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Kinetics and Mechanism of the Reduction of Dodecatungstocobaltate(III) by D-Fructose, D-Glucose, and D-Mannose: Comparison between Keto- and Aldo-hexoses

Mala Gupta, Swapan K. Saha, and Pradyot Banerjee*
Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India

The kinetics of reduction of dodecatungstocobaltate(III) by D-fructose, D-glucose, and D-mannose in aqueous media have been investigated. A pseudo-zero-order rate was obtained with the ketose and the reaction was acid-dependent. On the contrary, pseudo-second-order rates were obtained for the aldose reactions. The reactions were catalysed by metal ions in the supporting electrolyte; the cation catalytic order $K^+ > Na^+ \geqslant Li^+$ observed for aldose oxidations is explained on the basis of electrostatic considerations. A mechanism for the ketose oxidation is offered based on keto–enol tautomerism; the aldose oxidations are explained in terms of a transition state formed *via* ion-induced dipole bridging.

A number of studies relating to the interaction of dodecatungstocobaltate(III) with a broad spectrum of electron donors have been reported recently.[1–9] However, there is no report of the reduction of this polyanion by sugars. This paper describes experiments designed to examine pathways for electron transfer from D-fructose, D-glucose, and D-mannose to dodecatungstocobaltate(III). The interaction of this polyanion with these sugars is interesting since (i) D-fructose and D-glucose are regarded as model reducing sugars, (ii) carbohydrate units are constituents of nucleic acids,[10] and (iii) carbohydrates play an important role in mammalian food supply and metabolism.[11]

The kinetics of oxidative degradation of sugars by metal complexes have been the subject of numerous investigations (Table 1).[12–15] These however did not show any significant mechanistic dissimilarity betwen keto- and aldo-sugars. We report an example where the modes of oxidation of keto- and aldo-sugars with the same heteropolyanion are completely different.

Table 1. Previous kinetic studies of the oxidation of sugars

Oxidant	Reducing sugar	Ref.
Ce^{IV}	D-Glucose, D-galactose, D-mannose, L-rhamnose, L-arabinose, D-xylose	12, 15
Cu^{II}	Eleven reducing sugars including D-glucose, D-mannose, and D-fructose	13
H_2O_2	D-Fructose, L-sorbose	14
V^V	D-Glucose, D-mannose, D-galactose, D-xylose, L-arabinose, D-erythrose, D-fructose, L-sorbose, D-ribose, DL-glyceraldehyde	16, 18, 19, 20, 21, 22, 25
Cr^{VI}	D-Galactose, D-mannose, L-arabinose, D-xylose, D-glucose, D-ribose, D-erythrose, DL-glyceraldehyde, D-fructose, L-sorbose	17, 19, 20, 21
Pyridinium fluorochromate	D-Glucose	23
N-Bromosuccinimide	D-Arabinose, D-xylose, D-mannose	24
(Ru^{III}-catalysed)	D-Glucose	

Experimental

The methods of preparation[26] and characterisation[27] of the potassium salts of dodecatungstocobaltate(III) $[CoW_{12}O_{40}]^{5-}$ and dodecatungstocobaltate(II) $[CoW_{12}O_{40}]^{6-}$ (henceforth designated $Co^{III}M$ and $Co^{II}M$, respectively) were reported earlier. Doubly recrystallised D-glucose, D-mannose (Sigma), and D-fructose (Riedel-de Haën) were used for the kinetic studies. Cations were varied by using doubly recrystallised sodium perchlorate, potassium nitrate, and lithium nitrate. Perchloric acid and nitric acid of high purity were used for the $[H^+]$ variation study. Sugar solutions were always used on the same day as made.

Kinetic Studies.—A Pye–Unicam SP8-150 spectrophotometer fitted with a thermostatically controlled cell compartment was used to follow the disappearance of $Co^{III}M$ at 388 nm. A few kinetic runs conducted at 625 nm (the absorption maximum of $Co^{II}M$) gave identical results. Dissolved oxygen did not show any effect. pH Measurements were performed with a Systronics 335 digital pH meter.

Polymerisation Studies.—Reaction solutions were degassed with dinitrogen before initiation of the reaction and addition of acrylonitrile to the reaction mixture. In the D-fructose oxidation, polymerisation started quickly, but for D-glucose and D-mannose, polymerisation started after *ca.* 30 min. Blank experiments from which either $Co^{III}M$ or sugar was excluded gave no detectable polymerisation, demonstrating that the reactions of $Co^{III}M$ with all the carbohydrates proceed *via* free radicals.

Stoicheiometry and Products.—Several reaction mixtures with $[Co^{III}M] > [sugar]$ at fixed $[H^+]$ were prepared. After the completion of reactions the $[Co^{II}M]$ produced was determined spectrophotometrically. In all the cases the reaction stoicheiometry was found to be 2:1 (complex:sugar); thus the reactions may all be represented by equation (1).

$$C_6H_{12}O_6 + 2Co^{III}M \longrightarrow 2Co^{II}M + \text{other products} \qquad (1)$$

The organic products were identified by paper chromatography.[17] The D-glucose and D-mannose oxidation products were characterised as arabinose by matching with a standard sample. To characterise the products of D-fructose oxidation, a series of aldopent- and hex-oses were oxidised separately with nitric acid and bromine water[28] and the purified products were

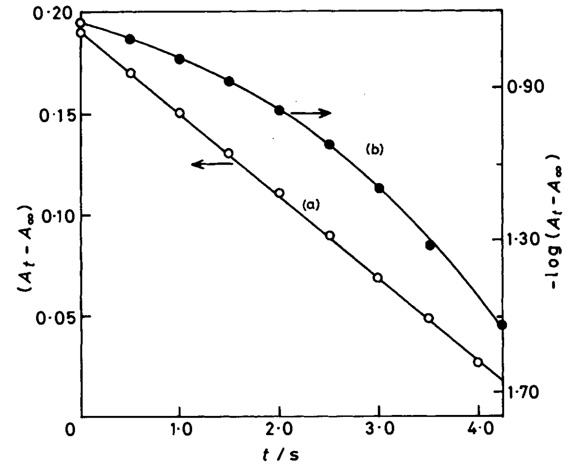


Figure 1. Representative kinetic plots of (a) $(A_t - A_\infty)$ *versus* time and (b) $-\log(A_t - A_\infty)$ against time for the oxidation of fructose by $Co^{III}M$ at 60 °C. $[Co^{III}M] = 2 \times 10^{-4}$ mol dm^{-3}, [Fru] = 0.80 mol dm^{-3}, $[NaClO_4] = 1.0$ mol dm^{-3}, $[H^+] = 0.10 \pm 0.01$ mol dm^{-3}

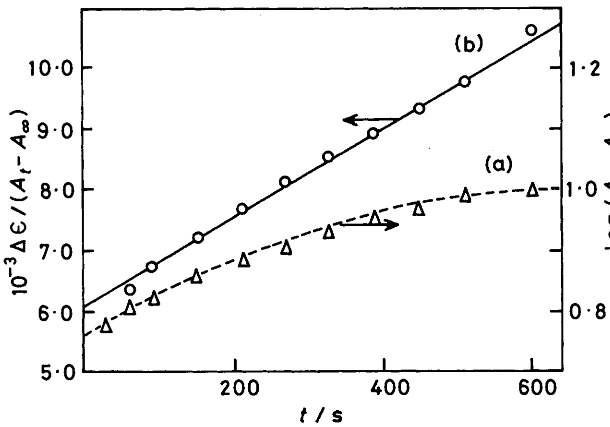


Figure 2. Plots of (a) $-\log(A_t - A_\infty)$ against time and (b) $\Delta\varepsilon/(A_t - A_\infty)$ *versus* time for a representative run of the reaction of $Co^{III}M$ with glucose at 60 °C. $[Co^{III}M] = 2 \times 10^{-4}$ mol dm^{-3}, [Glu] = 0.80 mol dm^{-3}, $[K^+]_T = 1.0$ mol dm^{-3}, $[H^+] = 0.10$ mol dm^{-3}. In all cases a quartz cell of 1 cm path length was used

used as standards in the chromatographic procedure. Thus the aldonic acid corresponding to arabinose was identified as one of the products of the D-fructose oxidation. The distillates obtained from all the reaction mixtures at 100—101 °C were collected and tested for formic acid. For both the aldoses and the ketose, the distillate responded to the test with chromotropic acid,[29] indicating the presence of formic acid.

Results and Discussion

Kinetics.—Spectral scanning during the reactions of $Co^{III}M$ with all the sugars gave a clear isosbestic point at 510 nm, indicating the absence of any appreciable quantities of reaction intermediates. For the D-fructose oxidation, the plots of $-\log(A_t - A_\infty)$ *vs.* time (t), where A_∞ and A_t denote absorbances at infinite time and time t, respectively, were all curved. However the plot of $(A_t - A_\infty)$ *vs.* time (Figure 1) showed linearity up to 85% reaction. This indicates that the oxidation rate is zero-order with respect to $[Co^{III}M]$. For the D-glucose and D-mannose oxidations, neither plots of $(A_t - A_\infty)$ nor $-\log(A_t - A_\infty)$ *vs.* time gave a straight line, but a plot[30,31] of $\Delta\varepsilon/(A_t - A_\infty)$ *vs.* time [$\Delta\varepsilon$ is the difference in molar extinction coefficients of $Co^{III}M$ and $Co^{II}M$ at the experimental wavelength (388 nm)] was always linear (Figure 2) up to 80% of the reaction, showing a second-order dependence on $Co^{III}M$. Values of the pseudo-zero-order rate constants for D-fructose and the pseudo-second-order-rate constants for D-glucose and D-mannose oxidations were obtained from the slopes of the respective plots at various concentrations of the reducing sugars.

Dependence on Substrate Concentration.—The dependence of rate on substrate concentration was studied for each sugar at 60 °C, with $[H^+] = 0.10$ mol dm^{-3} and constant alkali metal ion concentration ($[Na^+] = 1.00$ mol dm^{-3}) (Table 2). All the reactions showed first-order dependence on the concentration of sugar. In view of the stoicheiometry of the reactions, the rate laws may be formulated as (2)—(4), where k_1 is the apparent

$$-d[Co^{III}M]/dt = 2k_1[Fru] \tag{2}$$

$$-d[Co^{III}M]/dt = 2k_2[Glu][Co^{III}M]^2 \tag{3}$$

$$-d[Co^{III}M]/dt = 2k_3[Man][Co^{III}M]^2 \tag{4}$$

first-order rate constant for D-fructose oxidation and k_2 and k_3 are the apparent third-order rate constants for D-glucose and D-mannose oxidations, respectively.

Dependence on $[H^+]$.—Acid dependence studies were carried out for all the sugars, with [Fru] = 0.50 mol dm^{-3}, $[Na^+] = 1.00$ mol dm^{-3}, $T = 60$ °C, and $[H^+] = 0.05$—0.25 mol dm^{-3}; [Glu] = 0.80 mol dm^{-3}, $[Na^+] = 1.00$ mol dm^{-3}, $T = 60$ °C, and $[H^+] = 0.01$—0.30 mol dm^{-3}; [Man] = 0.50 mol dm^{-3}, $[Na^+] = 1.00$ mol dm^{-3}, $T = 60$ °C, and $[H^+] = 0.10$—1.00 mol dm^{-3}. The oxidation of D-fructose was found to be catalysed by acid, but the oxidations of the aldo-sugars were unaffected (Table 3). The D-fructose oxidation showed a first-order dependence on $[H^+]$.

Dependence on Alkali Metal Ions and Ionic Strength.—To examine the possibility of catalysis by alkali metal ions (encountered in our previous studies[8,9]), both the nature and the concentration of metal ions were varied for all the sugar oxidations, at constant pH and substrate concentration. The D-fructose oxidation was unaffected, but the aldo-sugar oxidations responded markedly to changes in both concentration and nature of the alkali metal ions.

To discover whether the increase in rate was due to the ionic strength effect or to metal ion catalysis, the results of metal ion variations were subjected to the extended Brønsted relationship treatment [equations (5) and (6), where k is the rate constant at

$$\log k = \log k_0 + 2Az_Az_B\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + BI \tag{5}$$

$$\log k'_0 = \log k - 2Az_Az_B\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} \tag{6}$$

a particular ionic strength (I), k_0 is the rate constant at zero ionic strength, and B is a constant]. Combining (5) and (6) gives equation (7).

$$\log k'_0 = \log k_0 + BI \tag{7}$$

Since one of the reacting species (D-glucose or D-mannose) is uncharged, $z_Az_B = 0$; therefore $\log k'_0 = \log k$. Plots of $\log k'_0$ *vs.* I (which is equivalent to the concentration of metal ions) deviate from linearity (Figure 3). This type of behaviour is

Table 2. Kinetic data for the variation of sugar concentration in the reactions of $Co^{III}M$ with D-fructose, D-glucose, and D-mannose[a]

[Reductant]/ mol dm^{-3}	$10^7k_{obs.}$(Fru)/ mol dm^{-3} s^{-1}	$10^2k_{obs.}$(Glu)/ mol^{-1} dm^3 s^{-1}	$10k_{obs.}$(Man)/ mol^{-1} dm^3 s^{-1}
0.10			0.97
0.20	0.54	2.57	
0.40	1.13	4.83	4.27
0.50	1.28	6.46	5.71
0.60	1.61	7.38	
0.70			7.96
0.80	2.04	10.33	
0.90			10.03
1.00	2.72	12.65	

[a] $[Co^{III}M] = 2 \times 10^{-4}$ mol dm^{-3}, $T = 60$ °C, $[H^+] = 0.10$ mol dm^{-3}, $I = 1.00$ mol dm^{-3} ($NaClO_4$).

Table 3. Effects of $[H^+]$ variation on the reactions of $Co^{III}M$ with D-fructose, D-glucose, and D-mannose[a]

$[H^+]$/ mol dm^{-3}	10^7k_F[b]/ s^{-1}	10^2k_G[b]/ mol^{-2} dm^6 s^{-1}	$10k_M$[b]/ mol^{-2} dm^6 s^{-1}
0.01		13.23	
0.05	1.22		
0.10	2.56[c]	12.92	11.42
0.15	3.66	13.20	
0.20	4.80	13.29	
0.25	6.26		
0.30		12.65	11.72
0.50			11.18
0.60			11.33
0.80			12.04
1.00			

[a] At 60 °C, $I = 1.00$ mol dm^{-3} ($NaClO_4$) and [sugar] = 0.50 mol dm^{-3}. [b] k_F, k_G, and k_M denote the $k_{obs.}$ values divided by the respective sugar concentrations. [c] This is in close agreement with the enolisation rate for fructose at $[H^+]$ 0.1 mol dm^{-3} studied separately by iodination at 460 nm (k_{enol} 2.62×10^{-7} s^{-1} at 60 °C).

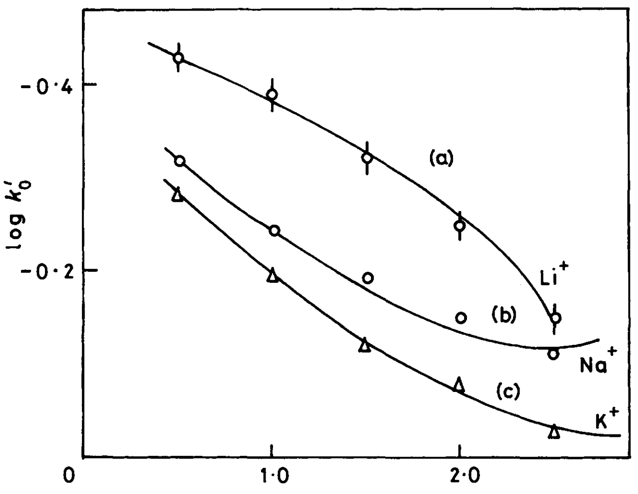


Figure 3. Brønsted–Christiansen–Scatchard plots showing the dependence of log k_0 on ionic strength for the electron-transfer reaction between $Co^{III}M$ and mannose at 60 °C in (a) $LiNO_3$, (b) $NaClO_4$, and (c) KNO_3 media

observed in metal-ion-catalysed reactions,[32,33] and indicates the existence of non-electrostatic interactions.

The individual effects of K^+, Na^+, and Li^+ on the reaction rates were studied thoroughly at $[H^+] = 0.10$ mol dm^{-3} for both D-glucose and D-mannose. When $k_{obs.}/2$[Glu] was plotted against metal ion concentration, a second-order dependence on both $[Li^+]$ and $[Na^+]$ and a first-order dependence on $[K^+]$ was observed, with cation catalysis order $K^+ > Na^+ > Li^+$, in the low metal concentration region, where almost a first-order dependence prevails for all the metal ions. A similar trend was observed for the D-mannose oxidation, where a second-order dependence on $[Li^+]$ but first-order dependence on $[Na^+]$ and $[K^+]$ was observed. The modified rate laws may therefore be described by equations (8)—(10) and (11)—(13) for D-glucose

$$k_{obs.} = 2(k^0_G + k'_G[K^+])[Glu] \quad (8)$$

$$k_{obs.} = 2(k^0_G + k''_G[Na^+]^2)[Glu] \quad (9)$$

$$k_{obs.} = 2(k^0_G + k'''_G[Li^+]^2)[Glu] \quad (10)$$

$$k_{obs.} = 2(k^0_M + k'_M[K^+])[Man] \quad (11)$$

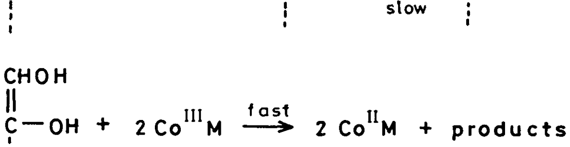
$$k_{obs.} = 2(k^0_M + k''_M[Na^+])[Man] \quad (12)$$

$$k_{obs.} = 2(k^0_M + k'''_M[Li^+]^2)[Man] \quad (13)$$

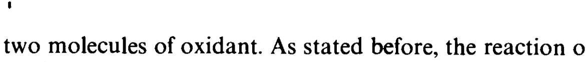
and D-mannose, respectively. The rates of spontaneous and cation-catalysed paths were obtained from the intercepts and slopes of the plots of $k_{obs.}/2$[sugar] *vs.* $[M^+]$ or $[M^+]^2$ (Table 4).

From the results it is apparent that the mode of reaction of D-fructose differs from that of D-glucose and D-mannose. Since the interaction of D-fructose with $Co^{III}M$ is independent of $[Co^{III}M]$, it is evident that the electron-transfer rate does not control the rate of oxidation. It is known that ketones like cyclohexanone,[33] diethyl ketone,[34] *etc.* exhibit keto–enol tautomerism in acid media. Littler *et al.* showed that the oxidation of cyclohexanone[33] by Hg^{2+}, Tl^{3+}, or Mn^{7+} in acid medium occurs through the formation of an enol. Singh *et al.*[13] studied the oxidation of a number of monomeric sugars, *e.g.* D-glucose, D-fructose, D-mannose, *etc.*, by Cu^{2+} in alkaline medium. They suggested a mechanism involving OH^--catalysed formation of an enediol, which reacts in a fast step with Cu^{2+} leading to products; the reaction was found to show zero-order dependence on the oxidant, but in our case the oxidation was catalysed by acid.

A reasonable interpretation of our observations of D-fructose oxidation involves rate-determining acid-catalysed enolisation of D-fructose, followed by fast reaction of the enediol thus formed with $Co^{III}M$ to give the redox products [equations (14) and (15)]. In this scheme one molecule of enediol reacts with two molecules of oxidant. As stated before, the reaction occurs *via* free radicals. Thus it may be assumed that the fast enediol reaction produces a free radical and one molecule of $Co^{II}M$. The free radical in turn reacts rapidly with another molecule of $Co^{III}M$ to give products.


(14)

$$(CH_2OH)C{=}O + H^+ \rightleftharpoons (H{-}CHOH)C{=}OH^+ \xrightarrow[\text{slow}]{k} (CHOH){=}C{-}OH$$


(15)

$$(CHOH){=}C{-}OH + 2\,Co^{III}M \xrightarrow{\text{fast}} 2\,Co^{II}M + \text{products}$$

Table 4. Kinetic data for the variation of metal ion in the reactions of $Co^{III}M$ with glucose and mannose at 60 °C and $[H^+] = 0.10$ mol dm^{-3}

Reductant	$[M^+]$/ mol dm^{-3}	$5k_{obs.}[Sugar]^{-1}$/mol^{-2} dm^6 s^{-1} $[Li^+]$	$[Na^+]$	$[K^+]$
Glucose[a]	0.50	0.50	0.53	0.61
	1.00	0.56	0.80	0.75
	1.50	0.97	1.56	0.87
	2.00	1.30	2.20	0.99
	2.25	1.44		1.06
	2.50		2.92	
Mannose[b]	0.50	3.73	4.80	5.15
	1.00	4.03	5.71	6.25
	1.50	4.78	6.40	7.52
	2.00	5.59	7.07	8.26
	2.50	7.07	7.65	9.24

$k^0_G = (4.5 \pm 0.40) \times 10^{-2}$ mol^{-2} dm^6 s^{-1} $k'''_G = (2.09 \pm 0.10) \times 10^{-2}$ mol^{-4} dm^{12} s^{-1}

$k''_G = (4.05 \pm 0.10) \times 10^{-2}$ mol^{-4} dm^{12} s^{-1} $k'_G = (2.55 \pm 0.06) \times 10^{-2}$ mol^{-3} dm^9 s^{-1}

$10k^0_M = 3.85 \pm 0.31$ mol^{-2} dm^6 s^{-1} $10k'''_M = 0.56 \pm 0.04$ mol^{-4} dm^{12} s^{-1}

$10k''_M = 1.41 \pm 0.09$ mol^{-3} dm^9 s^{-1} $10k'_M = 2.04 \pm 0.20$ mol^{-3} dm^9 s^{-1}

[a] [Glucose] = 0.80 mol dm^{-3}, [b] [Mannose] = 0.5 mol dm^{-3}.

The rate law in the presence of H^+ may therefore be represented by equation (16).

$$-d[Co^{III}M]/dt = 2k_1[Fru][H^+] \quad (16)$$

In contrast, the aldose oxidations are catalysed by metal ions and not by acid. The spontaneous and catalysed processes for D-glucose oxidation may therefore be described by equations (17)—(19). The rate expression for the uncatalysed path thus

$$Co^{III}M^{5-} + Glu \underset{}{\overset{K_1}{\rightleftharpoons}} Co^{III}M^{5-},Glu \quad (17)$$

$$Co^{III}M^{5-},Glu \overset{K_2}{\rightleftharpoons} [Co^{II}M^{6-},Gl\dot{u}]^{\ddagger} + H^+ \quad (18)$$

$$Co^{III}M^{5-} + [Co^{II}M^{6-},Gl\dot{u}]^{\ddagger} \xrightarrow{k_s} 2Co^{II}M^{6-} + H^+ + \text{products} \quad (19)$$

may be given as equation (20). Similarly, for the cation-assisted

$$-d[Co^{III}M]/dt = 2k_sK_1K_2[Co^{III}M]^2[Glu] \quad (20)$$

path in presence of K^+ ion, the mechanism† (21)—(23) may be

$$Co^{III}M^{5-} + Glu + K^+ \overset{K_3}{\rightleftharpoons} KCo^{III}M^{4-},Glu \quad (21)$$

$$KCo^{III}M^{4-},Glu \overset{K_4}{\rightleftharpoons} [KCo^{II}M^{5-},Gl\dot{u}]^{\ddagger} + H^+ \quad (22)$$

$$[KCo^{III}M^{5-},Gl\dot{u}]^{\ddagger} + Co^{III}M^{5-} \xrightarrow{k_c} 2Co^{II}M^{6-} + H^+ + \text{products} \quad (23)$$

suggested. The overall rate expression for the spontaneous and catalysed paths, therefore, may be given as equations (24) and (25) [similar to equation (8)]. Thus by comparing these two

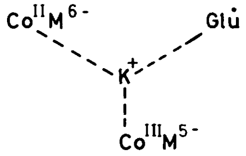
$$-d[Co^{III}M]/dt = 2\{k_sK_1K_2[Co^{III}M]^2[Glu] + k_cK_3K_4[Co^{III}M]^2[K^+][Glu]\} \quad (24)$$

$$k_{obs.} = 2\{k_sK_1K_2 + k_cK_3K_4[K^+]\}[Glu] \quad (25)$$

equations one can write equations (26).

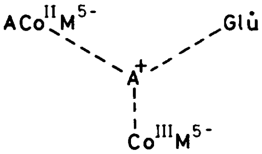
$$k^0_G = k_sK_1K_2 \quad \text{and} \quad k'_G = k_cK_3K_4 \quad (26)$$

The transition state for the metal-ion-catalysed oxidation is assumed to be a free-radical-bound activated species and may be represented as (A). With Na^+ and Li^+ the reaction scheme will



(A)

be similar to that for K^+, the only difference being the second-order dependence on metal ion which may be explained by incorporating another metal ion (A^+) in the transition state (**B**).



(B)

A similar mechanism may be suggested for the oxidation of D-mannose. Outer-sphere equilibrium association has also been suggested in our previous studies[8,9] and for oxidations of L-cysteine, mercaptoacetic acid, *etc.*,[2] by the same $Co^{III}M$ polyanion. Second-order dependence on $Co^{III}M$ has also been observed in the reaction of formate[9] with the same polyanion and has been explained by similar mechanism.

The most interesting feature of this study is the difference in order of reaction between the keto- and aldo-sugars. We are unaware of any precedent in the redox chemistry of sugars. The zero-order dependence of $Co^{III}M$ in the D-fructose oxidation is unique in the sense that the reaction is catalysed by acid. Previously, enediol formation in sugar oxidation in alkaline medium has been suggested,[13] but not in the presence of acid. Enol formation is supported by our recent observation that the reaction of $Co^{III}M$ with 1,3-dihydroxyacetone[35] is zero-order with respect to the oxidant and is catalysed by acid. Again, the

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† The predicted reversible electron-transfer mechanism does not specify the exact nature or stability of the second intermediate produced by equations (18) or (22), but we assume it to be less reactive than the Glů itself. The value of the thermodynamic redox potential for the couple Glu/Glů is not known.

second-order dependence on [complex] in the case of the aldose oxidations is interesting; this has not been reported hitherto in the oxidation of any sugar. The metal ion catalysis for the aldosugars may be explained by outer-sphere complex formation *via* an ion-induced-dipole-type interaction; this type of catalysis is rare in redox reactions involving a neutral species. At very low pH, the reaction of $Co^{III}M$ with malonic acid[36] has been found to be catalysed by alkali-metal ions. In aldose oxidations, D-mannose has been found to be more reactive than D-glucose. Mehrotra *et al.*[16] showed that the increase in reactivity is related to the increase in the percentage of free aldehyde form in the equilibrium mixture. However, such a correlation does not hold good in our case.

The cation catalytic order observed for the aldose oxidations may be explained on the basis of the stability of the transition state. The radii of hydrated metal ions fall in the order $Li^+ > Na^+ > K^+$; consequently the potential in the vicinity of the hydrated ion will follow the same order. Thus K^+ will be most effective in bridging the negatively charged reacting species. The same cation catalytic order has been observed previously in the decomposition of dodecatungstosilicate[37] in base and in many other outer-sphere electron-transfer processes.[38–42]

Appendix

Comparison of Oxidation Rate with Mutarotation.—In aqueous acidic solution, D-glucose exists predominantly as a dynamic equilibrium mixture of α- and β-pyranose forms, with the free aldehyde form as intermediate[17] [equation (27)]. The

$$\alpha\text{-glucose} \underset{k''}{\overset{k'}{\rightleftharpoons}} \beta\text{-glucose} \qquad (27)$$
$$\text{where } K = k'/k''$$

rate of mutarotation, k_m, is $0.0096 + 0.258[H^+]$ at 25 °C.[43] At 0.10 mol dm^{-3} $HClO_4$ and 25 °C, k_m is calculated as 5.9×10^{-4} s^{-1}. Again, $k_m = k' + k''$ and $K = 1.77$ at 25 °C.

Using this value of K and equation (27), one obtains $k' = 2.12 \times 10^{-4}$ s^{-1} at 25 °C. At 60 °C, k' is calculated from equation (28), with $E = 23$ kcal mol^{-1} (ref. 44) as 12.67×10^{-3} s^{-1}.

$$\log k_1 - \log k_2 = -\frac{E}{4.576}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (28)$$

Since the D-glucose oxidation has a second-order dependence on $Co^{III}M$ and a first-order dependence on D-glucose, the disappearance of $Co^{III}M$ may be expressed by equation (29),

$$-d[Co^{III}M]/dt = k[Co^{III}M]^2[Glu] \qquad (29)^*$$

where k is the third-order rate constant. As one mole of glucose reduces two moles of $Co^{III}M$ one can write equation (30). The

$$-d[Co^{III}M]/dt = -2d[Glu]/dt \qquad (30)$$

value of the first-order rate constant with respect to $[Co^{III}M]$ can be calculated by substitution in equation (31) as $k_g = 2.53 \times 10^{-9}$ s^{-1}. A comparison of the respective values of k_g and k' indicates that the rate of transformation of α-glucose into β-glucose is many times greater than the rate of glucose oxidation with respect to glucose. The observed rate therefore depends on the total contribution of α- and β-forms in addition to a possible contribution from the free aldehyde form in the dynamic equilibrium.

$$k_g = k_{obs.}[Co^{III}]^2/2[Glu] \qquad (31)^\dagger$$

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* Equation (29) is similar to (3) where $k = 2k_2$

† Equation (31) is derived from equations (29) and (30).