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Note

Kinetics of oxidation of D-glucose 6-phosphate by hexachloroiridate(IV) and tetrachloroaurate(III)

KALYAN KALI SENGUPTA*, UMA CHATTERJEE,
Department of Chemistry, Jadavpur University, Calcutta-700032 (India)

AND SAMARENDRA NATH BASU
Department of Chemistry, Ashutosh College, Calcutta-700026 (India)

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The kinetics of the oxidation of D-glucose by some metal-ion oxidants[1-3] have been reported, but no data are available on such oxidations of D-glucose 6-phosphate. The oxidation of D-glucose 6-phosphate by iridium(IV) and gold(III) is now reported.

The reactions were studied at various $[\text{iridium(IV)}]_o$ or $[\text{gold(III)}]_o$, but at constant $[\text{substrate}]_o$, $[\text{acid}]_o$, and temperature. The pseudo-first-order rate constant is independent of $[\text{oxidant}]_o$. The double reciprocal plots (Fig. 1) indicate that the reaction between D-glucose 6-phosphate and iridium(IV) takes place through a 1:1 intermediate-complex. At higher concentrations (>mM) of substrate, the rate of the reaction decreases in the oxidation by iridium(IV). This may be due to the fact that more than one substrate molecule complexes with a metal ion and one of the complexes resists oxidation. The results plotted in Fig. 2*a*, on the other hand, indicate that the order with respect to D-glucose 6-phosphate is one for oxidations by gold(III).

The effect of variation of pH (3.72–4.63) on the rate of reaction was studied at 50° with $[\text{Ir(IV)}]_o = 50\ \mu\text{M}$, $[\text{substrate}]_o = 100\ \mu\text{M}$, and $\mu = 0.1\text{M}$. The rate of oxidation of D-glucose 6-phosphate increased with the increase in pH, and the slope of the log k_{obs} against pH plot is 0.3. The variation of hydrogen ion concentration (by the addition of HCl) did not influence the pseudo-first-order rate constant in the pH range (1.0–1.7) for the other reaction.

The reaction rate was enhanced considerably when sodium chloride was added to the reaction mixture having fixed $[\text{D-glucose 6-phosphate}]_o$, $[\text{iridium(IV)}]_o$, $[\text{acid}]_o$, and temperature. The pseudo-first-order rate constant increased to the extent of 172% in 0.3MNaCl. The reaction rate, on the other hand,

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*To whom all correspondence should be addressed.

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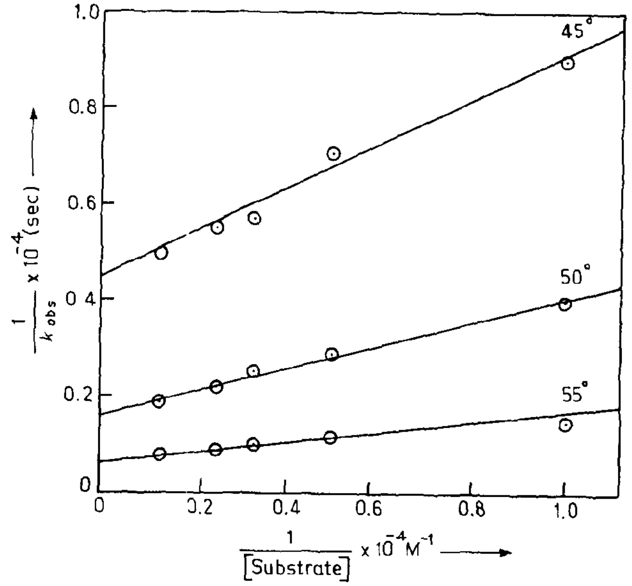


Fig. 1. Oxidation of D-glucose 6-phosphate by iridium(IV). Plots of $1/k_{obs}$ against 1/[substrate] at different temperatures. $[Ir(IV)] = 50\mu M$; pH = 4.63.

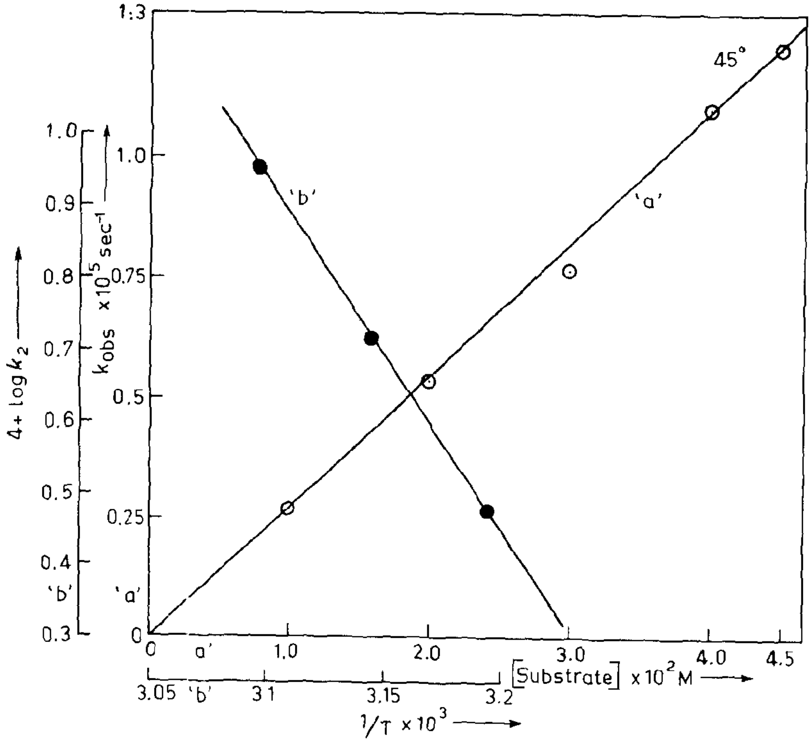


Fig. 2. Oxidation of D-glucose 6-phosphate by gold(III). (*a*) Plot of k_{obs} against [substrate]. (*b*) Plot of $\log k_2$ against $1/T$. $[Au(III)] = 251\mu M$; pH = 2.0.

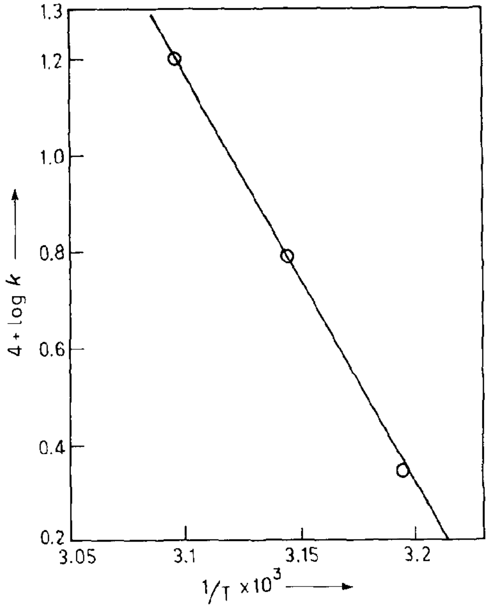


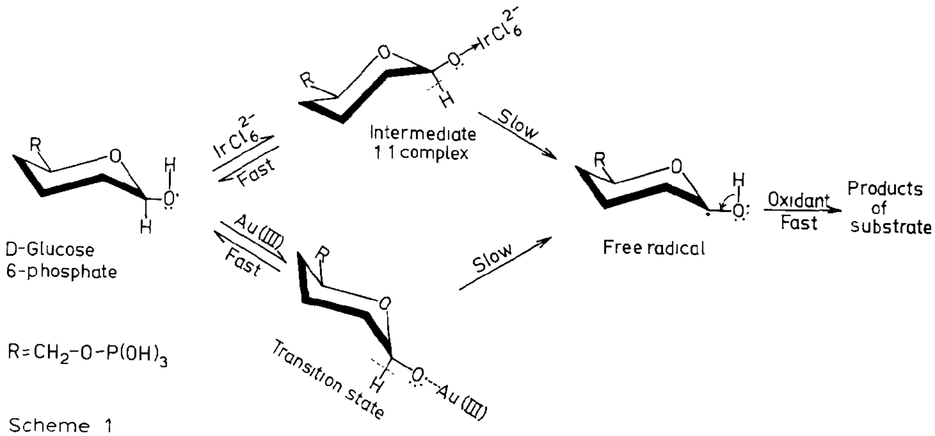
Fig. 3. Influence of temperature on the rate of oxidation of D-glucose 6-phosphate by iridium(IV). Plot of log k against 1/T.

was independent of sodium chloride concentration (≤M) when the substrate was oxidised by gold(III).

The values of k (disproportionation constant) for the former reaction were obtained from the intercepts of the double reciprocal plots (Fig. 1). The value of k_2 (average of 4–5 determinations) at different temperatures were used to calculate the activation energy for the other reaction. The values of E_a (calculated from Fig. 3) and $\Delta S^{\ddagger}$ are 162.8 kJ.mol^{-1} and 206.6 J.K^{-1}.mol^{-1}, respectively, for the former reaction. The corresponding values for the other reaction are 76.0 kJ.mol^{-1} (calculated from Fig. 2*b*) and −81.3 J.K^{-1}.mol^{-1}, respectively.

The reaction has been studied in the pH range 3.72–4.63. Consequently the chances of protonation of the ethereal oxygen and the hydroxyl groups are remote, and the reactive form of the substrate[4,5] is believed to be unprotonated. Hexachloroiridate(IV), which is fairly stable, reacts with the substrate[6,7].

The oxidation of D-glucose 6-phosphate by hexachloroiridate(IV) seems to proceed *via* the formation of an unstable 1:1 intermediate-complex. The exact nature of the complex cannot be determined on the basis of the present data. It is possible that a chlorine atom from the chloro complex of iridium(IV) acts as a bridge between iridium(IV) and a hydroxyl group of the substrate, but the formation of an unstable 1:1 seven-co-ordinated complex[8] cannot be totally ruled out. The formation of the complex is corroborated by kinetic evidence. The complex decomposes by rupture of the C-H bond of H-C-OH, rather than the O-H bond, as evidenced in the oxidation of secondary alcohols by such one-electron-transfer oxidants[9] as



Scheme 1

vanadium(V), cerium(IV), and iridium(IV), to give free radicals (shown by the positive polymerisation test with acrylamide). The free radical then undergoes fast oxidation by another unit of iridium(IV) to yield lactones (see Scheme 1).

It has been shown[10,11] that $HAuCl_4$ remains in equilibrium with H^+ and $AuCl_4^-$ in acid solution. Since the rate of oxidation is independent of added Cl^-, further aquation of $AuCl_4^-$ to give $AuCl_3(H_2O)$ and Cl^- does not occur. The absence of an effect of $[H^+]$ on k_{obs} indicates that both species of Au(III), *viz.*, $HAuCl_4$ and $AuCl_4^-$, have the same kinetic properties. D-Glucose 6-phosphate forms a "transition state" with gold(III). The transition state then decomposes slowly into a free-radical intermediate and gold(II). The formation of the free radical is substantiated by the formation of a polymeric suspension when acrylamide was added to the reaction mixture. The transient free-radical is then further oxidised by another unit of gold(III) in a fast step to give products (Scheme 1). The gold(II) formed disproportionates[12] to form gold(I) and gold(III).

Unlike the present reactions, the oxidations of D-glucose by these metal ions[3] were studied at much higher concentrations (0.2–1.0M) of substrate, since they were too slow to be studied at much lower concentrations (<10mM) of substrate. The presence of a bulkier group at C-5 gives rise to greater non-bonded interactions with the reactive group of the intermediate, thus making the intermediate more unstable and consequently highly reactive. This is probably the reason for the higher rate of oxidation with D-glucose 6-phosphate by these metal ions.

EXPERIMENTAL

All kinetic studies were carried out under pseudo-first-order conditions, with concentrations of D-glucose 6-phosphate (Sigma) in large excess over that of oxidant. The reactions were followed spectrophotometrically, using a Perkin–Elmer spectrophotometer (digital), as described earlier[3]. The oxidation of D-glucose 6-phosphate by iridium(IV) was studied in sodium acetate–acetic acid buffer, and that by gold(III) in hydrochloric acid. The pseudo-first-order rate constants (k_{obs}) were calculated as usual, and the reproducibility was better than ±5%.

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