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Reactivity of some sugars and sugar phosphates towards gold(III) in sodium acetate–acetic acid buffer medium

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Abstract

The kinetics of the oxidation of some aldoses and aldose phosphates have been studied spectrophotometrically in sodium acetate–acetic acid buffer medium at different temperatures. The reactions are first order with respect to [Au(III)] and [substrate]. Both H^+ and Cl^- ions retard the reaction. The reactions appear to involve different gold(III) species, viz. $AuCl_4^-$, $AuCl_3(OH_2)$ and $AuCl_3(OH)^-$. The results are interpreted in terms of the probable intermediate formation of free radicals and Au(II). Aldoses react with gold(III) in the order: triose > tetrose > pentose > hexose. The sugar phosphates react with gold(III) at a faster rate than the parent sugars except glucose-1-phosphate, which reacts at slower rates than glucose. A tentative reaction mechanism leading to the formation of products has been suggested.

Keywords: Kinetics; Sodium acetate–acetic acid; Gold(III); Sugars and sugar phosphates

1. Introduction

Trivalent gold are mostly complexes and are powerful oxidising agents. The redox potential for the system ($Au^{3+} + 2e \rightleftharpoons Au^+$) is about 1.29 V at 298 K.[1] There have been comparatively few reports on the kinetics of oxidation by gold(III). Although the kinetics of oxidation of some aldoses[2–13] by some oxidants have been published, there are no literature data involving the oxidation of aldoses and sugar phosphates by gold(III). Gold compounds have been used[14,15] in medicine for centuries, an application known as chrysotherapy. However, complexes of gold have also been used[16] most successfully to treat arthritic disorders in humans and other animals. Au(I) compounds are currently the only class of pharmaceuticals known to halt the progression of rheumatoid arthritis.[17] However, the mechanism of the reactions involving gold(III) with biologically important organic molecules is yet to be understood. The present investigation on the reduction of gold(III) by aldoses and sugar phosphates in sodium acetate–acetic acid medium was carried out in order to throw light upon the reactivity of aldoses and aldose phosphates towards gold(III).

2. Experimental

Reagents.—Aldoses were obtained from BDH, E. Merck, or Sigma. D-Glucose 1-phosphate, D-glucose 6-phosphate, D-ribose 5-phosphate, D-erythrose 4-phosphate and DL-glyceraldehyde 3-phosphate were of Sigma grade. Gold(III) was prepared using $HAuCl_4$ (Johnson Matthey) in a pyrex stoppered bottle and the concentration of gold(III) was esti-

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mated gravimetrically[18] as follows: To a known volume (5 mL) of the standard gold solution in a 150 mL beaker, was added dropwise with stirring, a 1 N solution of KOH until the yellow color was just discharged. A further 2 mL of KOH solution was added, followed by dilution to ca. 75 mL with distilled water. Then 5–6 mL of 1 N oxalic acid solution was added dropwise with stirring, and the contents were kept on a boiling water bath. The solution turned purple with a violet tinge when gold separated out. The beaker was kept on the water bath for about an hour with occasional stirring. The solution was filtered through a Whatman No. 42 (7 cm) filter paper. The precipitate was washed with distilled water, dried, ignited in a silica crucible and weighed as metal. The solution after estimation was stored in the dark. The other materials employed were of the highest purity available. All solutions were made in doubly distilled water. Buffer solutions were prepared[19] from a standard solution of sodium acetate and acetic acid. The pH of the solution was checked against standard buffer solution with an Elico (LI 120) pH meter (India).

Kinetic measurements.—Gold(III) has a strong absorption in the 280–355 nm region with an absorption maximum at 313 nm ($\epsilon_{max} = 4.86 \times 10^3$ M^{-1} cm^{-1}). When aqueous solutions of $AuCl_3$ or $HAuCl_4$ are exposed to UV light, colloidal gold is formed,[20] which may be enhanced in the presence of reducing species. Consequently, the reactions were monitored at $\lambda = 400$ nm using higher gold(III) concentrations in order to minimize error due to colloidal gold formation. The kinetic investigations were carried out in a Systronics (India) UV–Vis spectrophotometer using a thermostated cell of 1 cm path length. The water was circulated from the bath maintained at the required temperature (± 0.1 °C). The pseudo-first-order rate constants (k_{obs}) were obtained from linear $\log A$ (A = absorbance) versus time plots. The linearity further indicated that the redox reaction is not complicated by the formation of colloidal gold. The k_{obs} values were reproducible to within $\pm$ 5%.

Stoichiometry and product analysis.—The reactions occur according to the following stoichiometric equation:

$$RCHO + Au(III) + H_2O \rightarrow RCOOH + Au(I) + 2H^+ \quad (1)$$

where, $R = -(CHOH)_4CH_2OH$

After the kinetic experiments, the reaction mixtures of the aldoses and the aldose phosphates were acidified and treated with 2,4-dinitrophenylhydrazine hydrochloride. The absence of any yellow precipitate (except in the case of glucose 1-phosphate) indicated that neither the $-CH_2OH$ nor the =CHOH group is oxidized. On the other hand, iron(III) chloride solution that had been colored violet with phenol and the violet-colored compound when added to the reaction mixture gave a bright yellow coloration.[2] This indicates that aldonic acids are formed in the oxidation of the aldoses. Similar yellow coloration has also been obtained in the oxidation products of aldose phosphates (other than glucose 1-phosphate) with the above-mentioned reagents. The ^{13}C NMR spectrum of the oxidation product with glucose in D_2O was recorded on a Bruker DPX-300 Spectrometer (75 MHz), and the appearance of a peak[21] at 178.8 ppm, confirmed the presence of the –COOH group in the oxidation product. The oxidation product of glucose 1-phosphate when treated with 2,4-DNP gave a yellow precipitate. The yellow derivative was filtered, washed several times with water, dried and then analyzed: mp 175–178 °C, lit. mp[22] 175–180 °C, Anal. Calcd for $C_{12}H_{15}N_4O_{12}P$: C, 32.9; H, 3.42; N, 12.78. Found: C, 33.1; H, 3.47; N, 12.8. These results indicate that the $-CH_2OH$ group of glucose 1-phosphate is oxidized to –CHO. After the experiments, part of the reaction mixture was treated with excess NaOH when a greyish-violet[23] solid was obtained that was insoluble in H_2SO_4 but soluble in HCl. On the other hand, the addition of NaOH to gold(III) failed to give any such greyish-violet precipitation. Gold(I) was found to be product of reduction of gold(III).

Test for free radicals.—Involvement of free radicals in the reaction mixture has been tested by the following experiments.

1. *Using $HgCl_2$*: When mercuric chloride solution was added to the reaction mixture, an immediate precipitation of mercurous chloride occurs. This is to be expected if a reducing intermediate like free radicals is generated.[24] $HgCl_2$ failed to give Hg_2Cl_2 when added to the substrate solutions.
2. *Using acrylamide*: Acrylamide (40% w/v) was added during the course of the reactions. An immediate haziness appeared during the oxidation of the substrates by gold(III). When an excess of methanol was added to the reaction mixture, a thick precipitate of polyacrylamide was formed.

Blank experiments in which either the oxidant or the substrates was excluded gave no polymeric suspension. Cationic and anionic polymerizations have been discounted under the conditions at which the reactions were studied. All these indicate that free radicals are generated during the reactions, and a one-step two-electron transfer process in the rate-determining step has been ruled out.

Table 1
Effect of [Au(III)] on the rate of oxidation at 298 K [a]

Substrate	$k_{obs} \times 10^3$ (s^{-1})
D-Glucose	1.88 ± 0.06
D-Ribose	2.40 ± 0.08
D-Erythrose	3.35 ± 0.1
DL-Glyceraldehyde	4.56 ± 0.2
D-Glucose 1-phosphate	1.48 ± 0.05
D-Glucose 6-phosphate	6.02 ± 0.2
D-Ribose 5-phosphate	7.04 ± 0.3
D-Erythrose 4-phosphate	9.42 ± 0.1
DL-Glyceraldehyde 3-phosphate	12.6 ± 0.07

[a] [Substrate] $= 2.0 \times 10^{-3}$ mol dm^{-3}, [Au(III)] $= (0.5–3) \times 10^{-4}$ mol dm^{-3}, [Cl^-] $= 1.96 \times 10^{-3}$ mol dm^{-3}, pH 3.72.

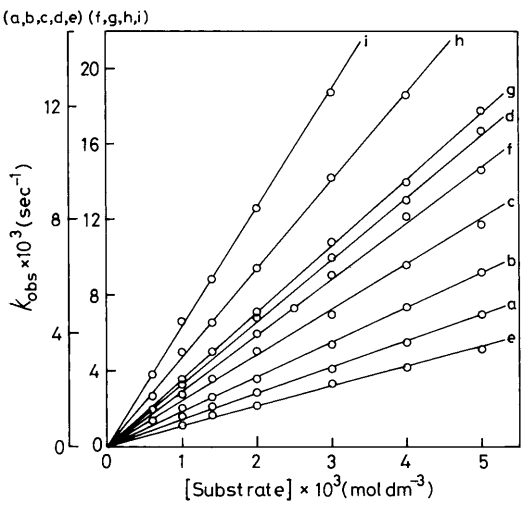


Fig. 1. Variation of the reaction rate constant with [substrate]. Plots of k_{obs} vs. [substrate] at [Au(III)] $= 3.0 \times 10^{-4}$ mol dm^{-3}, [Cl^-] $= 1.96 \times 10^{-3}$ mol dm^{-3} pH 3.72 and temperature 298 K. (a) D-Glucose; (b) D-ribose; (c) D-erythrose; (d) DL-glyceraldehyde; (e) D-glucose 1-phosphate; (f) D-glucose 6-phosphate; (g) D-ribose 5-phosphate; (h) D-erythrose 4-phosphate; (i) DL-glyceraldehyde 3-phosphate.

3. Results and discussion

Effect of reactant concentrations.—The reactions were studied at varying concentrations of Au(III) but at constant [substrate], [Cl^-], pH and temperature. The pseudo-first-order rate constant is independent of oxidant concentration in each reaction (Table 1).

The reactions were also studied at four different temperatures with variation of [substrate] from 0.6×10^{-3} to 5.0×10^{-3} mol dm^{-3}, keeping [Au(III)], [Cl^-] and pH constant at 3.0×10^{-4}, 1.96×10^{-3} mol dm^{-3} and 3.72, respectively. The plot of k_{obs} against [substrate] was found to be linear, passing through the origin at each temperature (Fig. 1), indicating that kinetic evidence for intermediate complex formation between the reactants is insignificant.

Effect of [H^+].—The rate of the reaction was studied at 298 K but at different pH values (3.42–4.45) using NaOAc–AcOH buffer while keeping [Au(III)], [substrate] and [Cl^-] constant. No attempt was made to keep ionic strength constant as the values of k_{obs} remain unchanged at different ionic strengths, $(0.3–2.0) \times 10^{-1}$ mol dm^{-3}, varied by the addition of sodium perchlorate. The oxidation rate decreases with an increase in [H^+]. The plot of k_{obs} versus 1/[H^+] is linear, making an intercept on the y-axis (Fig. 2).

Effect of [Cl^-].—The reaction was studied varying [NaCl] but at constant [Au(III)], [substrate], pH and temperature of 3×10^{-4}, 2×10^{-3} mol dm^{-3}, 3.72 and 298 K. The oxidation rate decreases with an increase of [Cl^-]. A plot of k_{obs} versus 1/[Cl^-] is linear making an intercept on the y-axis (Fig. 3).

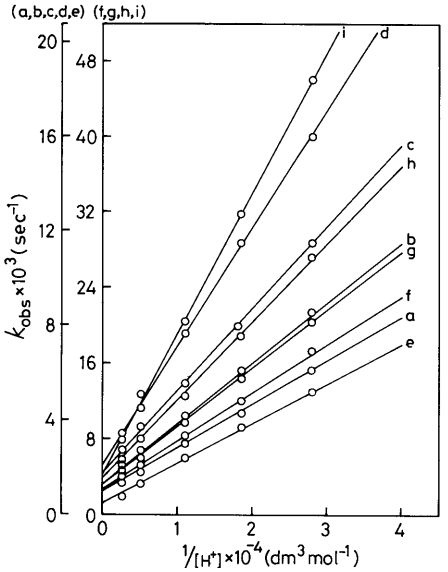


Fig. 2. Dependence of reaction rate constant on [H$^+$]. Plots of k_{obs} vs. 1/[H$^+$] at [substrate] = 2.0×10^{-3} mol dm^{-3}, [Au(III)] = 3.0×10^{-4} mol dm^{-3}, [Cl$^-$] = 1.96×10^{-3} mol dm^{-3} and temperature 298 K. (a) D-Glucose; (b) D-ribose; (c) D-erythrose; (d) DL-glyceraldehyde; (e) D-glucose 1-phosphate; (f) D-glucose 6-phosphate; (g) D-ribose 5-phosphate; (h) D-erythrose 4-phosphate; (i) DL-glyceraldehyde 3-phosphate.

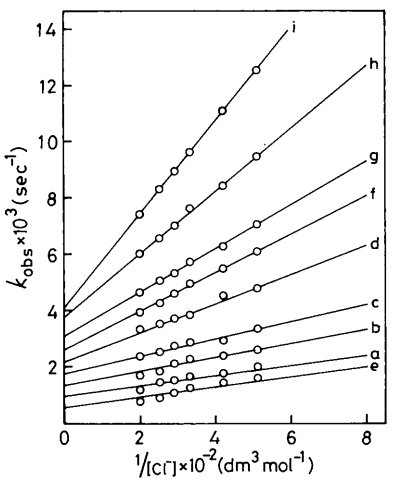


Fig. 3. Dependence of reaction rate constant on [Cl$^-$]. Plots of k_{obs} vs. 1/[Cl$^-$] at [substrate] = 2.0×10^{-3} mol dm^{-3}, [Au(III)] = 3.0×10^{-4} mol dm^{-3}, pH 3.72 and temperature 298 K. (a) D-Glucose; (b) D-ribose; (c) D-erythrose; (d) DL-glyceraldehyde; (e) D-glucose 1-phosphate; (f) D-glucose 6-phosphate; (g) D-ribose 5-phosphate; (h) D-erythrose 4-phosphate; (i) DL-glyceraldehyde 3-phosphate.

Activation parameters.—The second-order rate constants (k) for the oxidation of aldoses and sugar phosphates by gold(III) were determined at different temperatures. The enthalpy of activation ($\Delta H^{\neq}$) for the reactions were calculated from the plots of log (k/T) against ($1/T$) (Fig. 4), followed by entropy of activation ($\Delta S^{\neq}$) as mentioned in an earlier communication.[11,12] The activation parameters are recorded in Table 2.

The enthalpy of activation is linearly related with the entropy of activation[25] ($r = 0.9857$, Fig. 5) and the isokinetic temperature is 325 K. The isokinetic behaviour supported[26] by the linear plot of $\log k'$ versus $\log k$ ($r = 0.9794$), where k' and k are the second-order rate constants at the temperatures 298 and 293 K, respectively (Fig. 5). The isokinetic temperature was calculated from the relation $\beta = T_1T_2(1-f)/(T_1 - T_2f)$, where f is the slope of

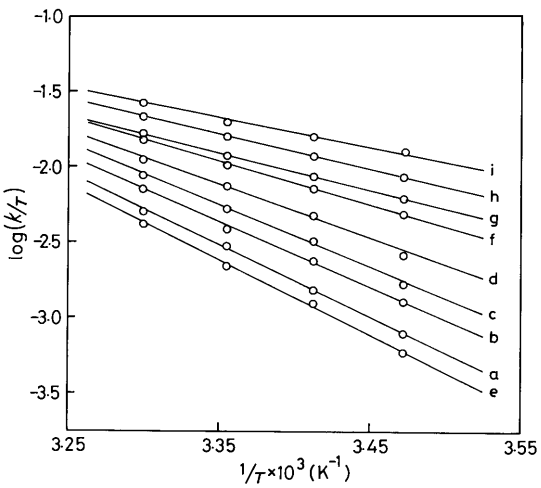


Fig. 4. Influence of temperature on second-order rate constant. Plots of log (k/T) vs. $1/T$. (a) D-Glucose; (b) D-ribose; (c) D-erythrose; (d) DL-glyceraldehyde; (e) D-glucose 1-phosphate; (f) D-glucose 6-phosphate, (g) D-ribose 5-phosphate, (h) D-erythrose 4-phosphate, (i) DL-glyceraldehyde 3-phosphate.

Table 2
Values of activation parameters of the oxidations of some aldoses and sugar phosphates

Substrate	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})
D-Glucose	88 ± 2	50 ± 7
D-Ribose	82 ± 2	32 ± 7
D-Erythrose	79 ± 3	23 ± 10
DL-Glyceraldehyde	67 ± 6	-14 ± 20
D-Glucose 1-phosphate	96 ± 4	73 ± 13
D-Glucose 6-phosphate	55 ± 3	-52 ± 10
D-Ribose 5-phosphate	46 ± 2	-80 ± 7
D-Erythrose 4-phosphate	43 ± 2	-86 ± 7
DL-Glyceraldehyde 3-phosphate	36 ± 2	-107 ± 7

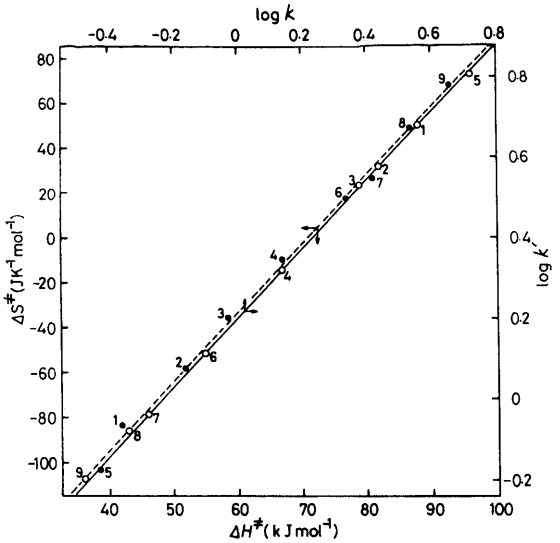


Fig. 5. Isokinetic plots for the oxidations of aldoses and aldoose phosphates by gold(III) in NaOAc–AcOH buffer medium. Plots of (i) $\Delta S^{\neq}$ vs. $\Delta H^{\neq}$ (ii) $\log k'$ vs. $\log k$. (1) D-Glucose; (2) D-ribose, (3) D-erythrose; (4) DL-glyceraldehyde; (5) D-glucose 1-phosphate; (6) D-glucose 6-phosphate; (7) D-ribose 5-phosphate; (8) D-erythrose 4-phosphate; (9) DL-glyceraldehyde 3-phosphate.

the Exner plot and β is 329 K. Since the value of β is above the experimental temperature (295), it can be concluded that enthalpy is a controlling factor[8] of the reaction.

Aldohexoses exist mainly in the pyranoid form,[27,28] whereas in aldopentoses the pyranoid form remains in equilibrium with the furanoid form. Though erythrose is known to exist in acyclic form,[29] literature evidence indicates that it can also exist in furanoid form.[30] In aqueous solution,[31] the composition of D-erythrose is 25% α-furanose, 63% β-furanose, ~2% aldehyde and 10% aldehydrol form. Again, crystalline form of DL-glyceraldehyde is dimeric with a 1,4-dioxane structure, but in aqueous solution it dissociates into the monomeric form, which remains in equilibrium with hydrated and nonhydrated forms. Since the concentration of water is constant, the proportions of aldehyde and hydrated form are also constant. Consequently, the reaction has been shown to occur between the hydrated form and oxidant.

Monosodium D-glucose 6-phosphate exists as a mononegative anion in aqueous solution, but under conditions of high acidity (2.5 mol dm^{-3}), it is rapidly protonated to yield D-glucose 6-phosphate (Robinson's ester), which exists mainly in the cyclic hemiacetal form. The apparent ionisation constants of D-glucose 6-phosphate are known.[32] The pK_a values (pK_{a1} 0.94, pK_{a2} 6.11) indicate that it exists preponderantly in the β-pyranose form, and the unusually strong ionisation of the first acidic hydrogen has been attributed[32] to the formation of a hydrogen bond[33] between the ring oxygen of the sugar moiety and the second acid hydrogen of the phosphate group.

Disodium D-ribose 5-phosphate exists as a dinegative anion in aqueous solution, but under highly acid conditions (2.5 mol dm^{-3}), fast diprotonation to yield D-ribose 5-phosphate is believed to occur, which also exists[34] mainly as the furanose form where intramolecular hydrogen bonding involving the ring oxygen atom and the phosphate group can occur. Because of intramolecular hydrogen bonding between HO-2 and O-1, the α anomer is expected to be the preponderant form.

D-glucopyranose 1-phosphate (pK_{a1} 1.10, pK_{a2} 6.13) suggests the formation of a hydrogen bond between the oxygen of the sugar moiety in the β configuration and the second acidic hydrogen atom of the phosphate group.[33] Again, D-glucopyranose 1,6-diphosphate practically does not undergo substantial oxidation under comparable conditions, indicating that C-1 and C-6 are the reactive sites. The reactive site of glucose 1-phosphate is believed to be C-6 since C-1 is blocked by the phosphate group.

Dilute solution of tetrachloroauric acid is known[35–37] to involve the following equilibria

$$HAuCl_4 \overset{K_1}{\rightleftharpoons} H^+ + AuCl_4^- \quad (2)$$

$$AuCl_4^- + H_2O \overset{K_2}{\rightleftharpoons} AuCl_3(OH_2) + Cl^- \quad (3)$$

$$AuCl_3(OH_2) \overset{K_3}{\rightleftharpoons} AuCl_3(OH)^- + H^+ \quad (4)$$

where K_1, K_2 and K_3 are 1.0, 9.5×10^{-6} and 0.25, respectively, at 298 K. Consequently four different species, viz. $HAuCl_4$, $AuCl_4^-$, $AuCl_3(OH)_2$ and $AuCl_3(OH)^-$, may oxidize the substrate under the present experimental conditions. $HAuCl_4$ dissociates to give H^+ and $AuCl_4^-$ in the pH range studied. But in a solution of $[H^+]$ of $\sim 10^{-4}$ mol dm^{-3}, $[HAuCl_4]$ is practically insignificant compared with $[AuCl_4^-]$, and further aquation of $AuCl_4^-$

may be prevented if the reactions occur at high [Cl^-] of 3×10^{-2} mol dm^{-3}, which has been noticed[38] in the oxidation of α-hydroxy compounds by gold(III). Since the present reactions have been studied at [Cl^-] of 1.96×10^{-3} mol dm^{-3}, it is suggested that all the three species, namely $AuCl_4^-$, $AuCl_3(OH_2)$ and $AuCl_3(OH)^-$ participate during the reaction. This is in keeping with the observations made earlier[39] in the oxidation of glycolaldehyde by gold(III). It may therefore be proposed that $AuCl_4^-$, $AuCl_3(OH_2)$ and $AuCl_3(OH^-)$ oxidize the substrates.

Gold(III) is known[36] to behave as a one- or two-electron transfer oxidant, depending upon the nature of the substrate and the experimental conditions. In the present investigation, the reaction mixture gave a polymeric suspension in the presence of acrylamide, indicating the involvement of free-radical intermediates during the reaction. The formation of unstable gold(II) as an intermediate has been predicted by a number of workers.[40–43] Consequently reduction of gold(III) to gold(I) in a one-step, two-electron process has been ignored. A free-radical intermediate may also be produced by the reaction between substrates with gold(I). However such a possibility has been ruled out, since neither colloidal gold nor any precipitate of gold(0) was detected under kinetic conditions. Therefore gold(II) appears to be more reactive than gold(I). The reaction steps involving substrates and different species of gold(III) may be shown as mentioned below (where $R = -(CHOH)_nCH_2OH$ and $n = 4$, 3, 2 and 1 for glucose, ribose, erythrose and glyceraldehyde, but $R = -(CHOH)_nCH_2OP(O)(OH)O^-$ when $n = 4$, 3, 2 and 1 for six-, five-, four- and three-membered rings, respectively).

$$RCHO + AuCl_4^- \xrightarrow[\text{slow}]{k_1} R\text{–}\dot{C}{=}O + AuCl_4^{2-} + H^+ \quad (5)$$

$$R\text{–}\dot{C}{=}O + AuCl_4^- \xrightarrow[\text{followed by hydrolysis}]{\text{electron transfer}} RCO_2H + AuCl_4^{2-} + H^+ \quad (6)$$

$$RCHO + AuCl_3(OH)_2 \xrightarrow[\text{slow}]{k_2} R\text{–}\dot{C}{=}O + AuCl_3(OH_2)^- + H^+ \quad (7)$$

$$R\text{–}\dot{C}{=}O + AuCl_3(OH_2) \xrightarrow[\text{followed by hydrolysis}]{\text{electron transfer}} RCO_2H + AuCl_3(OH_2)^- + H^+ \quad (8)$$

$$RCHO + AuCl_3(OH)^- \xrightarrow[\text{slow}]{k_3} R\text{–}\dot{C}{=}O + AuCl_3(OH)^{2-} + H^+ \quad (9)$$

$$R\text{–}\dot{C}{=}O + AuCl_3(OH)^- \xrightarrow[\text{followed by hydrolysis}]{\text{electron transfer}} RCO_2H + AuCl_3(OH)^{2-} + H^+ \quad (10)$$

Au(II) undergoes fast disproportionation into Au(I) and Au(III).

$$2\,AuCl_4^{2-} \xrightarrow{\text{fast}} AuCl_2^- + AuCl_4^- + 2\,Cl^- \quad (11)$$

$$2\,AuCl_3(OH_2)^- \xrightarrow{\text{fast}} AuCl_2^- + AuCl_4^- + 2\,H_2O \quad (12)$$

$$2\,AuCl_3(OH_2)^{2-} + 2\,H^+ \xrightarrow{\text{fast}} AuCl_2^- + AuCl_4^- + 2\,H_2O \quad (13)$$

According to the suggested mechanism, the rate of disappearance of [Au(III)] may be expressed as

$$-\mathrm{d[Au(III)]}/\mathrm{d}t = \{k_1[AuCl_4^-] + k_2[AuCl_3(OH_2)] + k_3[AuCl_3(OH)^-]\}\ [S] \quad (14)$$

If $C_0 = [Au(III)]$, $x = [AuCl_3(OH_2)]$ and $y = [AuCl_3(OH)^-]$, Eq. (14) may be written as

$$-\mathrm{d[Au(III)]_t}/\mathrm{d}t = \{k_1C_0 + (k_2 - k_1)x + (k_3 - k_1)y\}\ [S] \quad (15)$$

Again, the value of K_2 indicates that $C_0 \gg x,y$, so that

$$K_2 = \frac{x[Cl^-]}{C_0 - x\text{-}y} \approx \frac{x[Cl^-]}{C_0}$$

$$\therefore\ x = \frac{K_2C_0}{[Cl^-]}$$

and

$$K_3 = \frac{y[H^+][Cl^-]}{K_2C_0} \quad \text{or} \quad y = \frac{K_2K_3C_0}{[H^+][Cl^-]}$$

Substitution of x and y in Eq. (15) gives

Table 3
Rate-determining steps for the oxidations of the aldoses and sugar phosphates by different gold(III) species at 298 K [a]

Substrate	k_1 (dm^3 mol^{-1} s^{-1})	k_2 (dm^3 mol^{-1} s^{-1})	k_3 (dm^3 mol^{-1} s^{-1})
D-Glucose	0.467	0.494	0.543
D-Ribose	0.667	0.694	0.770
D-Erythrose	0.867	0.935	1.00
DL-Glyceraldehyde	1.067	1.13	1.27
D-Glucose 1-phosphate	0.266	0.294	0.337
D-Glucose 6-phosphate	1.30	1.50	1.52
D-Ribose 5-phosphate	1.53	1.74	1.80
D-Erythrose 4-phosphate	1.86	2.17	2.25
DL-Glyceraldehyde 3-phosphate	2.03	2.44	2.61

[a] [Au(III)] = 3.0×10^{-4} mol dm^{-3}, [substrate] = 2.0×10^{-3} mol dm^{-3}, [Cl$^-$] = 1.96×10^{-3} mol dm^{-3} pH 3.72.

$$k_{obs} = -\frac{1}{[Au(III)]}\frac{d[Au(III)]}{dt} = \left\{k_1 + \frac{(k_2-k_1)K_2}{[Cl^-]} + \frac{(k_3-k_1)K_2K_3}{[Cl^-]}.\frac{1}{[H^+]}\right\} \times [S] \quad (16)$$

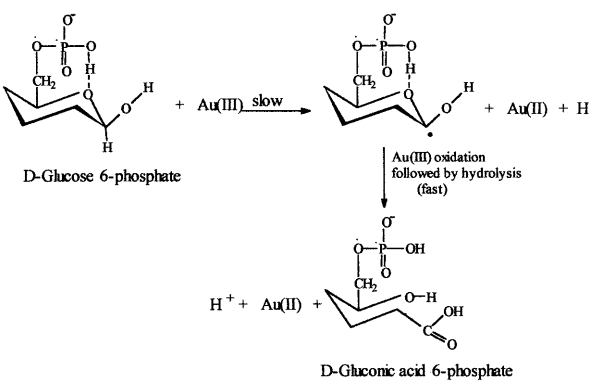
Eq. (16) predicts a linear plot of k_{obs} against [S] passing through the origin at constant [Au(III)], [H$^+$] and [Cl$^-$]. This has been verified experimentally (Fig. 1). Eq. (16) further indicates that the addition of Cl$^-$ decreases the concentrations of $AuCl_3(OH_2)$ and $AuCl_3(OH)^-$, thereby increasing the concentration of the less reactive species, $AuCl_4^-$, and, hence, the retarding effect of the Cl$^-$ ion on the reaction rate. From the linear plot of k_{obs} against 1/[Cl$^-$] at a constant temperature and from the intercept of the plot (Fig. 3), the values of k_1 at 298 K for different substrates were evaluated (Table 3).

The reactions are inhibited by H$^+$ ions at a constant [Cl$^-$], indicating the fact that $AuCl_3(OH)^-$ is the most reactive amongst different Au(III) species. The linear plot of k_{obs} versus 1/[H$^+$] at 298 K (Fig. 2) conforms to Eq. (16)). From the intercept and slope of the straight line and using the value of k_1 obtained earlier, the values of k_2 and k_3 have been evaluated at 298 K (Table 3). Of the three different gold(III) species, $AuCl_3(OH)^-$ appears to be the most reactive species, and $AuCl_4^-$ is the least reactive species. Reactivity of $AuCl_3(OH_2)$ lies between these two species, in keeping with the observation made earlier.[44] Substituting the values of k_1, k_2 and k_3 into Eq. (16) the values of k_{obs} were calculated under different experimental conditions. The calculated and experimental values (Table 4), which are not widely different, justify the involvement of three different gold(III) species in the reactions with sugars and sugar phosphates.

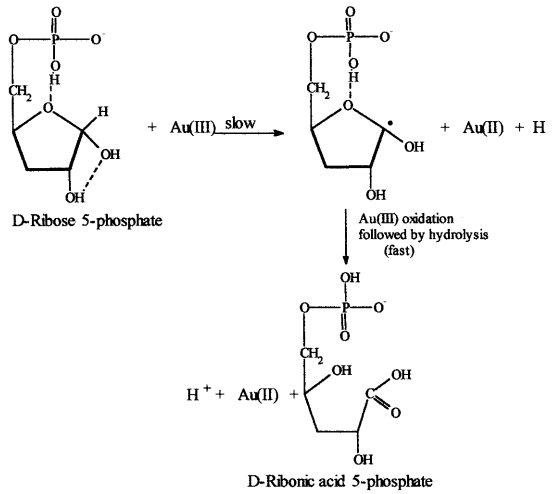
Table 4
Measured and calculated pseudo-first-order rate constants of the oxidations of some aldoses and sugar phosphates by gold(III) at 298 K [a]

Substrate	$k_{obs}\times10^{-3}$ (s^{-1})	$k_{cal}\times10^{-3}$ (s^{-1})
D-Glucose	1.87	1.90
D-Ribose	2.45	2.65
D-Erythrose	3.39	3.46
DL-Glyceraldehyde	4.59	4.72
D-Glucose 1-phosphate	1.46	1.43
D-Glucose 6-phosphate	5.98	5.41
D-Ribose 5-phosphate	7.02	6.42
D-Erythrose 4-phosphate	9.39	8.63
DL-Glyceraldehyde 3-phosphate	12.3	11.4

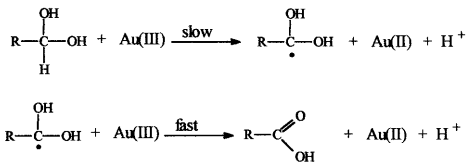
[a] [Au(III)] = 3.0×10^{-4} mol dm^{-3}, [substrate] = 2.0×10^{-3} mol dm^{-3}, [Cl$^-$] = 1.96×10^{-3} mol dm^{-3} pH 3.72.



Scheme 1.



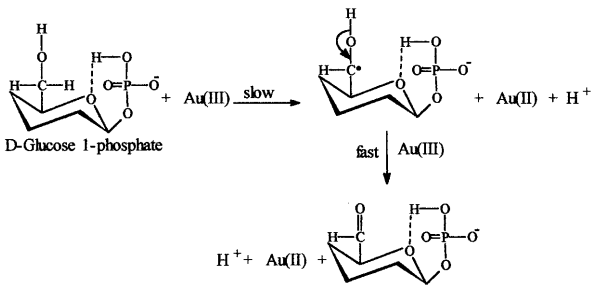
Scheme 2.



R=–(CHOH)$_2$CH$_2$OP(O)(OH)O$^-$ for D-erythrose 4-phosphate

R=–CHOHCH$_2$OP(O)(OH)O$^-$ for DL-glyceraldehyde 3-phosphate

Scheme 3.



Scheme 4.

The electron transfer from the aldoses to the oxidant leading to the formation of aldonic acids have been shown earlier.[11] The reaction steps involving sugar phosphates leading to the formation of products of oxidation in cyclic and acyclic sugar phosphates are shown in Schemes 1–4.

The results of the oxidation of aldose and aldose phosphates by gold(III) under comparable conditions are shown in the Table 1. The plots of $\log k_{obs}$ verses 'n' where (n = asymmetric centre) are linear with slopes of 0.13 and 0.11, respectively. The reactions follow the order: D-glyceraldehyde > D-erythrose > D-ribose > D-glucose. On the other hand, the sugar phosphates react with gold(III) at a faster rate than the parent sugars, except for glucose 1-phosphate, which reacts at slower rate than glucose, thereby indicating that sugars are not stronger ligands for gold(III) in comparison with sugar phosphates. The aldose and aldose phosphates (except glucose 1-phosphate) are oxidized to give aldonic acids and phosphoaldonic acids by similar mechanisms. The reaction product obtained in the oxidation of glucose 6-phosphate failed to give any 2,4-DNP derivative, indicating that C-2, C-3 and C-4 are unreactive towards gold(III) under the kinetic conditions of these experiments. On the other hand, when C-1 is blocked by phosphate group, the oxidation product gave a 2,4-DNP derivative. The higher rate of oxidation of glucose 6-phosphate than glucose 1-phosphate is to be expected since C-1 has a potential –CHO group whereas C-6 possesses a –CH_2OH group. Thus the oxygen atom of the ring exerts a $-I$ effect,[45] which is more pronounced on the nearer C-1 position than that at C-6.

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