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Kinetic behaviour and relative reactivities of some aldoses, amino sugars, and methylated sugars towards platinum(IV) in alkaline medium

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Abstract

The kinetic behaviour and relative reactivities of some carbohydrates (aldoses, amino sugars and methylated sugars) towards platinum(IV) in alkaline medium have been investigated. The reactions are first order with respect to [substrate] and [Pt(IV)]. The rates increase with the increase in $[OH^-]$. The reactions show pseudo-first-order dependence on $[OH^-]$. The oxidation rates in alkaline medium follow the order triose > tetrose > pentose > hexose. Activation parameters of the reactions have been calculated. Mechanisms have been proposed for the reactions. © 1998 Elsevier Science Ltd. All rights reserved

1. Introduction

The mechanism for the oxidations of some aldoses by chromium(VI) [1], vanadium(V) [2], cerium(IV) [3], manganese(III) [4], iridium(IV) [5], gold(III) [6] and periodic acid [7] have been investigated in acidic media. The kinetics of the oxidation of aldoses by halogens [8,9], chloramine-T [10], bromamine-T [11] (sodium *N*-bromo-*p*-toluenesulfonamide), osmium tetroxide [12] and hexacyanoferrate(III) [13] have been reported in alkaline media. However, no data are available on the reactivities of aldoses, amino sugars, and methylated sugars with hexachloroplatinate(IV) in alkaline medium. The reactions of platinum(IV) with some aldoses represented by the general formula $C_nH_{2n}O_n$ ($n = 3$–6), as well as reactions with some amino sugars, have been carried out in alkaline medium.

2. Experimental

Reagents.—The sugars and hydrochlorides of the amino sugars were obtained from BDH, E. Merck, or Sigma Chemical Co. Reagent grade sodium hexachloroplatinate (Johnson-Matthey, London) was used as supplied. The platinum(IV) content of the salt was determined by an iodometric method [14].

Instrumentation.—Spectral measurements were recorded in the UV-vis region using a Systronics (India) spectrophotometer. IR spectra were recorded on KBr discs using a Perkin–Elmer 783 ratio-recording infrared spectrophotometer. Thermogravimetric analysis was performed in a Shimadzu Corporation (Japan) a TG 50 instrument at normal atmospheric environment by heating a sample (21.39 mg) at the rate of 15 °C min^{-1} up to 200 °C.

Kinetic measurements.—The platinum(IV) solution has a maximum absorption at 400 nm. Beer's

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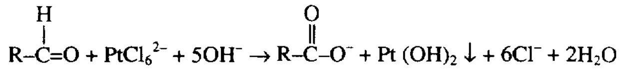
law is valid in the concentration range $(1.00–10.0)\times10^{-3}\,\mathrm{mol\,dm^{-3}}$. The kinetic studies were carried out under pseudo-first-order conditions with the concentration of substrates in large excess $(2\times10^{-2}\,\mathrm{mol\,dm^{-3}})$ relative to that of platinum(IV) concentrations. Hence, the rate of disappearance of platinum(IV) could be followed spectrophotometrically at 400 nm. The spectrophotometer had a cell compartment kept at constant temperature (±0.1 °C) by circulating water from a thermostat. The reactants were previously equilibrated to bath temperature. In each case, alkali was added to the substrate immediately before the kinetic experiment in order to minimise [15] isomerisation, degradation into substances with fewer carbon atoms than the original sugar, and internal oxidations and reductions. Platinum(IV) was then added to the mixture of aldose and alkali, the reaction mixture was transferred to the cell of path length 1 cm, and 8–10 experimental readings were taken in each run. Good straight lines were obtained for at least two half-lives. The pseudo-first-order rate constants, k_{obs}, were calculated from the plots of log A (A = absorbance) versus time. The rate constants were reproducible to within ±5%.

Stoichiometry and product analysis.—The reaction mixtures containing a known excess of [Pt(IV)] over [glucose] at fixed $[\mathrm{OH^-}]$ were made. After completion of the reactions the unreacted platinum(IV) was determined, showing that one mole of glucose consumed one mole of Pt(IV). The reaction stoichiometry may thus be represented as follows:



$$\mathrm{R{-}\overset{H}{\overset{|}{C}}{=}O + PtCl_6^{2-} + 5OH^- \rightarrow R{-}\overset{O}{\overset{\|}{C}}{-}O^- + Pt(OH)_2\downarrow + 6Cl^- + 2H_2O}$$

After the kinetic experiments, the reaction mixtures of the aldoses and the amino sugars were acidified and treated with 2,4-dinitrophenylhydrazine hydrochloride. The absence of any yellow precipitate indicated that neither the $-\mathrm{CH_2OH}$ nor the =CHOH group was oxidised. Iron(III) chloride solution that had been coloured violet with phenol when added to the reaction mixture gave a bright-yellow colouration [1], indicating that aldonic acids are formed in the oxidation of the aldoses. The aldoses were oxidized separately by the oxidant under kinetic conditions and then acidified. After purification and concentration, the products were confirmed [16] by paper chromatography (PC) by comparison with the products of the respective aldoses from bromine-water oxidation. PC was carried out in the descending mode with Whatman No.1 paper in 4:1:5 (upper layer) butanol–AcOH–$\mathrm{H_2O}$, and the sugars were detected by alkaline silver nitrate. The PC of the syrup obtained by oxidation of aldoses indicated the presence of aldonic acids. Similar experiments when carried out with the oxidation products of the amino sugars gave yellow colourations with the above iron(III) reagent. It may be mentioned [17] that amino sugars are also oxidised by HgO to give aldosaminic acids, and that when iron(III) chloride solution coloured violet with phenol is added to an aldosaminic acid solution, a yellow colouration is also obtained. However, the addition of alkaline hydroxylamine solution to the reaction mixtures and subsequent addition of 2% $\mathrm{FeCl_3}$ and 1% Hcl failed to give any blue colouration, which indicated that no lactone formation was taking place during the reaction [18]. It is to be mentioned that the primary products in the oxidation of cyclic aldoses are aldonic acids or γ- or δ-lactones in acidic solutions, but at pH > 2.5 the proportion of lactones is reduced because of the formation of aldonic acid anions that displace the equilibrium away from the lactones [19]. Consequently, the lactones which are formed in the rate-determining steps are hydrolyzed to form the aldonic acid anions in alkaline media in a fast step. The black product obtained in the oxidations by platinum(IV) is hydrated PtO as indicated by thermogravimetric and IR spectral analysis [20]. There is also literature evidence [21] to indicate that platinum(II) oxide exists as $\mathrm{Pt(OH)_2}$. This is supported by the thermogravimetric analysis of the solid product, which indicates that loss of water takes place in one step. The weight loss calculation based on $\mathrm{Pt(OH)_2}$ confirmed the loss of only one water molecule. The IR spectrum of the thermogravimetric residue identified it as PtO by the presence of ν(Pt–O) at around $570\,\mathrm{cm^{-1}}$ and the absence of ν(O–H) in the $3600–3400\,\mathrm{cm^{-1}}$ region. The IR spectrum of an authentic sample of PtO was compared with that of the PtO obtained as a reaction product.

3. Results and discussion

The reactions were investigated at different [Pt(IV)] and at constant [substrate], $[\mathrm{OH^-}]$, and temperature. The pseudo-first-order rate constants remain unaltered in the region of [Pt(IV)] of $(1–5)\times10^{-3}\,\mathrm{mol\,dm^{-3}}$ (Table 1). These indicate that the rate is first order with respect to [Pt(IV)]. At constant [Pt(IV)], $[OH^-]$, and temperature, the rate increases with increase in [substrate]. The results plotted in Fig. 1 indicate that each reaction is first-order with respect to [substrate] and that the slope of each line is one.

The influence of hydroxide ion on the reaction rates was investigated at different hydroxide ion concentrations but at constant [substrate] and temperature. The rate increased with increase in $[OH^-]$. Plots of log k_{obs} versus log $[OH^-]$ gave a slope of each line that was one, which indicates that the reaction is first order (Fig. 2).

The reactions were studied at constant [Pt(IV)], [substrate], $[OH^-]$, and 303 K at different $[Cl^-]$ (0.6–4×10^{-2} mol dm^{-3}), which was varied by the addition of NaCl. The values of k_{obs} were found to be independent of sodium chloride concentrations.

Table 1
Effect of [Pt(IV)] on the rate of oxidation rate at 303 K; $[Pt(IV)] = (1-5)\times10^{-3}$ mol dm^{-3}, $[OH^-] = 1.0\times10^{-2}$ mol dm^{-3}, [substrate] = 2.0×10^{-2} mol dm^{-3}

Substrate	$k_{obs}\times10^4$ (s^{-1})
D-Glucose	0.54 ± 0.01
D-Mannose	0.61 ± 0.01
D-Galactose	0.69 ± 0.02
D-Xylose	0.96 ± 0.02
L-Arabinose	1.08 ± 0.01
D-Ribose	1.28 ± 0.02
D-Erythrose	3.3 ± 0.02
D-Glyceraldehyde	40.1 ± 0.03
D-Glucosamine	1.27 ± 0.01
D-Mannosamine	4.8 ± 0.02
D-Galactosamine	9.6 ± 0.01

The influence of temperature on the rate was determined for each reaction (Table 2). The values of k_3 ($k_3 = k_{obs}/[\text{substrate}][OH^-]$) were calculated (Table 3) at different temperatures from 298–318 K. Least-squares treatment of the log k_3/T against $1/T$ plots were used to obtain the best straight lines from which the enthalpies of activation ($\Delta H^{\neq}$) and entropies of activation ($\Delta S^{\neq}$) were calculated using the theory of absolute reaction rate, the equation being $k_3 = (RT/Nh)e^{-\Delta H^{\neq}/RT}.e^{\Delta S^{\neq}/R}$. The activation parameters are recorded in Table 4. The activation enthalpies are in the order hexose > pentose > tetrose > triose. The values of $\Delta S^{\neq}$ for aldohexoses, which are higher than those of aldopentoses, are also in keeping with the idea of Hammett and Price [22] who showed that $\Delta S^{\neq}$ is related to the rigidities of the transition states. The enthalpy of activation is linearly related with the entropy of activation [23] ($r = 0.9939$, Fig. 3), and the isokinetic temperature is 333 K. The isokinetic behaviour supported [24] by the linear plot of log k_2' versus log k_2 ($r = 0.9925$) where k_2' and k_2 are the second-order rate constants at the temperatures 308 and 303 K, respectively (Fig. 3). The isokinetic temperature was calculated from the relation $\beta = T_1T_2(1-f)/(T_1 - T_2f)$, where f is the slope of the Exner plot, and β is 348 K. Since the value of β

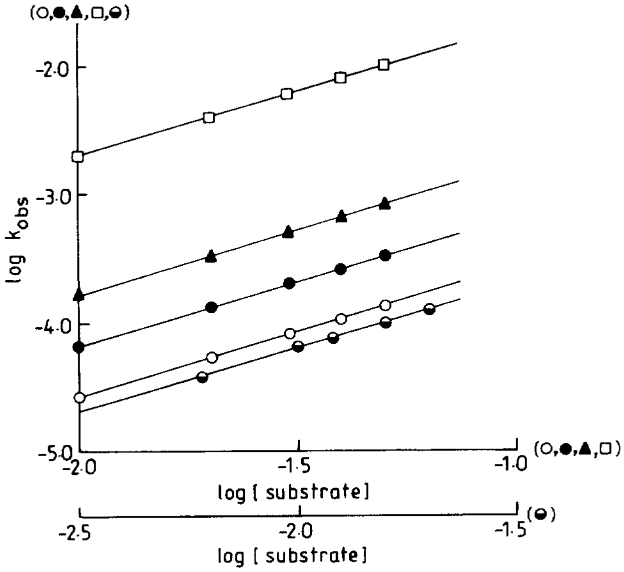


Fig. 1. Variation of the reaction rate with [substrate]. Plots of log k_{obs} versus log [substrate] at $[OH^-] = 1\times10^{-2}$ mol dm^{-3} and temperature = 303 K. (○) D-glucose, (●) D-ribose, (▲) D-erythrose, [□] DL-glyceraldehyde, (⊖) D-glucosamine.

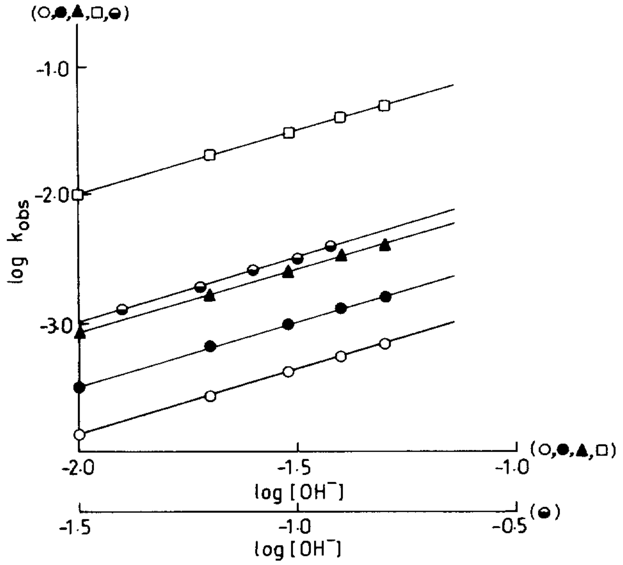


Fig. 2. Dependence of the reaction rate on $[OH^-]$. Plots of log k_{obs} versus log $[OH^-]$ at [substrate] = 5×10^{-2} mol dm^{-3} and temperature = 303 K. (○) D-glucose, (●) D-ribose, (▲) D-erythrose, [□] DL-glyceraldehyde, (⊖) D-glucosamine.

is above the experimental temperature (305 K), it can be concluded that enthalpy is a controlling factor [11] of the reaction.

Cyclic aldoses exist [25] mainly in their cyclic hemiacetal forms in equilibrium with the open-chain forms. Again aldoses which predominantly exist as a β-anomer of the pyranoid form are converted to anions in alkaline medium. Erythrose is known to exist in acyclic form, although literature evidence [26] indicates that it can also exist in 88% cyclic furanoid form with the β-anomer predominating. DL-Glyceraldehyde in aqueous solution exists in acyclic monomeric form that remains in equilibrium with hydrated and nonhydrated forms [27]. Since the experiments were performed at low concentrations ($\leq 5.0\times10^{-2}$ mol dm^{-3}) of substrates, it is likely that the hydrated monomeric forms should be preponderant, although the oxidation via the nonhydrated form cannot be ruled out.

Again, there is literature evidence [14] to indicate that in alkaline medium (pH > 8) $PtCl_6^{2-}$ changes to $PtCl_5(OH)^{2-}$ in a fast step.

$$PtCl_6^{2-} + OH^- \rightarrow PtCl_5(OH)^{2-} + Cl^-$$

The addition of Cl^- to the reaction mixture failed to inhibit the rate, which indicates that the above

Table 2
The values of pseudo-first-order rate constants ($k_{obs} \times 10^4$ s^{-1}) of the oxidations of some aldoses and amino sugars at different temperatures; [Pt(IV)] = 2×10^{-3} mol dm^{-3}, [OH$^-$] = 1×10^{-2} mol dm^{-3}, [substrate] = 2×10^{-2} mol dm^{-3}

Temperature (K)	a	b	c	d	e	f	g	h	i	j	k
298	0.25					0.80	2.21	29.2			
303	0.54	0.61	0.69	0.96	1.08	1.28	3.30	40.1	1.27	4.80	9.60
308	1.10	1.23	1.28	1.74	1.86	1.99	4.84	54.2	1.79	7.25	15.3
313	2.22	2.50	2.30	3.14	3.29	3.34	7.02	73.5	2.53	10.9	24.9
318		4.94	4.10	5.66	5.54				3.48	16.7	39.2

(a) D-glucose, (b) D-mannose, (c) D-galactose, (d) D-xylose, (e) L-arabinose, (f) D-ribose, (g) D-erythrose, (h) DL-glyceraldehyde, (i) D-glucosamine, (j) D-mannosamine, (k) D-galactosamine.

Table 3
Influence of temperature on the oxidations of some aldoses and amino sugars in alkaline medium (k_3 in mol^{-2} dm^6 s^{-1})

Temperature (K)	k_3^a	k_3^b	k_3^c	k_3^d	k_3^e	k_3^f	k_3^g	k_3^h	k_3^i	k_3^j	k_3^k
298	0.127					0.395	1.107	14.5			
303	0.27	0.300	0.350	0.480	0.540	0.640	1.65	20.0	0.633	2.40	4.80
308	0.546	0.614	0.640	0.868	0.930	0.995	2.42	27.1	0.893	3.63	7.67
313	1.11	1.25	1.15	1.57	1.64	1.67	3.51	36.7	1.27	5.458	12.5
318		2.47	2.05	2.83	2.77				1.733	8.38	19.6

(a) D-glucose, (b) D-mannose, (c) D-galactose, (d) D-xylose, (e) L-arabinose, (f) D-ribose, (g) D-erythrose, (h) DL-glyceraldehyde, (i) D-glucosamine, (j) D-mannosamine, (k) D-galactosamine.

Table 4
Values of activation parameters of the oxidations of aldoses and amino sugars

Substrates	$\Delta H^{\neq}$(kJ mol^{-1})	$\Delta S^{\neq}$(JK^{-1} mol^{-1})	$\Delta G^{\neq}$(kJ mol^{-1})
D-Glucose	113 ± 8	117 ± 27	77.55 ± 0.1
D-Mannose	107 ± 4	99 ± 13	77.00 ± 0.06
D-Galactose	91 ± 4	47 ± 13	76.76 ± 0.06
D-Xylose	90 ± 4	46 ± 13	76.06 ± 0.06
L-Arabinose	86 ± 4	31 ± 12	76.6 ± 0.3
D-Ribose	73 ± 8	-8 ± 26	75.42 ± 0.1
D-Erythrose	56 ± 4	-56 ± 13	72.97 ± 0.06
DL-Glyceraldehyde	47 ± 4	-65 ± 13	66.70 ± 0.06
D-Glucosamine	55 ± 2	-67 ± 7	75.30 ± 0.1
D-Mannosamine	64 ± 2	-27 ± 7	72.20 ± 0.1
D-Galactosamine	68 ± 2	-8 ± 7	70.4 ± 0.1

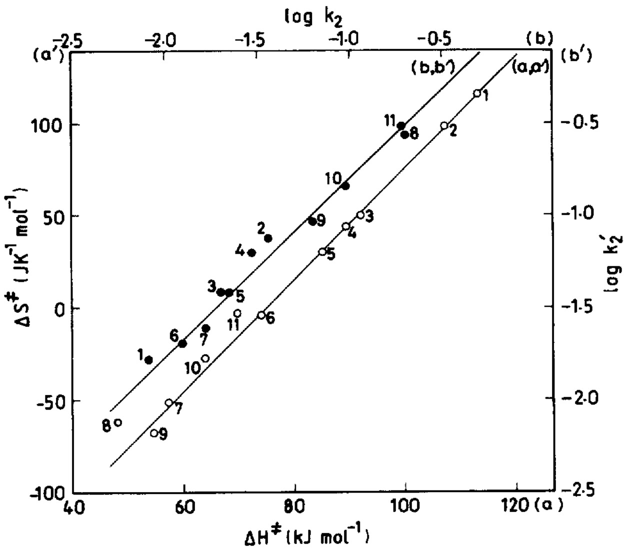


Fig. 3. Isokinetic plots for the oxidations of aldoses and amino sugars by platinum(IV) in alkaline medium. (a,a'), plot of $\Delta S^{\neq}$ versus $\Delta H^{\neq}$; (b,b'), plot of log k'_2 versus log k_2. (1) D-glucose, (2) D-mannose, (3) D-galactose, (4) D-xylose, (5) L-arabinose, (6) D-ribose, (7) D-erythrose, (8) DL-glyceraldehyde, (9) D-glucosamine, (10) D-mannosamine, (11) D-galactosamine.

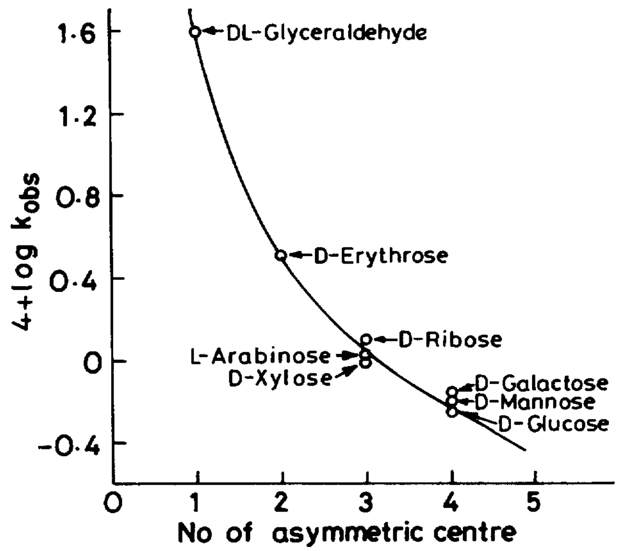


Fig. 4. Dependence of the reaction rate on the number of asymmetric centres (n). Plot of log k_{obs} against 'n'.

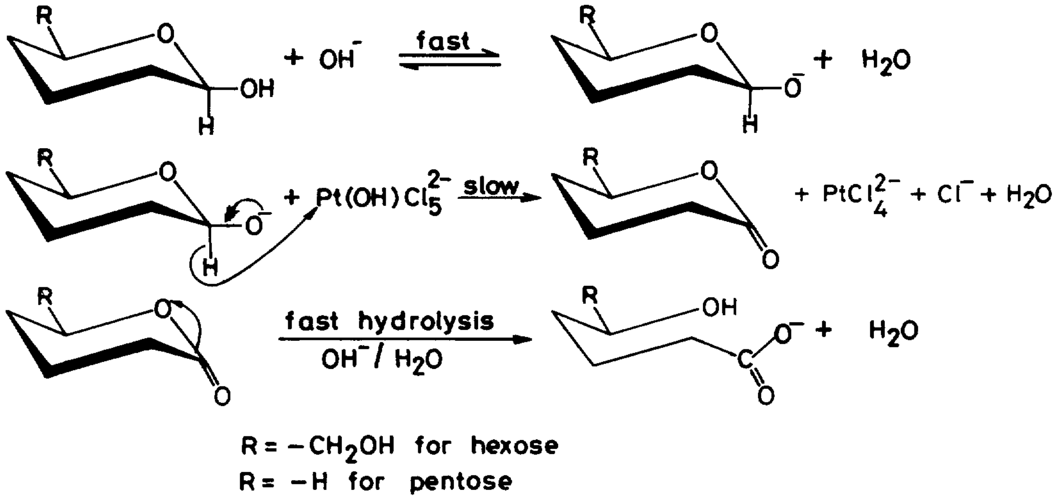
step is not reversible. The ligand replacement reaction between $PtCl_5(OH)^{2-}$ and OH^- to give $PtCl_4(OH)_2^{2-}$ and Cl^-, followed by the oxidation of aldose by $PtCl_4(OH)_2^{2-}$, can be ruled out since the dihydroxy platinum(IV) complex is unstable in aqueous solution and readily disproportionates [28] according to the following equation:

$$2\,PtCl_4(OH)_2^{2-} \rightarrow PtCl_6^{2-} + PtCl_2(OH)_4^{2-}$$

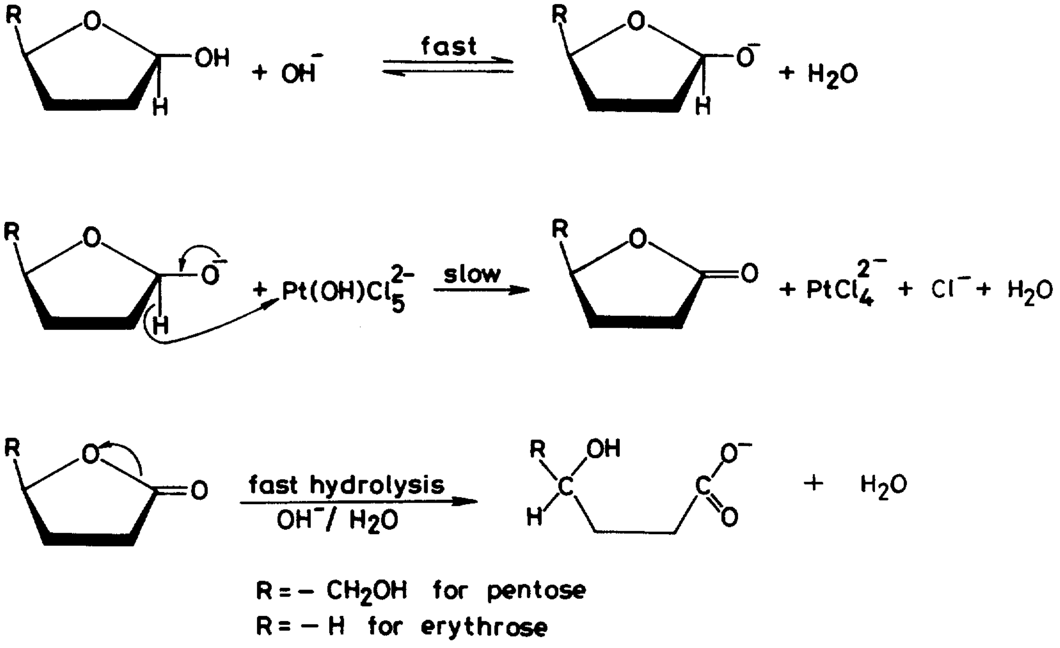
The path by which platinum(IV) is reduced by different reductants has been the subject of much discussion [29,30], which was mainly concerned with the possibility of platinum(III) as an intermediate. The reductions of some platinum(IV) complexes by different reductants have been shown to proceed via a free-radical mechanism [31,32]. However, the alternative mechanistic paths whereby platinum(IV) undergoes a two-electron reduction have also been reported [20,33,34].

The oxidation reactions of all the aldoses and the amino sugars that we have studied are kinetically similar. It appears that oxidation rates for substrates existing mainly in acyclic forms are higher than those existing in cyclic forms. The decrease in the rate with increase in asymmetric centre (n) is shown in Fig. 4. The plot of log k_{obs} versus 'n' is hyperbolic in character. The pseudo-first-order rate constants thus follow the order triose > tetrose > pentose > hexose. The presence of different substitutents 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 due to the inductive effect (–I), as well as the stabilising effect of the hydroxymethyl group in the former. The difference in the rates of oxidation of aldoses having the same substituents at C-5 seems to be due to the configurational variation at positions other than C-1 and C-5 [35]. There is literature evidence [10] to indicate that aldoses exist as enolate ions in alkaline medium. The dependence of the rate on the concentration of OH^- was explained as resulting from the anion of aldoses being much more reactive than the unionized form, which would require specific OH^- catalysis [36].

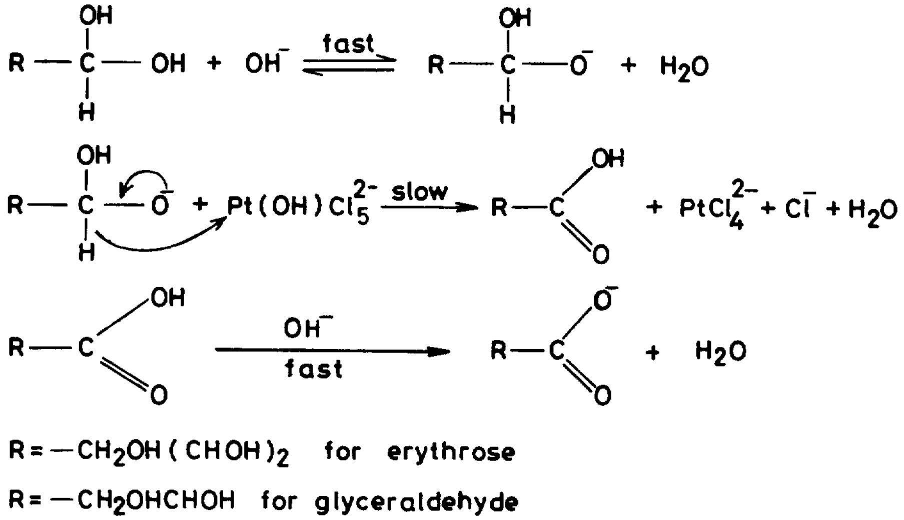
Again, aldoses may react [11,15] with hydroxide ion to form an enediol, followed by the reaction with the oxidant to form lower aldoses and formic acid. Under the pseudo-first-order conditions of a large excess of substrate over oxidant used in this study, the possibility of oxidation via the intermediate formation of an enediol has been discounted. This is supported by the formation of aldonic acid anions, which are formed [10] under kinetic conditions. It is believed that the anion of the aldose reacts with the oxidant to form products of oxidation. Attempts have also been made to determine rate constants for the oxidations of both methyl α-D-glucopyranoside and methyl β-D-glucopyranoside at high hydroxide ion concentrations and temperature. As it is known [37] that hydrolysis of methyl α-D-glucopyranoside and methyl β-D-glucopyranoside occurs in 2.0 M HCl and at 60 °C, it is unlikely that hydrolysis of the methyl glucosides takes place under the present experimental conditions. The values of k_{obs} obtained for the oxidations of the two methyl glucosides are 7.68×10^{-5} and $10.9\times10^{-5}\,s^{-1}$, for methyl α- and methyl β-D-glucosides, respectively, at [substrate] = $2.0\times10^{-2}\,mol\,dm^{-3}$, [Pt(IV)] = $1.0\times10^{-3}\,mol\,dm^{-3}$, $[OH^-]=0.10\,mol\,dm^{-3}$ and T = 328 K. The oxidations of methyl α- and methyl β-D-glucopyranoside are too slow to be studied under the conditions at which other substrates are oxidised. Consequently, C-1 of the aldoses appears to be more reactive [38] than C-6. The H-1 bonds of the cyclic and acyclic forms are ruptured, and two electrons are transferred to platinum(IV) to give the δ-lactone and the ketene, respectively. The latter compounds undergo fast alkaline hydrolysis to give aldonic acid anions [10]. The rate expression may be deduced as follows:



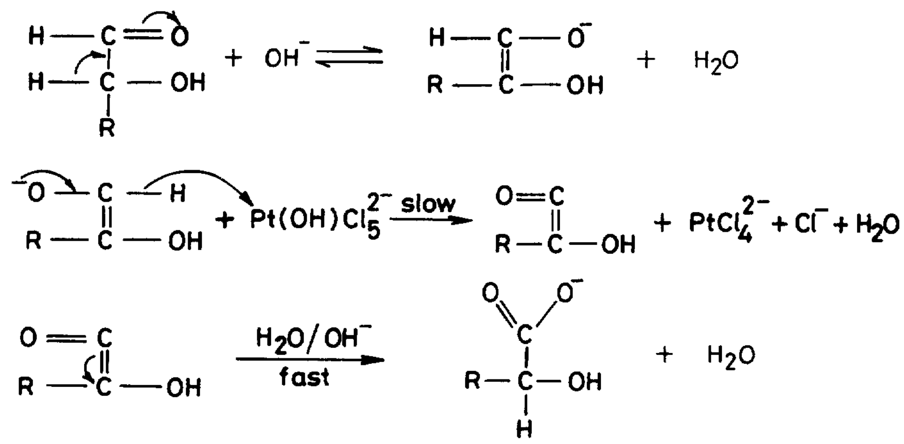
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

$$\text{Aldose} + \text{OH}^- \overset{K}{\rightleftharpoons} \text{Enolate} + \text{H}_2\text{O}$$

$$\text{Enolate} + \text{Pt(IV)} \xrightarrow{k} \text{products}$$

$$\therefore \frac{-\text{d[Pt(IV)]}}{\text{d}t} = k\text{[Pt(IV)][Enolate]}$$

$$\text{or } \frac{-\text{d [Pt(IV)]}}{\text{d}t} = k_3\text{[Pt(IV)][Aldose][OH}^-\text{]}$$

where $k_3 = kK$.

The reactions leading to the formation of aldonic acid anions may be expressed according to Schemes 1–4. When the reaction mixtures were allowed to stand for several hours, a black precipitate was obtained, presumably due to $PtCl_4^{2-}$, which is formed in alkaline medium and is transformed into hydrated PtO.

$$PtCl_4^{2-} + 2OH^- \rightarrow Pt(OH)_2\downarrow + 4Cl^-$$

Thus irrespective of whether the substrates are in cyclic or acyclic forms, oxidations of the aldoses take place to form aldonic acid anions. All the above-mentioned evidence provides adequate support to the proposed mechanism.

The rate of oxidation of the substrates by platinum(IV) increases with the first power of the concentration of [platinum(IV)], [substrate], and [OH$^-$]. Oxidations of these substrates by other oxidants [8–11] in alkaline medium are kinetically dissimilar, and hence, the present rate constant values cannot be compared with those obtained previously with other oxidants. However, from the results it appears that even in alkaline medium, oxidations of the substrates by platinum(IV) proceed at appreciable rates, and thus platinum(IV) can also be used as an effective oxidant in the oxidation of carbohydrate molecules.

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