

KINETICS OF OXIDATION OF D-GLUCOSE BY HEXACHLORO- IRIDATE(IV) AND TETRACHLOROAUROATE(III)

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ABSTRACT

Kinetic data for the oxidation of D-glucose by hexachloroiridate(IV) and tetrachloroaurate(III) are reported. The reactions have been studied spectrophotometrically over a wide range of experimental conditions. The activation parameters have been calculated and mechanisms are suggested.

INTRODUCTION

The kinetics of oxidation of some monosaccharides have been studied both in acidic¹⁻³ and alkaline media⁴. In some cases, the mechanistic approach was based on the formation of intermediate complexes; in other cases, the results were interpreted on the basis of the formation of free radicals. This suggests that the mechanism may depend on the nature of the oxidant and the substrate. The kinetics of oxidation of some organic compounds by hexachloroiridate(IV)⁵ and tetrachloroaurate(III)⁶ have been studied; iridium(IV) behaves as a one-electron-transfer oxidant and there is evidence⁷ to indicate that gold(III) also behaves in this way, although a two-electron reduction cannot be totally ruled out. The present investigation was undertaken in order to clarify the mechanism of oxidation of D-glucose by these oxidants.

EXPERIMENTAL

Reagents. — Sodium chloroiridate was used to prepare iridium(IV) solutions which were standardised spectrophotometrically⁸. Solutions of gold(III) were prepared from chloroauric acid and their concentrations were determined gravimetrically⁹ by the oxalic acid method; the solutions were stored in the dark and used in subdued light. All other reagents were of the highest purity available and the solu-

tions were prepared in doubly distilled water (second distillation from permanganate).

The oxidation of D-glucose by iridium(IV) was carried out in sodium acetate-acetic acid buffer, whereas that by gold(III) was studied in hydrochloric acid.

Absorption spectra of iridium(IV) and gold(III) solutions. — The absorption spectra of solutions of iridium(IV) were recorded in the visible region. The values λ_{\max} 488 nm (ϵ 4050) and λ_{\min} 460 nm accorded with literature values⁸. The IrCl_6^{3-} ion, or its hydrolysed product $\text{Ir}(\text{OH})_2\text{Cl}_4^-$ ion, does not absorb⁸ in the region of maximum absorption of IrCl_6^{3-} . The absorption spectra of solutions of gold(III) in 0.1–2.0M hydrochloric acid in the concentration range 25–150 μM were recorded in the u.v. region and showed two strong bands [227 (ϵ 35,750) and 315 nm (ϵ 5,400)]. The spectral pattern remained unaltered with changes in the concentration of gold(III). Beer's law was valid for both λ_{\max} absorptions.

Kinetic measurements. — The kinetic studies were carried out under pseudo-first-order conditions with the concentration of D-glucose in large excess compared to that of each oxidant. The reactions were studied spectrophotometrically at 488 or 315 nm as appropriate, using a Perkin-Elmer spectrophotometer (digital) equipped with a thermostatic cell compartment. Requisite volumes of the reactants at the appropriate temperature were mixed and the mixture was immediately transferred to a cell having a path length of 1 cm. The rate of decrease of iridium(IV) or gold(III) was followed for at least two half-lives. Pseudo-first-order rate constants (k_{obs}) were calculated in the usual manner. The maximum error in the measurement of rate constants was ± 1 –5%, depending upon the experimental conditions. However, for most experiments, duplicate measurements were reproducible to within $\pm 3\%$.

Identification of reaction products. — The oxidation products of D-glucose were identified by t.l.c. on silica gel G with 1-butanol-acetic acid-water¹⁰. Comparison with the products of the oxidation of D-glucose with bromine water and those with iridium(IV) or gold(III) indicated that gluconic acid (R_F 0.38) and lactones (R_F 0.70) were formed.

Polymerisation test. — When aqueous 40% acrylamide was added to the various reaction mixtures, the viscosity of the resulting solutions was greatly increased and polyacrylamide could be precipitated by the addition of methanol or 1,4-dioxane. The results indicated that free radicals were formed during the reaction. Blank experiments, in which either D-glucose or metal ion was excluded, gave no polymers.

RESULTS

Effect of variation of reactant concentrations. — The reaction was studied at various [oxidant], but at constant [D-glucose], acidity, and temperature. The pseudo-first-order rate constant (k_{obs}) was independent of initial [iridium(IV)] or [gold(III)], suggesting that the reaction is first order with respect to each [oxidant].

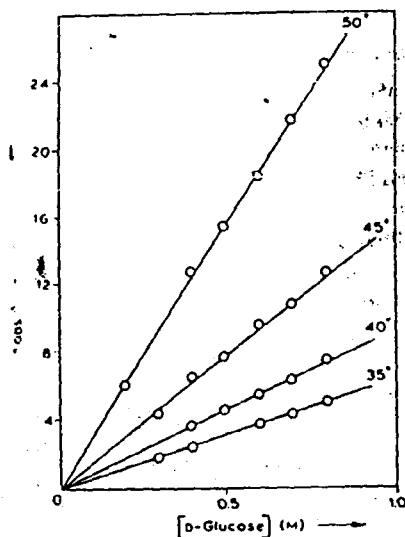


Fig. 1. Oxidation of D-glucose by iridium(IV). Plots of pseudo-first-order rate constants against [D-glucose] at various temperatures: [Ir(IV)] 152 μM, pH 4.63.

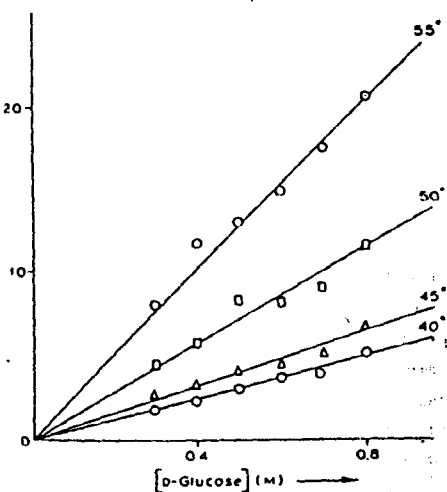


Fig. 2. Oxidation of D-glucose by gold(III). Plots of pseudo-first-order rate constants against [D-glucose] at various temperatures: [Au(III)] 251 μM, pH 2.0.

The plots of the pseudo-first-order rate constants against the concentration of D-glucose are linear and pass through the origin for both reactions (Figs. 1 and 2). The order with respect to the concentration of D-glucose is one in each case.

Effect of variation of pH. — The effect of pH on the rate of reaction was

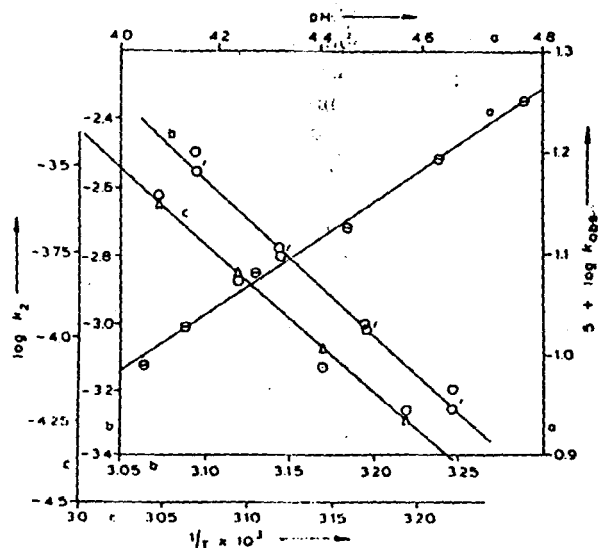


Fig. 3. (a) Effect of pH on the pseudo-first-order rate constants when iridium(IV) was used as oxidant: $[\text{Ir(IV)}] 152\mu\text{M}$, $[\text{D-glucose}] 0.2\text{M}$, 40° . (b) Variation of second-order rate constant with temperature for the oxidation of D-glucose by iridium(IV). Plot of $\log k_2$ against $1/T$: \circ , experimental points; \circ' , least-squares points. (c) Variation of second-order rate constant with temperature for the oxidation of D-glucose by gold(III). Plot of $\log k_2$ against $1/T$: \circ , experimental points; \triangle , least-squares points.

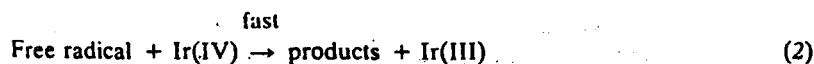
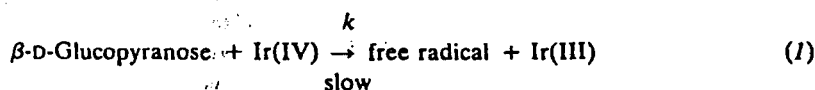
studied at 40° with $[\text{Ir(IV)}] 152\mu\text{M}$, $[\text{D-glucose}] 0.2\text{M}$, and $\mu 0.12\text{M}$. The pH of the reaction mixture was varied in the region 4.05–4.80. The rate of oxidation of D-glucose increased with increase in pH. The plot of $\log k_{obs}$ against pH was linear (Fig. 3) and the slope was 0.3. The pH of the gold(III) oxidations was varied by the addition of HCl. The reactions were carried out at $[\text{Au(III)}]$, $[\text{D-glucose}]$, and temperature values of $1.25\mu\text{M}$, 0.8M , and 50° , respectively. The added hydrogen ions did not influence the pseudo-first-order rate constant in the pH range 0.5–1.0.

Effect of variation of sodium chloride concentrations. — The reaction rate was enhanced considerably when sodium chloride was added to the reaction mixture containing D-glucose and iridium(IV), e.g., 50% in 0.4M salt. The rate of reaction was independent of NaCl concentration for oxidations with gold(III).

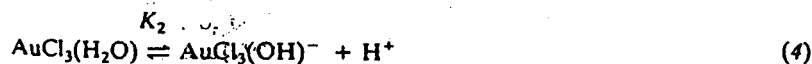
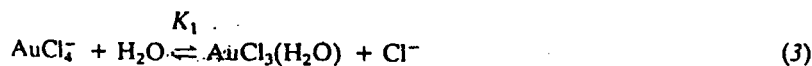
Effect of variation of temperature and activation parameters. — The values of second-order rate constants (k_2) at various temperatures were obtained from the slopes of plots of k_{obs} vs. $[\text{D-glucose}]$. The Arrhenius energy of activation was evaluated from the least-squares plot of $\log k_2$ against $1/T$ (Fig. 3). The values of E_a and ΔS^\ddagger for the oxidation of D-glucose by iridium(IV) were $88.7\text{ kJ}\cdot\text{mol}^{-1}$ and $-38.9\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively. The corresponding values for the oxidations with gold(III) were $84.6\text{ kJ}\cdot\text{mol}^{-1}$ and $-65.3\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

DISCUSSIONS

In aqueous solution, D-glucose exists mainly as cyclic hemiacetals² with only a small proportion of the aldehydo form. It has been suggested³ that it is the cyclic hemiacetal form rather than the aldehydo form which reacts with the oxidant. Moreover, the ⁴C₁ pyranoid form of D-glucose preponderates in aqueous solution and the β anomer (HQ-1 equatorial) is readily attacked by the oxidants. Hexachloroiridate(IV) is known to be stable¹¹ towards substitution or hydrolysis over a wide range of acidities. A study of the photochemical behaviour¹² of IrCl₆²⁻ in solution indicated that irradiation at 254 and 360 nm effected only the aquation reaction to give IrCl₅(H₂O)⁻. The photoreaction of IrCl₆²⁻ takes place¹² at high concentrations of both iridium(IV) and HCl. Moreover, the spectral pattern of hexachloroiridate(IV) remains unaltered with change in concentration of iridium(IV) in the range 28.3–242 μM. Thus, it is IrCl₆²⁻, and not IrCl₅(H₂O)⁻, which oxidises D-glucose. The increase in reaction rate with the increase in ionic strength could be consistent with the proposed mechanism involving a neutral molecule and an ion³. In oxidations¹³ by cerium(IV), D-glucose is converted into D-arabinose and formic acid. However, a negative chromotropic acid test indicated that formic acid was not formed in the present reaction. Therefore, it is suggested that the β-alldopyranose reacts with iridium(IV) to give an intermediate free-radical and iridium(III), and that the free radical reacts rapidly with another iridium(IV) to give gluconic acid and its lactones as follows.

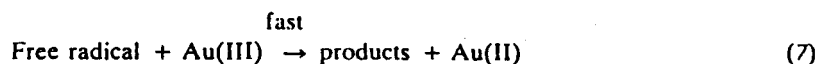
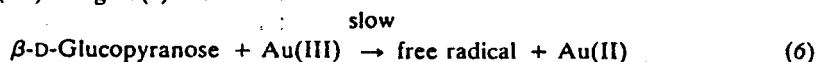


Halides of Au(III) which are soluble in water are partially hydrolysed¹⁴ to AuCl₃(OH)⁻ species at lower acidities. The rate of hydrolysis of tetrachloroaurate(III) in aqueous solution at chloride and hydrogen ion concentrations of 0.05–0.5M and 0.11–1.26 μM, respectively, has been studied¹⁵ and is as follows.



The dissociation constants K_1 and K_2 for the steps 3 and 4 are 9.5 μM and 0.25M at 25°, respectively. Since most of the reactions were carried out at [Cl⁻] 0.1M, it is

likely that the extent of aquation of AuCl_4^- would be small. Again, if $\text{AuCl}_3(\text{H}_2\text{O})$ were the reacting species in the present study, the rate would have depended on $[\text{Cl}^-]$. In the presence of various $[\text{Cl}^-]$, the change in the pseudo-first-order rate constant was insignificant, indicating that $\text{AuCl}_3(\text{H}_2\text{O})$ does not react with D-glucose. In HCl medium, AuCl_4^- or its protonated species HAuCl_4 reacts⁷ with some inorganic compounds, and HAuCl_4 remains in equilibrium with H^+ and AuCl_4^- in the hydrochloric acid medium. Since, in the present work, no H^+ dependence was found, both HAuCl_4 and AuCl_4^- appear to have the same kinetic properties. However, gold(III) reacts with D-glucose to give an intermediate free-radical and is reduced to gold(II). The free radical reacts with another gold(III) and, by a fast step, gives the products of reaction and gold(II). The latter disproportionates to give gold(III) and gold(I) as follows.



Methyl α - and β -D-glucopyranosides were oxidised by iridium(IV) and gold(III), with the latter reacting more rapidly, but gluconic acid or its lactones were not formed. It is possible that oxidation occurred at position 6 of these glycosides.

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