonated aldoses (SH^+), according[2] to Eqs. *4* and *5*, of which the former reaction is likely to predominate. For a reaction between an ion and a neutral molecule, the plot of log k_{obs} against μ (where μ is the ionic strength) is linear[9], which we have observed in oxidations of glucose and ribose by V(V).

$$S + VO(OH)^{2+} \rightarrow \text{Products} + VO^{2+} \qquad (4)$$

$$SH^+ + VO(OH)^{2+} \rightarrow \text{Products} + VO^{2+} \qquad (5)$$

Glucose and ribose, in aqueous solution, exist mainly as hemiacetal cyclic forms[10] which are in dynamic equilibrium with the aldehydo form[11]. The concentration of the aldehydo form markedly differs in these two aldoses, and there is a difference between the individual rates of oxidation of the aldoses by Cr(VI) and V(V). These differences may be considered to reflect the concentrations of the aldehydo forms of the aldoses. Whereas the relative proportion of the aldehydo form of D-ribose is several hundred times[11] greater than that of D-glucose, the rate of oxidation of the former is greater by a factor of <10 (Table VI). Thus, the aldehydo form does not seem to be the reactive species and, hence, the cyclic forms must be involved. The pyranoid forms in the $^4C_1$ conformation preponderate[13] in aqueous solutions of D-glucose, and the β anomer with HO-1 equatorial is expected[12] to be readily attacked by the oxidants. However, β-D-ribose exists[13] as an equilibrium mixture of $^4C_1$ and $^1C_4$ forms, of which the former preponderates. These aldoses are believed to be oxidised preponderantly in the $^4C_1$ β-pyranoid form, and hence the initial product should be the corresponding lactone. The reactions with chromium(VI) proceed as follows.

$$\begin{array}{lcl}
\text{Protonated } \beta\text{-aldopyranose} + \overset{\text{VI}}{\text{HCrO}_3^+} & \rightleftharpoons & \text{Protonated unstable} \\
 & & \text{intermediate} \\
 & & \quad\quad \downarrow \text{slow} \\
 & & \text{Products} + \overset{\text{IV}}{\text{H}_2\text{CrO}_3}
\end{array}$$

The above findings are not in agreement with the observation made earlier by Chandra and Mittal[14]. However, Cr(IV), which is generated in the slow step, is unstable, and reacts with Cr(VI), or disproportionates[15], to give Cr(V) which finally oxidises the reactive species of the aldoses and is reduced to the stable Cr(III). Cr(VI) has been reported to behave also as a three-electron transfer oxidant[16]. Since the order with respect to the aldose is one in the present study, simultaneous transfer of all the three electrons in the slow step is not feasible.

On the other hand, the reactions with vanadium(V) at higher acidities proceed mainly as follows.

$$\begin{array}{lcl}
\beta\text{-Aldopyranose} + \text{VO(OH)}^{2+} & \rightleftharpoons & \text{Transition state} \\
 & & \quad\quad \downarrow \text{slow} \\
\text{VO}^{2+} + \text{Products} & \xleftarrow{\text{VO(OH)}^{2+}} & \text{Intermediate free-radical} \\
 & & \text{from aldose} + \text{VO}^{2+}
\end{array}$$

This mechanism is supported by the fact that the addition of acrylamide to the reaction mixture indicated the generation of free radicals in V(V) oxidations, unlike Cr(VI) oxidations. This conclusion is also substantiated by the fact that the activation energies are widely different for Cr(VI) and V(V) oxidations of glucose and ribose.

The oxidations of all the aldohexoses and the aldopentoses that we have studied, using Cr(VI) as oxidant, are kinetically similar. Moreover, their second-order rate constants (k_2) are of the same order ($\sim 10^{-1}\text{M}^{-1}.\text{s}^{-1}$), indicating that similar mechanisms may be operative. Likewise, the V(V) oxidations are kinetically similar

TABLE VI

SECOND-ORDER RATE CONSTANTS FOR THE OXIDATIONS OF ALDOSES BY CHROMIUM(VI) AND VANADIUM(V) IN PERCHLORIC ACID MEDIUM AT 308K

Aldose	*Cr(VI)* $k_2 \times 10$ ($M^{-1}.s^{-1}$)	*V(V)* $k_2 \times 10^3$ ($M^{-1}.s^{-1}$)
D-Glucose	1.78	0.95
D-Mannose	2.14	1.17
D-Galactose	3.4	1.26
D-Xylose	6.6	9.29
L-Arabinose	3.7	5.94
D-Ribose	7.55	7.68

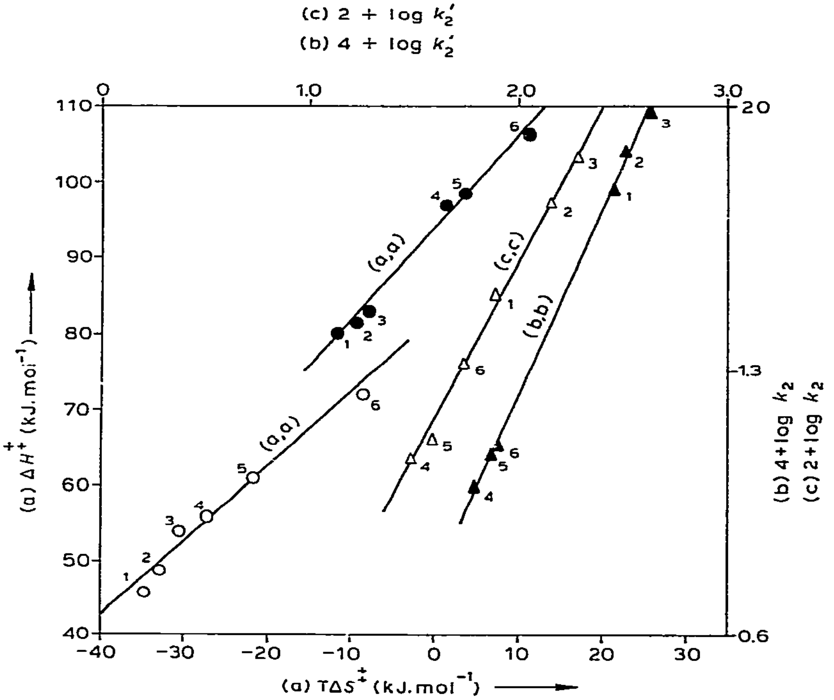

Fig. 3. Isokinetic plots for the oxidations of aldohexoses and aldopentoses by chromium(VI) and vanadium(V) in perchloric acid medium [○, △ Cr (VI); ●, ▲ V(V)]: 1, L-arabinose; 2, D-ribose; 3, D-xylose; 4, D-glucose; 5, D-mannose; 6, D-galactose.

and their k_2 values are of the same order ($\sim 10^{-3}M^{-1}.s^{-1}$), and hence they are believed to follow a similar mechanism. But, as the values of k_2 in Cr(VI) oxidations are very different from those obtained in V(V) oxidations (Table VI), the mechanisms of oxidations of these aldoses by Cr(VI) and V(V) are likely to be different. This view accords with the linear isokinetic plots[17,18] (Fig. 3) obtained by plotting $\Delta H^{\ddagger}$ *vs* $T\Delta S^{\ddagger}$ as well as log k_2 *vs* log k_2' (where k_2 and k_2' are the rate constants at the temperatures

TABLE VII

VALUES OF ENTHALPY AND ENTROPY OF ACTIVATION FOR THE OXIDATIONS OF ALDOSES BY CHROMIUM(VI) AND VANADIUM(V) IN PERCHLORIC ACID MEDIUM

Aldose	$\Delta H^{\ddagger}$ *(kJ.mol⁻¹)*		$\Delta S^{\ddagger}$ *(J.deg⁻¹.mol⁻¹)*	
	Cr(VI)	*V(V)*	*Cr(VI)*	*V(V)*
D-Galactose	72 ±4	106 ±6	−27.6 ±13	36.2 ±19.8
D-Mannose	61 ±5	98.5 ±4.2	−70.5 ±16	10.4 ±13.1
D-Glucose	56 ±4	97 ±5	−89.7 ±14	3.6 ±15
D-Xylose	54 ±2	82 ±2	−101 ± 9	−25.7 ± 6.6
D-Ribose	49 ±3	81 ±4	−108 ±10	−29.9 ±12
L-Arabinose	46 ±3.5	80 ±6.5	−114 ±13	−36.2 ±19.8

T and T′, respectively). Again, from our studies[1,2] of the oxidations of aldoses having the same conformation, the following points may be noted.

(*a*) The presence of different substituents at C-5 (*i.e.*, H or CH_2OH) affects the rate appreciably. The much lower rate for the aldohexoses in comparison to that for aldopentoses may be attributed to the inductive (—I) effect, as well as the stabilising effect, of the hydroxymethyl group in the former. The values of $\Delta S^{\ddagger}$ for aldohexoses, which are higher than those of aldopentoses (Table VII), are also in keeping with the idea of Hammett and co-workers[19], who showed that $\Delta S^{\ddagger}$ is related to the rigidities of organic compounds.

(*b*) There is a small difference in the rates of oxidations of aldoses having the same substituents at C-5, which seems to be due to the configurational variation at positions other than C-1 and C-5.

In our studies, Cr(VI) behaved as a two-electron transfer oxidant, whereas V(V) behaved as a one-electron transfer oxidant. Thus, polymerisation tests were positive only for V(V) oxidations. Moreover, the $\Delta H^{\ddagger}$ values were higher for the V(V) oxidations (Table VII), reflecting the involvement of high-energy free-radicals and according with observations on the oxidations of inorganic compounds[20].

The values of the second-order rate constants (k_2) were always higher (Table VI) for the Cr(VI) oxidations, although the acidity is higher in the V(V) oxidations. This fact conforms with the view that, for oxidants having similar redox potentials, two equivalent oxidations proceed faster than one[21].

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