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KINETICS AND MECHANISM OF OXIDATION OF D-FRUCTOSE AND L-SORBOSE BY CHROMIUM(VI) AND VANADIUM(V) IN PERCHLORIC ACID MEDIUM

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

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ABSTRACT

Kinetic data for the oxidations of D-fructose and L-sorbose by chromium(VI) and vanadium(V) in perchloric acid medium are reported. The addition of perchloric acid and sodium perchlorate increases the pseudo-first-order rate constants. Change of the reaction medium from water to deuterium oxide appreciably affects the rates of chromium(VI) oxidations, but does not affect those of vanadium(V) oxidations. The activation parameters are $\Delta H^{\ddagger} = 46.6 \pm 3.4$ (fructose) and 50.6 ± 6.3 (sorbose) $kJ.mol^{-1}$, and $\Delta S^{\ddagger} = -105 \pm 11$ (fructose) and -100 ± 20 (sorbose) $J.deg^{-1}.mol^{-1}$ for chromium(VI) oxidations, and, for the other reactions, $\Delta H^{\ddagger} = 53.2 \pm 4.2$ (fructose) and 52.3 ± 6.3 (sorbose) $kJ.mol^{-1}$, and $\Delta S^{\ddagger} = -139.0 \pm 14$ (fructose) and -137 ± 20 (sorbose) $J.deg^{-1}.mol^{-1}$. The kinetics of the oxidations of ketohexoses by chromium(VI) indicate no intermediate-complex formation, whereas those for vanadium(V) indicate the formation of a 1 : 1 intermediate complex between ketohexoses and vanadium(V).

INTRODUCTION

D-Fructose plays an important role in mammalian metabolism[1], and the recent tendency to use it as a substitute for sucrose, because of its nutritive qualities without risk[2], has led to investigations of its physicochemical properties in solution[3].

The mechanism of oxidation of ketohexoses by transition-metal ions in acid media[4a] has been little studied, although a few kinetic studies involving different oxidants[4b–d] in alkaline media have been reported. The oxidation of cyclic and acyclic forms of aldoses by chromium(VI) and vanadium(V) has been studied in detail[5–8], and we now report on the kinetics and mechanism of oxidations of D-fructose and L-sorbose by these reagents.

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*To whom correspondence should be sent.

EXPERIMENTAL

D-Fructose and L-sorbose were commercial products, and their aqueous solutions were freshly prepared in double-distilled water. The oxidants and other chemicals were as described earlier[7,8].

Kinetic measurements. — The kinetics of oxidation reactions were followed spectrophotometrically with a Perkin–Elmer spectrophotometer (digital) as previously described[7,8]. The reactions were performed in the presence of a large excess of each substrate. The reactions were initiated by mixing the requisite amounts of the oxidants with the reaction mixture.

Test for free radicals. — Gel formation in acrylamide was observed when vanadium(V) was used as oxidant, but neither fructose nor sorbose initiated visible polymerisation with chromium(VI). However, polymerisation did not take place when the monomer was added to separate solutions of vanadium(V) and of ketohexoses. The induced polymerisation of acrylamide added to the reaction mixtures in the vanadium(V) oxidations suggests the formation of free radicals.

Identification of reaction products. — The production of formic acid in the chromic acid oxidations of ketohexoses was confirmed by its reduction to formaldehyde by Zn/HCl followed by the preparation of the dimedone derivative. The dimedone derivative could be obtained directly from the reaction mixture in the oxidation of ketohexoses by vanadium(V), and the reduction by Zn/HCl was not necessary. This indicates that ketohexoses are oxidised directly by vanadium(V) to formaldehyde. The details of lactone products have been described previously[5].

RESULTS

Effect of variation of reactant concentrations. — The reactions were studied at various $[\text{oxidant}]_0$, maintaining a constant $[\text{ketohexose}]_0$, $[\text{HClO}_4]_0$, and temperature. The results indicated that the pseudo-first-order rate constant (k_{obs}) was independent of initial $[\text{oxidant}]_0$, suggesting that the reactions are first order with respect to [oxidant]. Likewise, k_{obs} was determined at different $[\text{ketohexose}]_0$, but at constant $[\text{oxidant}]_0$, $[\text{HClO}_4]_0$, and temperature. The reactions were first order with respect to both [fructose] and [sorbose] in chromium(VI) oxidations (Table I). The average values of the second-order rate constants, k_2 (where $k_2 = k_{\text{obs}}/[\text{ketohexose}]_0$, were $(6.99 \pm 0.2) \times 10^{-1}\text{M}^{-1}.\text{s}^{-1}$ and $(2.26 \pm 0.1) \times 10^{-1}\text{M}^{-1}.\text{s}^{-1}$ for the oxidations of D-fructose and L-sorbose at 35 and 31 °, respectively. For vanadium(V) oxidations, the orders with respect to [fructose] and [sorbose] were less than unity and can be expressed by the equation

$$\frac{-\,d\,[\text{V(V)}]}{dt} = \frac{kK\,[\text{V(V)}]\,[\text{ketohexose}]}{1 + K\,[\text{ketohexose}]},$$

where k and K are the disproportionation and equilibrium constants of a 1:1 inter-

TABLE I

EFFECT OF SUBSTRATE CONCENTRATION ON PSEUDO-FIRST-ORDER RATE CONSTANTS FOR OXIDATIONS BY CHROMIUM(VI)

[Fructose] × 10^3 (M)[a]	0.5	1.0	2.0	3.0	4.0	5.0
$k_{obs} \times 10^4$ (s^{-1})	3.50	6.83	13.60	21.18	28.80	35.30
$\frac{k_{obs}}{[\text{Fructose}]} \times 10$ ($M^{-1}.s^{-1}$)	7.00	6.83	6.80	7.06	7.20	7.06
[Sorbose] × 10^3 (M)[b]	0.5	1.0	2.0	3.0	4.0	5.0
$k_{obs} \times 10^4$ (s^{-1})	1.17	2.30	4.38	6.48	9.36	11.17
$\frac{k_{obs}}{[\text{Sorbose}]} \times 10$ ($M^{-1}.s^{-1}$)	2.34	2.30	2.19	2.16	2.34	2.23

[a] [Cr(VI)] = 1.67 × 10^{-4} M, [$HClO_4$] = 3.2M, and temperature = 35°. [b] [Cr(VI)] = 1.67 × 10^{-4} M, [$HClO_4$] = 3.2M, and temperature = 31°.

mediate complex. The values of k and K were calculated from the plots of $1/k_{obs}$ against 1/[ketohexose] (Figs. 1 and 2) as previously reported[9].

Effect of variation of perchloric acid concentration. — The effect of variation of acidity on k_{obs} was studied at constant ionic strength (maintained by the addition of $NaClO_4$). The results plotted in Fig. 3 indicate that the rate of oxidation of keto-

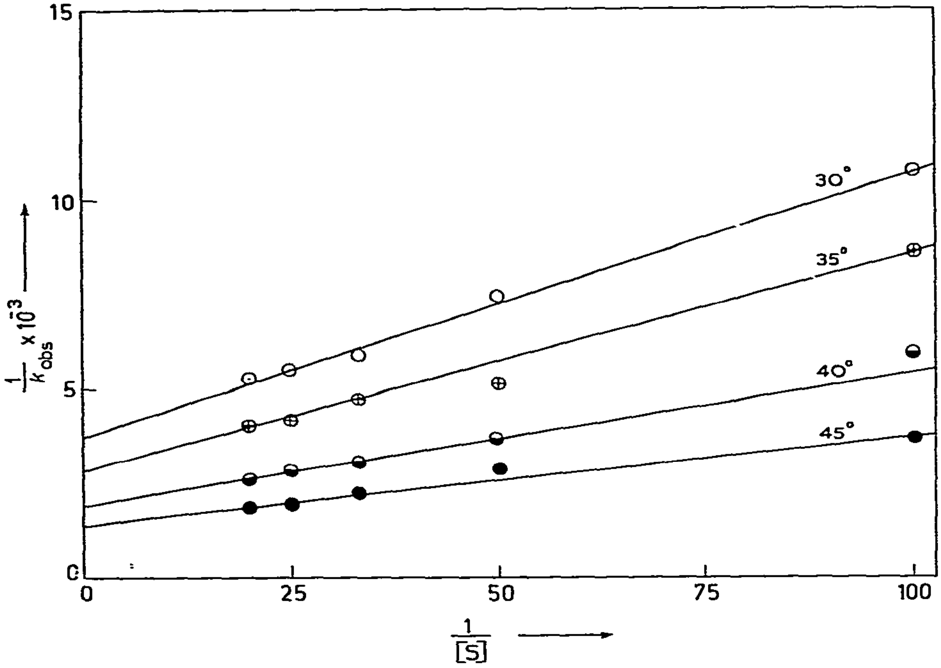

Fig. 1. Kinetic evidence for intermediate-complex formation between vanadium(V) and D-fructose. Plots of $1/k_{obs}$ against 1/[S] at different temperatures: [V(V)] = 1.0 × 10^{-3}M, [$HClO_4$] = 4.0M.

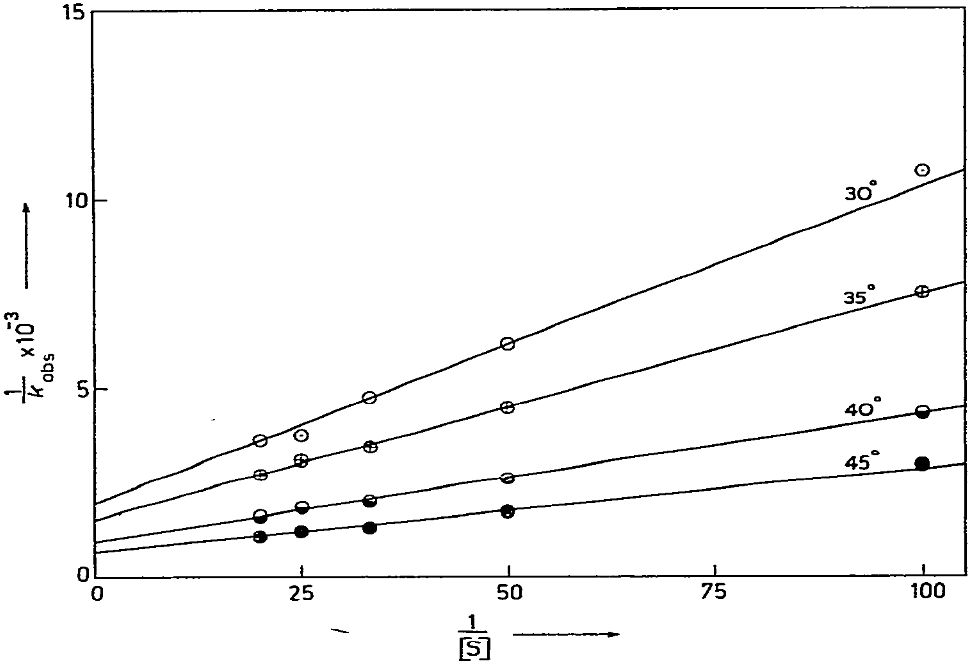

Fig. 2. Kinetic evidence for intermediate-complex formation between vanadium(V) and L-sorbose. Plots of $1/k_{obs}$ against $1/[S]$ at different temperatures: $[V(V)] = 1.0 \times 10^{-3}$M, $[HClO_4] = 4.0$M.

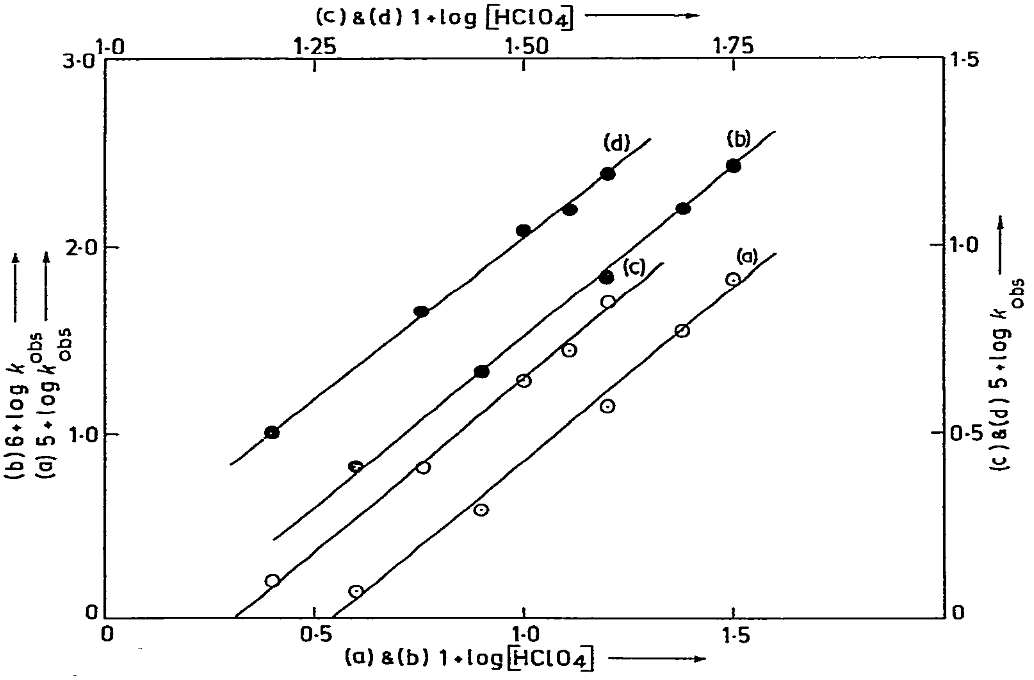

Fig. 3. Variation of pseudo-first-order rate constant with $[HClO_4]$ at 35°. Plots of $\log k_{obs}$ against $\log [HClO_4]$: (a) [Fructose] $= 1.0 \times 10^{-3}$M, [Cr(VI)] $= 1.67 \times 10^{-4}$M, and $\mu = 3.2$M; (b) [Sorbose] $= 1.0 \times 10^{-3}$M, [Cr(VI)] $= 1.67 \times 10^{-4}$M, and $\mu = 3.2$M; (c) [Fructose] $= 1.0 \times 10^{-2}$M, [V(V)] $= 1.0 \times 10^{-3}$M, and $\mu = 4.0$M; (d) [Sorbose] $= 1.0 \times 10^{-2}$M, [V(V)] $= 1.0 \times 10^{-3}$M, and $\mu = 4.0$M.

TABLE II

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

$NaClO_4$ (M)	$k_{obs} \times 10^4$ (s^{-1})		*$NaClO_4$ (M)*	$k_{obs} \times 10^5$ (s^{-1})	
	D-*Fructose*[a]	L-*Sorbose*[a]		D-*Fructose*[b]	L-*Sorbose*[b]
0.0	6.83	2.75	0.0	7.12	15.6
0.4	7.64	3.86	0.2	7.91	18.9
0.8	10.2	5.11	0.4	8.56	19.7
1.2	13.7	6.06	0.8	9.31	22.5
1.6	15.8	8.10	1.2	10.5	27.6

[a] [Cr(VI)] = 1.67 × 10^{-4}M, [ketohexose] = 1.0 × 10^{-3}M, [$HClO_4$] = 3.2M, and temperature = 35°.
[b] [V(V)] = 1.0 × 10^{-3}M, [ketohexose] = 1.0 × 10^{-2}M, [$HClO_4$] = 4.0M, and temperature = 35°.

hexoses increased with the increase in acid concentration. The slopes of the above plots are 1.85 and 1.80 for chromium(VI) oxidations of fructose and sorbose, respectively, whereas, for the other reactions, the values are 1.90 and 1.75, respectively.

Effect of variation of sodium perchlorate concentration. — The pseudo-first-order rate constants (k_{obs}) at different concentrations of sodium perchlorate are given in Table II. The values increased with the increase in sodium perchlorate concentrations as previously observed[5-8].

Solvent isotope effect. — The rates of oxidation were determined both in water and in deuterium oxide. The ratios k_{D_2O}/k_{H_2O} were calculated to be 3.7 and 3.9 for chromium(VI) oxidations of D-fructose and L-sorbose, respectively. A change in the reaction medium from water to deuterium oxide, however, does not seem to have any influence on the rates of oxidation by vanadium(V). It may be that one of the reactants, possibly vanadium(V), undergoes deuterium exchange and, as a result, the rate remains unaffected.

Effect of variation of temperature and activation parameters. — The plots of $\log k_2$ against 1/T were linear for chromium(VI) oxidation (Fig. 4), and the Arrhenius activation energies (E_a) followed by enthalpies of activation ($\Delta H^\ddagger$) were calculated. The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for chromium(VI) oxidation of D-fructose are 46.6 ±3.4 $kJ.mol^{-1}$ and -105 ± 11 $J.deg^{-1}.mol^{-1}$, respectively, whereas, for L-sorbose, the corresponding values are 50.6 ±6.3 $kJ.mol^{-1}$ and -100 ± 20 $J.deg^{-1}.mol^{-1}$. For the vanadium(V) oxidation of ketohexoses, the plots of $\log k$ (k = disproportionation constant) against 1/T (Fig. 4) were used to calculate activation parameters. The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are 53.2 ±4.2 $kJ.mol^{-1}$ and -139 ± 14 $J.deg^{-1}.mol^{-1}$ for fructose, whereas, for L-sorbose, the values are 52.3 ±6.3 $kJ.mol^{-1}$ and -137 ± 20 $J.deg^{-1}.mol^{-1}$, respectively. The equilibrium constants (K) were calculated to be 45.0, 48.7, 54.3, and 58.7M^{-1} at 30, 35, 40, and 45°, respectively, for the reaction involving D-fructose and vanadium(V), whereas, for the oxidation of L-sorbose by vanadium(V), the values are 24.0, 27.2, 30.1, and 33.8M^{-1} at the respective tempera-

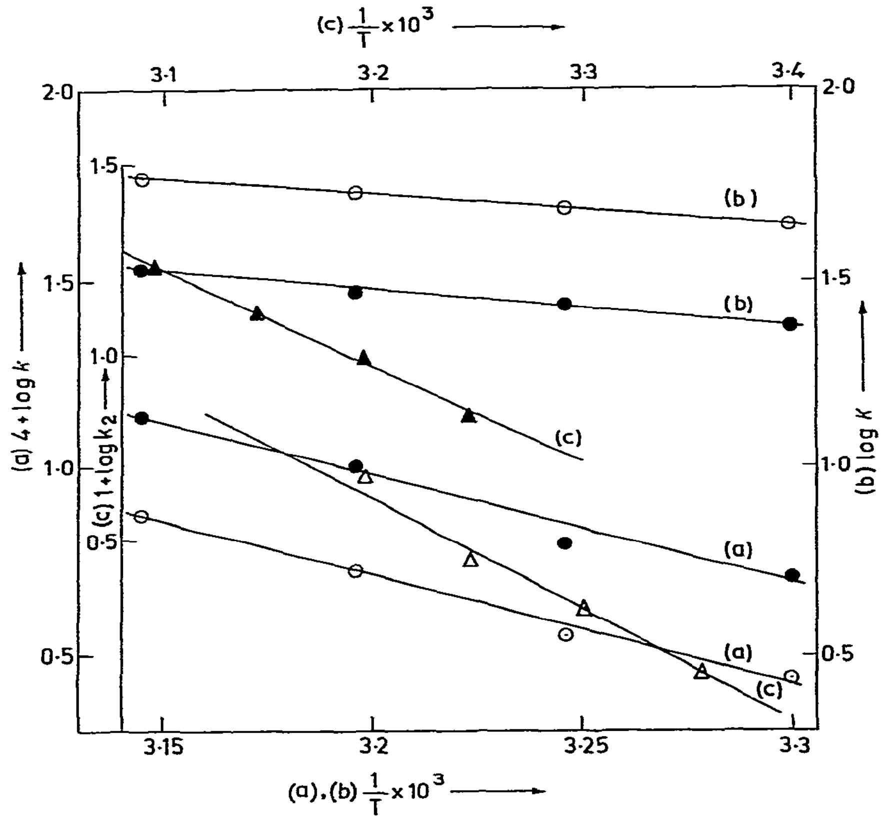

Fig. 4. Influence of temperature on different reactions. Plots of (a) log k against 1/T and (b) log K against 1/T for vanadium(V) oxidations. (○, D-Fructose; ●, L-Sorbose), and (c) log k_2 against 1/T for chromium(VI) oxidations (△, D-Fructose; ▲, L-Sorbose).

tures. The values of ΔH associated with the equilibrium (step 7) were calculated from the slopes of log K against 1/T plots (Fig. 4) and are found to be 16.4 ±2.1 and 18.3 ±2.1 kJ.mol^{-1} for vanadium(V) oxidations of D-fructose and L-sorbose, respectively.

DISCUSSION

In aqueous solution, D-fructose and L-sorbose exist mainly as cyclic hemiacetals which are in dynamic equilibrium with acyclic forms. Of the pyranoid and furanoid forms, the former is generally the most stable and exists mainly in a chair form. This is corroborated by a recent communication by Mathlouthi *et al.*[10] who showed by laser-Raman spectroscopic analysis that D-fructose in aqueous solution exists as 59% of pyranoid and 41% of furanoid forms, whereas, for L-sorbose, ^{13}C-n.m.r. spectroscopy revealed[11] 96–98% of pyranoid and 2–4% of furanoid forms.

The preponderant form of D-fructose is β-pyranoid, whereas, for L-sorbose, it is α-pyranoid[10,11].

The chromium(VI) oxidations of the ketohexoses were first order with respect to [oxidant] as well as [ketohexose], whereas the order with respect to [$HClO_4$] was ~2 in each reaction. Moreover, the rates of oxidation of D-fructose and L-sorbose by chromium(VI) are of the same order, thus indicating that a common mechanism may be operative in these reactions. Hence, the protonated chromic acid molecule, *i.e.*, $H_3CrO_4^+$, which is believed[12] to exist as the anhydride $HCrO_3^+$, reacts with the preponderant form of the substrate (S) molecule. The results in Table II further indicate that each reaction involves an ion and a neutral molecule[13], as shown in Eq. *1*.

$$S + HCrO_3^+ \rightarrow \text{Products} + Cr(III) \qquad (1)$$

The oxidation of these substrates, leading to the formation of lactone and formic acid, may be explained by either of Schemes 1 and 2. In Scheme 1, the substrate initially reacts with the protonated chromic acid molecule ($HCrO_3^+$) to give the lactone of the C_5-acid, and formaldehyde by C–C bond rupture as in diols[14], and chromium(VI) is reduced to chromium(IV). The chromium(IV) reacts further with chromium(VI) to give[15] chromium(V). Step *3* has also been proposed in chromic acid oxidations of some inorganic compounds[16–18], and the disproportionation of chromium(V) to give chromium(IV) and chromium(VI), which takes place at lower acidities[19], probably does not play an important role at higher acidities (>3M). Consequently, chromium(V) oxidises another substrate molecule, giving further lactone and formaldehyde, and is reduced to chromium(III). The formaldehyde which is formed in steps *2* and *4* is rapidly oxidised to formic acid (step *5*).

$$2\{S + Cr(VI) \rightarrow \text{Lactone} + HCHO + Cr(IV)\} \qquad (2)$$
$$2\{Cr(IV) + Cr(VI) \rightarrow 2Cr(V)\} \qquad (3)$$
$$S + Cr(V) \rightarrow \text{Lactone} + HCHO + Cr(III) \qquad (4)$$
$$3\{HCHO + Cr(V) \rightarrow HCOOH + Cr(III)\} \qquad (5)$$

Scheme 1

Alternatively, part of the chromium(IV) which is formed in step *2* undergoes disproportionation to yield chromium(V) and chromium(III), and the oxidation may then take place according to the steps in Scheme 2.

$$3\{S + Cr(VI) \rightarrow \text{Lactone} + HCHO + Cr(IV)\} \qquad (2)$$
$$2Cr(IV) \rightarrow Cr(V) + Cr(III) \qquad (6)$$
$$Cr(IV) + Cr(VI) \rightarrow 2Cr(V) \qquad (3)$$

followed by step *5*.

Scheme 2

For vanadium(V) oxidation of the ketohexoses, the orders with respect to [oxidant] and [$HClO_4$] are 1 and ~2, respectively, whereas, unlike chromium(VI), the order with respect to [substrate] is <1. This indicates that these reactions also follow a common mechanism. It is likely that diprotonated[20] vanadium(V), *i.e.*, $V(OH)_2^{3+}$ or the corresponding anhydride VO^{3+}, reacts with the substrate to form a 1:1 intermediate complex according to step *7* of Scheme 3. The kinetic evidence indicated the formation of a 1:1 intermediate complex, and this was corroborated by spectroscopy of the mixtures of ketohexoses and vanadium(V) at 313 nm. The ketohexoses do not absorb at this wavelength, and the increase in absorbancy of vanadium(V) on adding ketohexoses reflects the formation of complexes of ketohexoses and vanadium(V). No such increases were noticed in the chromium(VI) oxidations of the same substrates. However, the vanadium(V) complexes were not stable enough for determination of their equilibrium constants from spectral measurements. The intermediate complex decomposes slowly to give the lactone of the C_5-acid, a free radical ($\cdot CH_2OH$), and vanadium(IV) by rupture of the C–C bond, as in glycols[21]. The free radical reacts further with vanadium(V), to give formaldehyde and vanadium(IV), as shown in Scheme 3.

$$S + V(OH)_2^{3+} \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} \text{Intermediate complex} \tag{7}$$

$$\text{Intermediate complex} \underset{\text{slow}}{\overset{k}{\rightarrow}} \text{Lactone} + \cdot CH_2OH + V(IV) \tag{8}$$

$$\cdot CH_2OH + V(V) \underset{\text{fast}}{\rightarrow} HCHO + V(IV) \tag{9}$$

Scheme 3

The main difference between the products of oxidation of ketohexoses by chromium(VI) and vanadium(V) is that formic acid is the major product in chromium(VI) oxidations, whereas oxidations by vanadium(V) give formaldehyde. The redox-potential data for such couples as V(V)–V(IV), Cr(V)–Cr(III)[9], Cr(IV)–Cr(III)[22], and Cr(VI)–Cr(III), which are 1.00, $\geqslant 1.75$, 2.10, and 1.36 volts, respectively, provide information regarding their reactivities. Consequently, although the reaction of

TABLE III

ACTIVATION ENTHALPIES FOR THE OXIDATIONS OF BOTH ALDOHEXOSES AND KETOHEXOSES BY (*a*) CHROMIUM(VI) AND (*b*) VANADIUM(V) IN PERCHLORIC ACID MEDIUM

	(a) $\Delta H^{\ddagger}$ *(kJ.mol⁻¹)*	(b) $\Delta H^{\ddagger}$ *(kJ.mol⁻¹)*
Aldohexose	56 to 72	97 to 106
Ketohexose	47 to 51	52 to 53

formaldehyde with chromium(VI) or vanadium(V) is very slow[23], chromium(V), being a more powerful oxidant than chromium(VI) or vanadium(V), can oxidise formaldehyde to formic acid. The absence of polymeric product (when acrylamide was added in chromium(VI) oxidations) indicated that chromium(IV) does not participate in the reaction with each substrate, despite the fact that the redox potential of Cr(IV)–Cr(III) is higher than that of the Cr(V)–Cr(III) couple. In the oxidation of some hexoses by copper(II) in alkaline medium, it has been shown[4a] that fructose reacts at a higher rate than glucose, and that pretreatment of aldohexoses with alkali leads to an increase in the reaction rate. This has been interpreted in terms of a Lobry de Bruyn–Alberda van Ekenstein transformation[24] in which a ketose is formed from an aldose, and which therefore results in a faster oxidation. The data for enthalpy of activation, presented in Table III, also indicate that ketoses are more powerful reductants than aldoses.

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