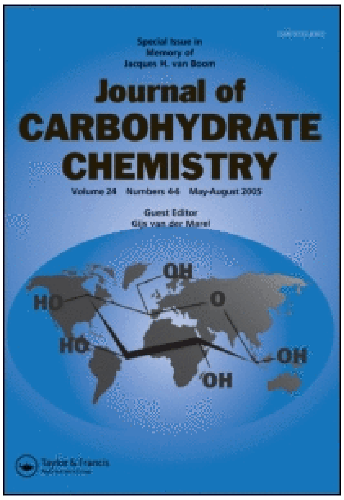

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KINETICS AND MECHANISM OF THE OXIDATION OF SOME ALDOSES BY CERIUM(IV)

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ABSTRACT

The kinetics of oxidation of some aldoses by cerium(IV) have been studied spectrophotometrically in sulphuric acid medium. The reactions are second order; first order with respect to both cerium(IV) and aldose concentration. The reaction rate decreases with increase in sulphuric acid concentration. The mechanisms for the reactions are discussed.

INTRODUCTION

The kinetics of oxidation of some aldoses by different oxidants in acid[1 - 9] as well as alkaline medium[10 - 12] have been carried out. Though the oxidation of D-glucose,[13 - 15] D-galactose,[16] L-arabinose,[16] and L-sorbose[17] by cerium(IV) has been studied, the reactions generally proceeded to give the corresponding lactones and aldonic acids. However, no attempt has been made to study the oxidation by cerium(IV) of lower members of the aldoses. It was, therefore, necessary to investigate the oxidations of aldoses like D-ribose, D-erythrose, and DL-glyceraldehyde in order to compare the results obtained with that for D-glucose. The kinetic investigations of the oxidation of D-glucose, D-ribose, D-erythrose, and DL-glyceraldehyde by cerium(IV) are reported in this paper.

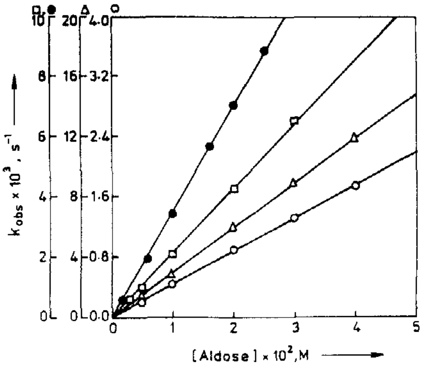


Fig. 1. Variation of pseudo first-order rate constant (k_{obs}) with aldose concentrations at [Cerium(IV)] = 1 x 10^{-3} M and [sulphuric acid] = 2.2 x 10^{-1} M.

○—○ D-Glucose (40 °C); Δ—Δ D-ribose (30 °C);

●—● D-Erythrose (25 °C); □—□ DL-glyceraldehyde (35 °C)

RESULTS AND DISCUSSION

The reactions were carried out at different cerium(IV) concentrations in the region (0.5 - 3.0) x 10^{-4} M, but at concentrations of aldose and sulphuric acid of 1.0 x 10^{-2} M and 2.2 x 10^{-1} M, respectively. The rate constants were independent of initial oxidant concentration in each reaction. The pseudo first-order rate constants (k_{obs}) were calculated at constant cerium(IV) concentration but at different aldose concentration. The results are plotted in Fig. 1 and indicate that the order in each aldose is unity.

Oxidation of the aldoses by cerium(IV) was carried out in solution containing different amounts of sulphuric acid. The reactions were studied at cerium(IV) and aldose concentrations of 1.0 x 10^{-3} and 1.0 x 10^{-2} M, respectively. Plots of log k_{obs} against log [sulphuric acid] are linear with negative slopes (data not shown). The slopes are not widely different (-0.6 - -0.7) for the oxidations of D-glucose, D-ribose, and D-erythrose, whereas for DL-glyceraldehyde, the slope is somewhat altered (-0.95). Hardwick and Robertson[18] have shown that cerium(IV) associates with bisulphate to form ceric sulphate complexes according to the equilibria.

$$Ce^{4+} + HSO_4^- \underset{}{\overset{K_1}{\rightleftharpoons}} Ce(SO_4)^{2+} + H^+ \qquad (1)$$

$$Ce(SO_4)^{2+} + HSO_4^- \overset{K_2}{\rightleftharpoons} Ce(SO_4)_2 + H^+ \qquad (2)$$

$$Ce(SO_4)_2 + HSO_4^- \overset{K_3}{\rightleftharpoons} Ce(SO_4)_3^{2-} + H^+ \qquad (3)$$

The values for the equilibrium quotients K_1, K_2, and K_3 are 3.5×10^3, 2×10^2, and 2×10, respectively, at 35 °C.

In order to understand the role of sulphuric acid on reaction rate, the experiments were performed at constant bisulphate concentration (μ= 1.0 M). From the results at constant hydrogen ion concentration and the K values quoted above, the plots of k_2 against $\{1 + K_2[HSO_4^-] + K_2K_3[HSO_4^-]^2\}^{-1}$ are not linear. On the other hand, the plots of k_2 against $\{1 + K_2[HSO_4^-]\}^{-1}$ are linear, passing through the origin for the oxidations of D-glucose, D-ribose, and D-erythrose. These are unlike that for DL-glyceraldehyde where the plot is not linear (Fig. 2). Thus the oxidations of D-glucose, D-ribose, and D-erythrose obey the following rate expression (4), indicating that a similar mechanism may be operative for the oxidation of all these aldoses.

$$\frac{-d[Ce(IV)]}{dt} = k\cdot[Ce(IV)][Aldose]\{1 + K_2\frac{[HSO_4^-]}{[H^+]}\}^{-1} \qquad (4)$$

The second-order rate constants (k_2) for the oxidations of aldoses were calculated at different temperatures. The activation parameters were then calculated using the relation (5).

$$\log (k_2/T) = \{\log(k/h) + \Delta S^{\neq}/2.303R\} - \Delta H^{\neq}/2.303\ RT \qquad (5)$$

The enthalpies of activation ($\Delta H^{\neq}$) were calculated from the slopes of the plots of log (k_2/T) against 1/T (Fig. 3), followed by the

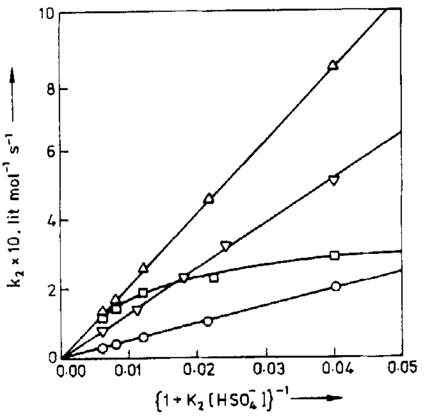


Fig. 2. Plots of k_2 against $\{1 + K_2[HSO_4^-]\}^{-1}$ at [Cerium(IV)] = 1 x 10^{-3} M, [Aldose] = 1 x 10^{-2} M at 35 °C.

O—O D-Glucose; Δ—Δ D-ribose; ∇—∇ D-erythrose;

□—□ DL-glyceraldehyde

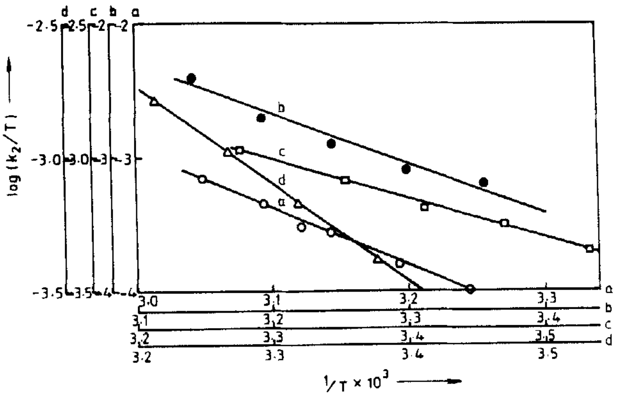


Fig. 3. Dependence of temperature on second-order rate constants for the oxidation of aldoses by cerium(IV). Plots of log (k_2/T) against 1/T.

O—O D-Glucose; ●—● D-ribose; □—□ D-erythrose;

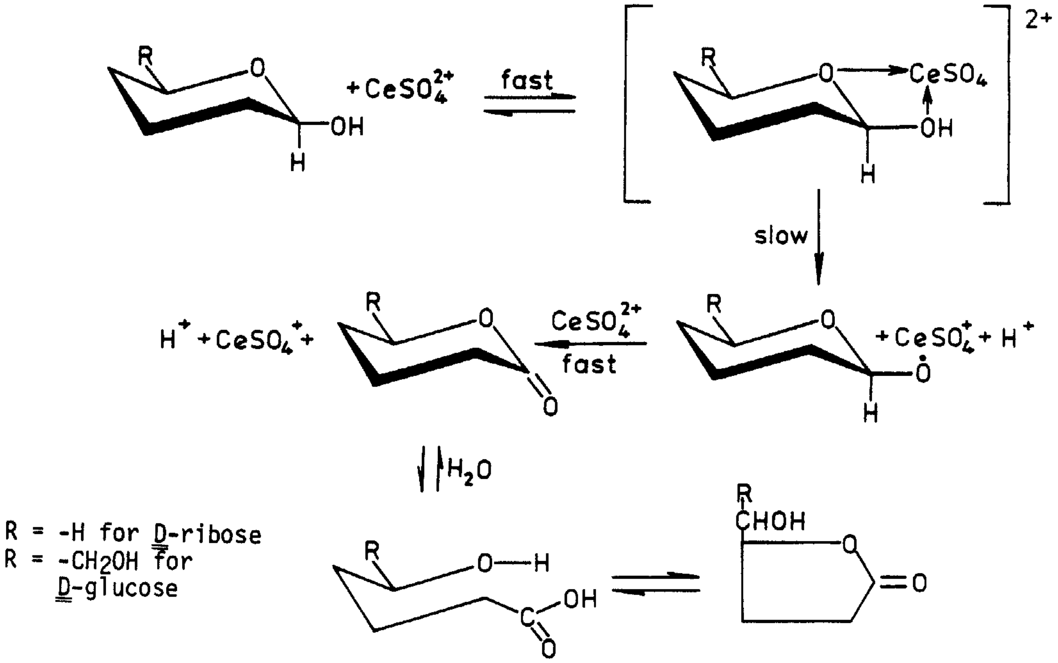
Δ—Δ DL-glyceraldehyde

Table 1. Activation Parameters for the Oxidation of Some Aldoses by Cerium(IV)

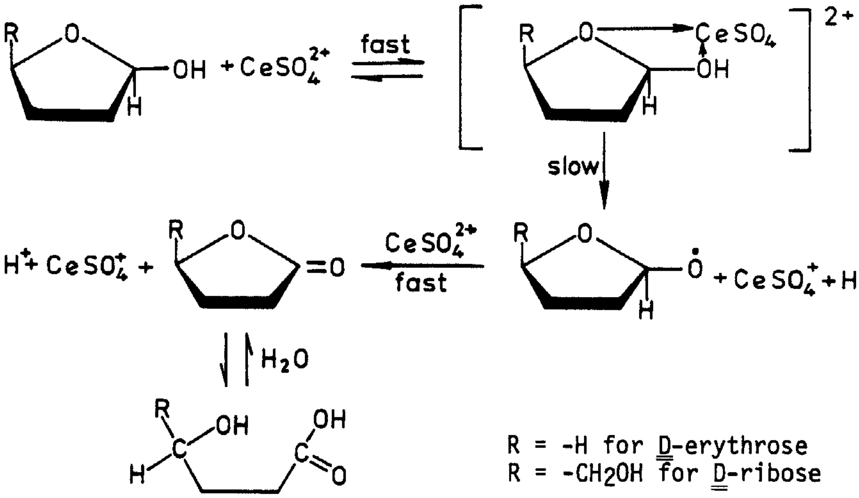
Aldose	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} deg^{-1})
D-Glucose	81.3	-4.8
D-Ribose	57.4	-65.6
D-Erythrose	27.8	-160.3
DL-Glyceraldehyde	70.8	-23.5

calculation of $\Delta S^{\neq}$ using equation (5). The results are recorded in Table 1.

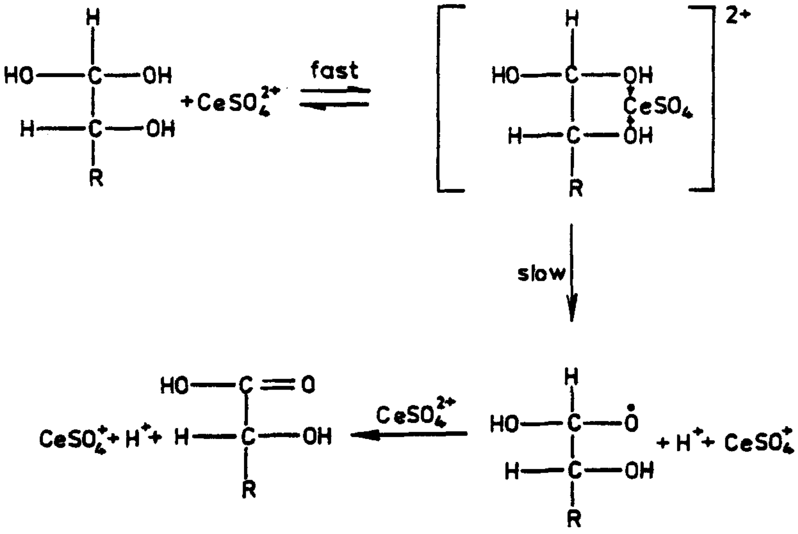
It has been shown[6,7] that cyclic pyranoid forms, and not the aldehydo forms, of D-glucose and D-ribose are involved in their oxidation with the metal ions. The pyranoid form in the $^4C_1$ conformation preponderates[19] in aqueous solution of D-glucose, and the β-anomer with the 1-OH equatorial is attacked by the oxidants.[20] However, β-D-ribose exists as an equilibrium mixture of $^4C_1$ and $^1C_4$ forms, of which the former preponderates. These aldoses are believed[9] to be preferentially oxidised in the $^4C_1$ β-pyranoid form, and hence the initial product should be corresponding lactone. Though D-erythrose is known to exist in acyclic form, literature evidence indicates that it can also exist in the cyclic form.[21] It has been shown[22] that D-erythrose exists in 88% furanoid form, with the β-anomer predominating. Again the crystalline form of DL-glyceraldehyde is dimeric with a 1:4 dioxane structure; however, in aqueous solution it dissociates into a monomeric form which remains in equibrium with the hydrated and non-hydrated form.[9] Cerium(IV) exists mainly as a mixture of several sulphato complexes like $CeSO_4^{2+}$, $Ce(SO_4)_2$, and $Ce(SO_4)_3^{2-}$ in sulphuric



Scheme 1



Scheme 2



R = $-CH_2OH$ for DL-glyceraldehyde

R = $-CHOH, CH_2OH$ for D-erythrose

Scheme 3

acid medium.[23] Among the various cerium(IV) sulphato species, the monosulphato species qualifies as an electrophile in the oxidation[23 - 25] of some organic compounds. It is suggested that the monosulphato complex is the kinetically relevant cerium(IV) species under our experimental conditions.

The reactions proceed through the intermediate formation of a free radical in the rate-determing step. The latter is then rapidly oxidised by another cerium(IV) to give the products. The mechanism appears to involve a direct attack of the cerium(IV) species on the aldose. The oxidation of the pyranoid form of D-glucose and D-ribose takes place through the formation of a free radical with cerium(IV) to give the δ-lactone, which on hydrolysis yields the aldonic acid. The latter remains in equilibrium with the γ-lactone[8] (Scheme 1). The oxidation of the furanoid form of D-ribose and D-erythrose takes place as shown in Scheme 2. The acyclic forms of D-erythrose and DL-glyceraldehyde are postulated to react with cerium(IV) to give carboxylic acid (Scheme 3).

The second-order rate constants for the oxidations of D-glucose, D-ribose, D-erythrose, and DL-glyceraldehyde are 4.38×10^{-2}, 29.5×10^{-2}, 34.8×10^{-2}, and 21.2×10^{-2} $l\ mol^{-1}\ s^{-1}$, respectively, as determined under comparable experimental conditions. The observed dependence of second-order rate constant on acidity and enthalpy data in the oxidation of DL-glyceraldehyde suggests that DL-glyceraldehyde is oxidised by a different mechanism. On the other hand, the oxidation of D-glucose, D-ribose, and D-erythrose by cerium(IV) are kinetically similar, and second-order rate constants follow the order D-erythrose > D-ribose > D-glucose, whereas the enthalpy of activations are in the order D-glucose > D-ribose > D-erythrose. The observed dependence of second-order rate constant on acidity and enthalpy data in the oxidation of DL-glyceraldehyde suggests that the latter is oxidised via a different mechanism. Thus it is unlikely that D-erythrose is oxidised by the mechanism as shown in Scheme 3, but the cyclic furanoid form of this compound is oxidised by cerium(IV) to give reaction products (Scheme 2).

EXPERIMENTAL

Reagents. Inorganic materials were of the highest purity available. Cerium(IV) in sulphuric acid solution was prepared by dissolving cerium(IV) ammonium sulphate (Merck) in sulphuric acid solutions, and the solution was titrated against ferrous ammonium sulphate. D-Glucose, D-ribose, and DL-glyceraldehyde were E. Merck's products. D-Erythrose was purchased from Koch-Light. All solutions were made up in doubly distilled water.

Kinetics. A large excess of aldose relative to cerium(IV) was employed. The reactions were studied at lower sulphuric acid concentrations ($\leq$ 1 M) in order to minimize the error due to its

reaction with the sugars. Oxidation of the aldoses was followed spectrophotometrically by noting the changes in absorption with time at 420 nm using a cell of 1-cm path length. [Cerium(IV) solution has absorption in the region 280 - 500 nm, while cerium(III) is transparent at 420 nm.[15,16]] Measured quantities of the solutions were rapidly mixed and poured into the cell, and the absorption of cerium(IV) was then measured at definite time intervals. The pseudo first-order rate constants (k_{obs}) were calculated from plots of log A (A = absorbance) versus time.

Product analysis. The aldoses were oxidised separately by cerium(IV) under kinetic conditions. After purification and concentration of the solutions, the products were identified[4] by paper chromatography using Whatman No. 1 paper with 4:1:5 (upper layer) n-butanol - acetic acid - water as the eluant and silver nitrate as the detection reagent.[26,27] The experiments indicated the presence of aldonic acid along with δ- and γ-lactone in the oxidations of D-glucose and D-ribose, whereas for D-erythrose and DL-glyceraldehyde, only aldonic acids were obtained. The results were compared with the products of the respective aldoses from oxidation by both bromine and nitric acid.

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