

Reactivity of Hexachloroiridate(IV) in Alkaline Medium

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The reduction of hexachloroiridate(IV) in alkaline medium was studied in the temperature range 298–313 K. The reaction is first order with respect to $[\text{IrCl}_6^{2-}]$ and $[\text{OH}^-]$. The rate increases with the increase in ionic strength. Plot of logarithm of rate constant against reciprocal of dielectric constant yields a good straight line with negative slope up to dielectric constant of *ca.* 44.4 beyond which the line bends. The values of ΔH^\ddagger and ΔS^\ddagger are $59 \pm 4 \text{ kJ mol}^{-1}$ and $-57 \pm 14 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively. Hexachloroiridate(IV) is reduced to hexachloroiridate(III) by outer sphere mechanistic path. The reaction appears to proceed through the intermediate formation of free radicals to give products.

INTRODUCTION

Hexachloroiridate(IV), undergoes slow reduction to the +3 state in weakly acidic solution.¹⁻³ The rate and extent of reduction appear to be dependent on pH. In basic solution, hexachloroiridate(IV) is rapidly and quantitatively reduced to iridium (+3). There is no literature data on the kinetics of decomposition of hexachloroiridate(IV) in alkaline medium. The decomposition reaction has been studied under different experimental conditions and are incorporated in this report.

EXPERIMENTAL

Reagent: Sodium hexachloroiridate(IV) hexahydrate (Aldrich) was used. The iridium(IV) content of the salt was estimated¹ by the addition of potassium iodide to solutions of weighed portions of iridium(IV) and titration of the liberated iodine with thiosulphate using starch as indicator. The average value obtained was 2.021×10^{-3} mequiv. of Ir(IV)/mg which corresponds to 97% of the theoretical value. Iridium trichloride (Loba, India) was used without any further purification. All other reagents were of analytical grade and all solutions were made in distilled water, redistilled from alkaline permanganate in an all-glass apparatus.

Absorption spectra of hexachloroiridate(IV): Spectral measurements were carried out in the visible and near ultraviolet region using a Shimadzu UV-160 spectrophotometer. The solution of hexachloroiridate(IV) ($2 \times 10^{-4} \text{ mol dm}^{-3}$) in the absence and presence of dilute sodium hydroxide ($2.0 \times 10^{-3} \text{ mol dm}^{-3}$) was scanned in the region 300–600 nm (Fig. 1). Sodium hexachloroiridate(IV) absorbs

maximum in aqueous medium at 488 nm ($\epsilon = 4050 \pm 10 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and minimum at 460 nm. Beer's law is found to be valid in the concentration ranges $(2-10) \times 10^{-4} \text{ mol dm}^{-3}$. The spectral pattern in alkaline medium changes with increase in time. This indicates reduction of IrCl_6^{2-} to the +3 state without formation of any aquochloro complexes of the +4 state, since the molar extinction coefficients of the aquochloro complexes of +4 state, are more than 10 times larger than the extinction coefficients of the corresponding +3 species.⁴ It may be mentioned that the spectral pattern of freshly prepared aqueous solution of iridium(III) chloride is different from that of hexachloroiridate(IV) in aqueous medium. Iridium(III) chloride is nearly transparent at 488 nm.

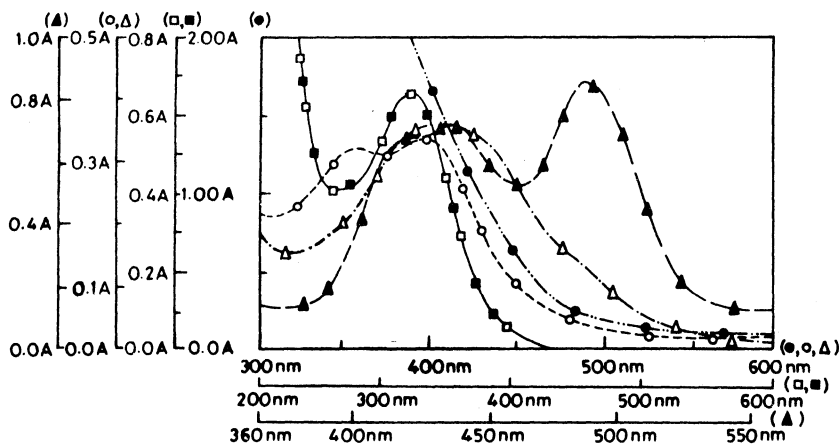


Fig. 1. Absorption spectra of Ir(IV) and Ir(III) solutions

- (i) \blacktriangle IrCl_6^{2-} in aqueous medium
- (ii) IrCl_6^{2-} in alkaline medium: Δ (30 s),
 \circ (4 h), \square (24 h), \blacksquare (48 h).
- (iii) \bullet IrCl_3 in aqueous medium.

Kinetic measurements: Kinetic measurements were carried out in the UV-visible region using a Systronics (India) spectrophotometer. The monitoring wavelength was 488 nm where hexachloroiridate(IV) absorbs to a considerably greater extent than any of the other reactants and products. The spectrophotometer had a cell compartment kept at constant temperature by circulating water from a thermostat. A large excess of sodium hydroxide concentration to that of iridium(IV) was used for all kinetic measurements. The reactants previously equilibrated to bath temperature were mixed and the mixture was then transferred to the cell of path length 1 cm. Generally, 10–15 experimental readings were taken in each run. The pseudo-first-order rate constants were calculated from the plots of $\log (A = \text{absorbance})$ vs. time. The rate constants were reproducible to within $\pm 5\%$.

Polymerization: Acrylonitrile (60% v/v) was added during the course of the reaction. The precipitation of white polyacrylonitrile appeared after a few hours. This indicates that free radicals intervene during the reaction. Blank experiments

from which either iridium(IV) or hydroxyl ion was excluded gave no detectable polymers. While these experiments do not serve to identify free radical species, they do indicate that the reaction between IrCl_6^{2-} and OH^- produces species which are capable of the initiation of acrylonitrile polymerization.

RESULTS AND DISCUSSION

The influence of iridium(IV) dependence on the rate was studied at $[\text{OH}^-]$ and temperature of $3.0 \times 10^{-3} \text{ mol dm}^{-3}$ and 298 K respectively by varying the concentrations of $[\text{Ir(IV)}]$ from $(2-6) \times 10^{-4} \text{ mol dm}^{-3}$. The pseudo-first-order rate constants are $(1.16 \pm 0.02) \times 10^{-3} \text{ s}^{-1}$. This indicates that the pseudo-first-order rate constant is independent of $[\text{Ir(IV)}]$.

The effect of variation of $[\text{OH}^-]$ on the pseudo-first-order rate constant was studied at constant $[\text{Ir(IV)}]$ and at different temperatures of $2 \times 10^{-4} \text{ mol dm}^{-3}$ and 298–313 K respectively. The plots of k_{obs} vs. $[\text{OH}^-]$ are linear passing through the origin (Fig. 2) indicating that the reaction is first order with respect to $[\text{OH}^-]$.

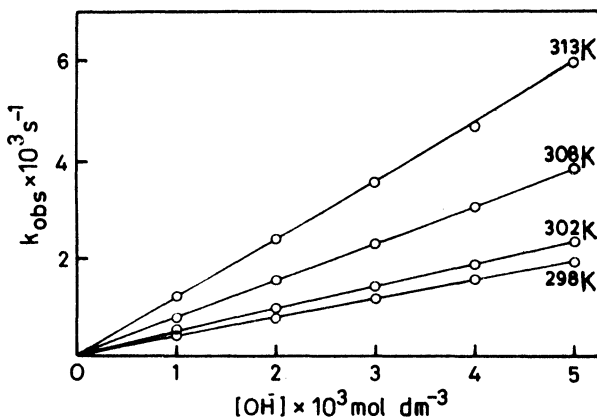


Fig. 2 Variation of pseudo-first-order rate constant with $[\text{OH}^-]$. Plots of k_{obs} against $[\text{OH}^-]$ at different temperatures. $[\text{Ir(IV)}] = 2 \times 10^{-4} \text{ mol dm}^{-3}$

The pseudo-first-order rate constants were determined at different ionic strengths (μ) by using sodium chloride at 298 K. The influence of ionic strength was studied at constant $[\text{OH}^-]$ and $[\text{Ir(IV)}]$ of 2×10^{-3} and $2 \times 10^{-4} \text{ mol dm}^{-3}$ respectively. The rate increases with the increase in ionic strength. The plot of $\log k_{\text{obs}}$ against $\{\sqrt{\mu}/(\sqrt{\mu} + 1) - 0.05 \mu\}$ based on Davies equation⁵ is shown in Fig. 3. This indicates that the reaction takes place between ions of similar charge.

The effect of changing dielectric constant (D) on the rate of the reaction has been studied. For a reaction between two ions A and B of charges Z_A and Z_B respectively, the dependence of the rate constant (k_{obs}) on the dielectric constant (D) is given by Bronsted-Christiansen-Scatchard⁶ equation (I), where e is the electronic charge, N the Avogadro number, T the temperature (K) and r the radius of the activated complex.

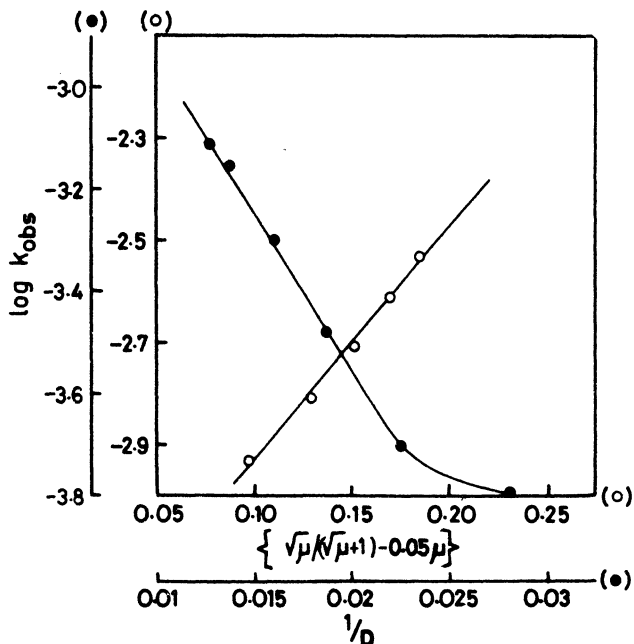


Fig. 3. Influence of ionic strength and dielectric constant on the pseudo-first-order rate constant at 298 K.

Plot of $\log k_{\text{obs}}$ against $\{\sqrt{\mu}/(\sqrt{\mu} + 1) - 0.05\mu\}$ (○) and plot of $\log k_{\text{obs}}$ against $1/D$ (●)
 $[\text{Ir(IV)}] = 2 \times 10^{-4} \text{ mol dm}^{-3}$
 $[\text{OH}^-] = 2 \times 10^{-3} \text{ mol dm}^{-3}$

$$\ln k_{\text{obs}} = \ln k_{\text{obs}}^0 - \frac{NZ_A Z_B e^2}{DRT} \quad (1)$$

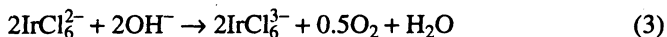
The rate decreases with the increase in solvent composition varied by the addition of dioxane (v/v %). The values of dielectric constant (D) at 298 K were taken from the work of King and Josephs.⁷ The plot of $\log k_{\text{obs}}$ against $1/D$ (Fig. 3) for water-dioxane mixture yield a good straight line with negative slope up to a dielectric constant of *ca.* 44.4 beyond which the line bends. Theoretical considerations would suggest a reaction between two similarly charged ions. The result of solvent effect is conclusive with respect to step (2).

The influence of temperature on the rate of reaction was studied in the range 298 K to 313 K. The values of k_2 ($k_{\text{obs}}/[\text{OH}^-]$) are 0.38, 0.46, 0.77 and 1.18 $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298, 302, 308 and 313 K respectively. Activation parameters were calculated from the Eyring equation

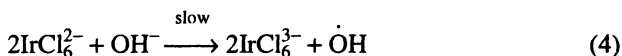
$$k_2 = \frac{RT}{Nh} \exp\left(\frac{-\Delta H^\ddagger}{RT}\right) \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (2)$$

A least square treatment of $\log k_2/T$ against $1/T$ plot (Fig. 4) was used to obtain the best straight line from which the enthalpy of activation (ΔH^\ddagger) was calculated followed by the evaluation of entropy of activation (ΔS^\ddagger). The values of ΔH^\ddagger and ΔS^\ddagger are $59 \pm 4 \text{ kJ mol}^{-1}$ and $-57 \pm 14 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively.

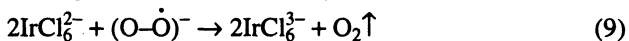
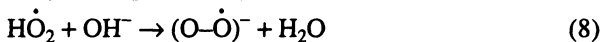
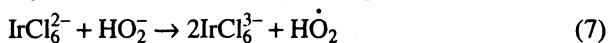
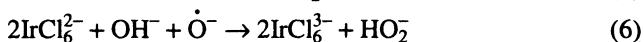
Hexachloroiridate(IV) is known to be stable⁸ toward substitution or hydrolysis over a wide range of acidities. In basic solution, the reduction of hexachloroiridate(IV) occurs much faster than succeeding hydroxylation and oxidation reaction. Mass spectrometry was employed earlier¹ to obtain quantitative identification of gaseous reaction products in basic solution. The gaseous products detected were oxygen and water vapour. In addition to this, vapour phase chromatography was employed to obtain quantitative measurements of evolved oxygen.¹ The results indicated the liberation of 0.25 mol of oxygen per mol of hexachloroiridate(IV). The stoichiometry is expressed as:



The reaction is first order with respect to $[\text{IrCl}_6^{2-}]$ and $[\text{OH}^-]$. The first order behaviour may be explained as follows:



Evidence for the existence of $\dot{\text{O}}\text{H}$ as a reaction intermediate has been cited in various studies.⁹ The step (4) is followed by the successive fast steps from 5 to 9. The species HO_2^- , HO_2 ($\text{O}-\dot{\text{O}}^-$) are also known in the literature.⁹⁻¹²



The entropy decrease as found in this study is to be expected since for ions of the same sign, the transition state will be a more highly charged ion which would be expected to be strongly solvated so that more solvent molecules might be required than for the separate ions.¹³ This would lead to decrease in entropy in forming the transition state. The activation entropies as found in this study are not widely different from those found¹⁴⁻¹⁷ for reactions which occur between two negatively charged ions. When hexachloroiridate(III) was allowed to stand for several hours in alkaline medium spectral characteristics of iridium(III) species changed possibly due to the formation of different aquo or hydroxo species.^{2, 4} The three aquo species of iridium(III) chloride which have been characterized in aqueous solution are $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$, $[\text{IrCl}_4(\text{H}_2\text{O})_2]^-$ and $[\text{IrCl}_3(\text{H}_2\text{O})_3]$. On the other hand there is also literature evidence¹⁸ to indicate that IrCl_6^{3-} in alkaline medium gives $[\text{Ir}(\text{OH})_6]^{3-}$.

After the reaction has been studied kinetically, potassium oxalate was added to the product solution; the appearance of a reddish orange colour due to the formation of tris-oxalato complex¹⁹ confirms that the reaction occurs by outer-sphere mechanistic path.

ACKNOWLEDGEMENT

Thanks are due to ICCR fellowship to Bilkis A.B. and to UGC New Delhi for J.R.F. to Nandini Bhattacharjee. Bilkis A.B. is also thankful to the authorities of Bangladesh Atomic Energy Commission for granting her leave.

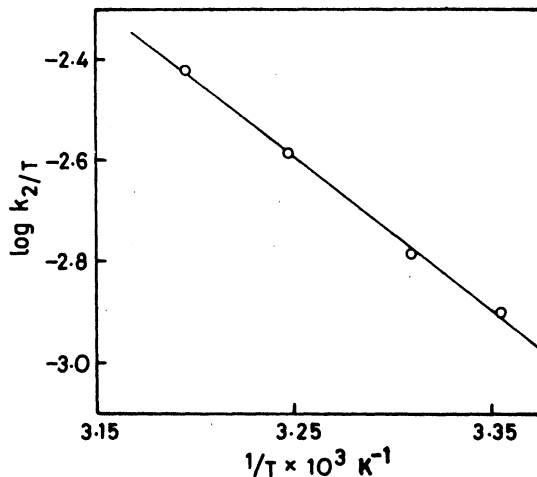


Fig. 4. Variation of second order rate constant with temperature. Plot of $\log(k_2/T)$ against $1/T$.
 $[\text{Ir(IV)}] = 2 \times 10^{-4} \text{ mol dm}^{-3}$.

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