

Kinetics & Mechanism of Osmium Tetroxide Catalysed Oxidation of Benzylphenylglycollic Acids by Alkaline Hexacyanoferrate (III)

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The kinetics of osmium tetroxide catalysed oxidation of benzylphenylglycollic acid and four substituted benzylphenylglycollic acids by alkaline hexacyanoferrate (III) have been studied in 30% (v/v) *t*-butanol-water mixture at a constant ionic strength. The reaction is found to be first order each in [substrate], [Os(VIII)] and [OH⁻] ([OH⁻] < 0.02 mol dm⁻³) but independent of [hexacyanoferrate (III)]. The rates of reaction decrease with decrease in dielectric constant and increase with increase in ionic strength of the medium. The entropy of activation is found to be negative. The mechanism involves the formation of an intermediate complex between the acid anion and Os(VIII) which rapidly decomposes followed by a fast reaction between the reduced osmium species and hexacyanoferrate (III).

In continuation of our earlier work on the kinetics of osmium tetroxide catalysed oxidation of chalcones¹ and pyridinium salts² by alkaline hexacyanoferrate (III), we report herein the kinetics of osmium tetroxide catalysed oxidation of benzylphenylglycollic acids by alkaline hexacyanoferrate (III). In the absence of the catalyst, the reaction is extremely slow or does not proceed at all.

Materials and Methods

Benzylphenylglycollic acids (BPGAs) were prepared and purified by the literature methods³. *t*-Butanol, hexacyanoferrate (III), potassium chloride and potassium hydroxide were of AR (BDH) grade. The solution of osmium tetroxide (0.004 mol dm⁻³) was prepared by dissolving known weight of OsO₄ (Johnson & Mathey) in KOH solution (0.05 mol dm⁻³). Ionic strength was adjusted with potassium chloride.

Kinetic measurements

Reaction mixture containing the requisite quantities of benzylphenylglycollic acid (BPGA), OsO₄ and KOH, and a solution of hexacyanoferrate (III) were thermally equilibrated separately for about 30 min at 30°C. A known volume of hexacyanoferrate (III) was then transferred to the reaction mixture and aliquots were removed at regular time intervals and the amount of hexacyanoferrate (II) formed during the reaction was estimated by titrating against a standard solution of ceric salt using ferroin as an indicator. The standard zero order rate constants (k_0) reported are average values of duplicate runs. No oxidation of the solvent occurred under the condition employed.

Stoichiometry

Stoichiometric investigation, carried out using a known excess of hexacyanoferrate (III) at 30°C, showed that 1 mol of benzylphenylglycollic acid required 2 mol of hexacyanoferrate (III) to give deoxybenzoin as the final product of oxidation. The product was characterised by direct comparison (m.m.p.) with an authentic sample of deoxybenzoin and by its IR data; m.p. and m.m.p. 58°.

Results and Discussion

The reaction is zero order in [hexacyanoferrate (III)] as shown by the constant values of k_0 over a ten-fold variation of [hexacyanoferrate (III)]. For example under the conditions [BPGA] = 5×10^{-3} mol dm⁻³, [OH⁻] = 2×10^{-2} mol dm⁻³, [OsO₄] = 1.55×10^{-7} mol dm⁻³, $\mu = 0.1$ mol dm⁻³ and temp. = 30°C, $k_0 \times 10^5$ remained constant at 12.20 ± 0.2 mol dm⁻³ min⁻¹ when [hexacyanoferrate (III)] was varied from 0.5×10^3 to 5×10^3 mol dm⁻³. The values of k_0 /[BPGA] and k_0 /[Os(VIII)] were found to be fairly constant showing first order dependence each on [BPGA] and [Os(VIII)]. At low [OH⁻] (< 0.02 mol dm⁻³) the reaction is first order in [OH⁻]. However, it becomes zero order at [OH⁻] > 0.02 mol dm⁻³.

Increase in ionic strength increases the rate constant. For example under the conditions [hexacyanoferrate (III)] = 1×10^{-3} mol dm⁻³, [4-methoxyBPGA] = 5×10^{-3} mol dm⁻³, [OsO₄] = 1.5×10^{-7} mol dm⁻³ and temp. = 30°C, $k_0 \times 10^5$ increased from 0.20 to 6.55 mol dm⁻³ min⁻¹ when ionic strength was changed from 0.02 to 0.2 mol dm⁻³. The plot of $\log k_0$

Table 1—Reaction Rates and Arrhenius Parameters for the Alkaline Hexacyanoferrate(III) Oxidation of BPGA in *t*-Butanol Water Mixture

{[Hexacyanoferrate (III)] = 1.0×10^{-3} mol dm $^{-3}$; [OH $^{-}$] = 2.0×10^{-2} mol dm $^{-3}$; [substrate] = 5.0×10^{-3} mol dm $^{-3}$; μ = 0.1 mol dm $^{-3}$; solvent = 30% (V/V); *t*-butanol}

Substrate	$k_0 \times 10^5$ mol dm $^{-3}$ min $^{-1}$			E_a (kJ mol $^{-1}$)	ΔS^\ddagger (J mol $^{-1}$ K $^{-1}$)	ΔH^\ddagger (kJ mol $^{-1}$)
	30°	35°	40°			
4-OCH $_3$	18.3	28.5	39.5	32.74	214.70	30.15
4-CH $_3$	15.9	23.3	32.8	28.85	229.14	26.26
H	12.2	19.5	26.5	25.09	242.76	22.54
4-Cl	10.5	16.1	21.7	21.95	254.68	19.36
2,4-Dichloro	5.2	6.6	8.3	18.65	272.83	16.05

versus $\sqrt{\mu}$ was linear. Added hexacyanoferrate(II) did not have any effect on the rate of oxidation.

The rate data of substituted BPGAs at different temperatures and the Arrhenius parameters obtained are recorded in Table 1. The observed reactivities of the substituted BPGAs conform to the following order: 4-OCH $_3$ > 4-CH $_3$ > H > 4-Cl > 2,4-dichloro. It is evident that electron-releasing substituents on the benzene nucleus increase the rate while electron-attracting groups retard it. The logarithm of the rate constants at 35°C correlate well with σ^+ values⁴. A similar correlation between $\log k_0$ and σ^+ has been observed by Rout and coworkers⁵ for Ce(IV) oxidation of benzylphenylglycollic acids. The above order of reactivities is in agreement with the negative values of ρ^+ . A common mechanism is envisaged for the substituted BPGAs as the free energy of activation values are of same order of magnitude.

A linear relationship between the entropy of activation (ΔS^\ddagger) and enthalpy of activation (ΔH^\ddagger) has been observed. The values of ΔH^\ddagger_0 and β are found to be 84.68 kJ mol $^{-1}$ and 330 K respectively.

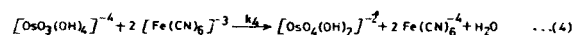
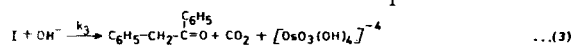
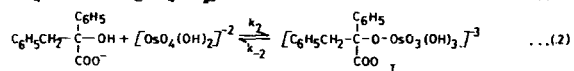
No induced polymerization of acrylonitrile or reduction of HgCl $_2$ has been observed. Hence a free radical mechanism is ruled out.

BPGA is easily oxidised to deoxybenzoin by Ce(IV). The redox potential of Ce(IV)/Ce(III) couple is 1.61 V which is high enough to oxidise the substrate. The oxidation of the same substrate by alkaline hexacyanoferrate (III) on the other hand, does not proceed in the absence of the catalyst. This is possibly because the oxidation potential of hexacyanoferrate (III)/hexacyanoferrate (II) couple is very low (−0.36 V) and does not appear to differ appreciably from that of BPGA/deoxybenzoin couple, the data for which are lacking in the literature. However, the oxidising or reducing ability of a substance can be altered by diminishing the activity of the oxidised or the reduced form of the redox couple and this can be achieved by the addition of a suitable complexing agent. The

catalyst osmium tetroxide which is necessary to promote the reaction possibly plays a role in lowering the redox potential of BPGA/deoxybenzoin couple.

It is worthwhile to mention that if only BPGA and OsO $_4$ are taken in alkaline medium, the colour of the osmium tetroxide immediately disappears and if this solution is acidified and titrated against standard ceric sulphate, then 2 mol of ceric are required for one mol of OsO $_4$. This proves that it is the reduced osmium which is first oxidised to its original octavalent state by alkaline hexacyanoferrate(III). It has already been pointed out that the oxidation of BPGA with ceric sulphate is not appreciable under these conditions and hence it is possibly the Os(VI) which reacts rapidly with hexacyanoferrate (III) ion. The alkali dependence of oxidation process clearly indicates that the oxidation of BPGA takes place through the formation of a complex anion between OsO $_4$ and OH $^{-}$ ion. Since the uncatalysed oxidation does not proceed at all and hexacyanoferrate (III) is consumed without taking part in the rate law, it is assumed that hexacyanoferrate(III) does not react directly until after the rate determining step. It is the reduced osmium which is first oxidised to its original octavalent state. Further according to the proposed rate law, the rate determining step involves the interaction between two negatively charged ions or between a negatively charged ion and a polar molecule and thus should correspond to a negative entropy change^{6,7}.

Keeping the results such as (i) the rate is independent of initial [hexacyanoferrate (III)] but proportional to [BPGA], [OH $^{-}$] and [OsO $_4$], (ii) rate increases with increase in ionic strength and (iii) entropy of activation is negative as also the ρ^+ , a mechanism shown in Scheme 1 can be proposed. The mechanism involves formation of a soluble complex between acid anion and Os(VIII). This complex then decomposes to give deoxybenzoin and Os(VIII) ion is regenerated by the oxidation of Os(VI) by two molecules of hexacyanoferrate (III) ion (Scheme 1).



Scheme 1

On the basis of this mechanism and applying steady state approximation, we get,

$$\begin{aligned} \text{Rate} &= -\frac{d}{dt} [\text{Fe}(\text{CN})_6]^{-3} \\ &= \frac{k_2 k_3 [\text{BPGA}] [\text{Os(VIII)}] [\text{OH}^-]}{k_{-2} + k_3 [\text{OH}^-]} \\ &= -\frac{d}{dt} [\text{Fe}(\text{CN})_6]^{-3} \\ &= \frac{k_2 [\text{BPGA}] [\text{Os(VIII)}] [\text{OH}^-]}{\frac{k_{-2}}{k_3} + [\text{OH}^-]} \end{aligned} \quad \dots (5)$$

Assuming $[\text{OH}^-]$ to be low, such that

$$\frac{k_{-2}}{k_3} > [\text{OH}^-] \text{ and } \left\{ \frac{k_{-2}}{k_3} + [\text{OH}^-] \right\} \approx \frac{k_{-2}}{k_3}$$

the rate law (5) approximates to Eq. (6).

$$\text{Rate} = \frac{k_2 k_3}{k_{-2}} [\text{BPGA}] [\text{Os(VIII)}] [\text{OH}^-] \quad \dots (6)$$

At high $[\text{OH}^-]$, $[\text{OH}^-] \gg \frac{k_{-2}}{k_3}$

such that $\left\{ \frac{k_{-2}}{k_3} + [\text{OH}^-] \right\} \approx [\text{OH}^-]$.

Rate law (5) reduces to rate law (7)

$$\begin{aligned} \text{Rate} &= \frac{k_2 [\text{BPGA}] [\text{Os(VIII)}] [\text{OH}^-]}{[\text{OH}^-]} \\ &= k_2 [\text{BPGA}] [\text{Os(VIII)}] \end{aligned} \quad \dots (7)$$

Thus Eqs (6) and (7) explain the experimental results, i.e. first order and zero order dependence of the rate on $[\text{OH}^-]$ at low and high $[\text{OH}^-]$ respectively.

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