

Relativity of Hexachloroplatinate(IV) in Alkaline Medium: Influence of Ionic Strength, Dielectric Constant and Temperature on the Reaction

KALAYAN KALI SEN GUPTA* and BILKIS ARA BEGUM

*Department of Chemistry
Jadavpur University, Calcutta 700 032, India*

The reactivity of hexachloroplatinate(IV) in alkaline medium was studied in the temperature range 308–323 K. The reaction is first order with respect to $[\text{PtCl}_6^{2-}]$ and $[\text{OH}^-]$. The rate increases with the increase in dielectric constant as well as ionic strength of the medium. The values of ΔH^\ddagger and ΔS^\ddagger are $34 \pm 4 \text{ kJ mol}^{-1}$ and $-195 \pm 14 \text{ J K}^{-1}$ respectively. The reaction appears to proceed through the replacement of Cl^- in the coordination sphere of hexachloroplatinate(IV) by OH^- to give products.

INTRODUCTION

Hexachloroiridate(IV) is known¹ to undergo slow reduction in +3 state. The reduction is rapid in basic solutions which is quantitatively reduced to iridium(III). Recently the reactivity of hexachloroiridate(IV) was studied in alkaline medium² under different experimental conditions. There is also literature evidence^{3,4} to indicate that hexachloroplatinate(IV) reacts with OH^- . It was therefore interesting to see whether PtCl_6^{2-} is reduced by OH^- to give PtCl_4^{2-} or chloride ions of PtCl_6^{2-} are replaced by OH^- . The present report deals with the reactivity of hexachloroplatinate(IV) towards OH^- under different experimental conditions.

EXPERIMENTAL

Reagents: Sodium hexachloroplatinate(IV) (Fluka A.G.) was used. The platinum(IV) content of the salt was estimated by the addition of potassium iodide to solutions of weighed portions of platinum(IV) and titration of the liberated iodine with thiosulphate using starch as indicator. All other reagents were of analytical grade and all solutions were made in doubly distilled water.

Kinetic measurements: The rate of disappearance of platinum(IV) was followed spectrophotometrically at 400 nm where platinum(IV) absorbs appreciably. Beer's law is found to be valid at this wavelength in the concentration range $(1-10) \times 10^{-3} \text{ mol dm}^{-3}$. The spectrophotometer had a cell compartment kept at constant temperature by circulating water from a thermostat. An electrically operated thermostatic water bath was used. It was provided with heater and stirrer with proper cooling arrangement. The temperatures were recorded with the help of an accurate sensitive thermometer reading to one-tenth of a degree. The reactants were previously equilibrated to bath temperature. The reaction mixture was then transferred to the cell of path length 1 cm. The progress of reaction was followed by observing the disappearance of platinum(IV) and the decrease in absorbance at

regular intervals of time was noted spectrophotometrically. The pseudo-first order rate constants were calculated from the plots of $\log A$ ($A = \text{absorbance}$) versus time. The rate constants were reproducible to within $\pm 5\%$.

Product Analysis: When the solution after kinetic measurements is kept for a few days, the product solution becomes colloidal in nature and then precipitates as a yellow product. The solution on evaporation yields a black residue. The residual black powder is believed to be a mixture of oxides of platinum(II) and platinum(IV).

We carried out some experiments to ensure whether platinum(IV) is reduced to platinum(II) or chloride ions are replaced by hydroxyl ions to give hydroxo products of platinum(IV). Consequently to a proton⁵ of the reaction product hydrazine sulphate solution was added and the evolution of nitrogen gas indicates that platinum remains in +4 state. All these indicate that during the kinetic experiments, Cl^- ions of PtCl_6^{2-} are replaced by OH^- ions to give products of oxidation.

RESULTS AND DISCUSSION

The influence of platinum(IV) on the rate was studied at $[\text{OH}^-]$ and temperature of $4 \times 10^{-3} \text{ mol dm}^{-3}$ and 308 K respectively by varying the concentrations of platinum(IV) in the range $(0.78-2.6) \times 10^{-3} \text{ mol dm}^{-3}$. The pseudo-first order rate constants are $(1.70 \pm 0.02) \times 10^{-4} \text{ s}^{-1}$ which indicate that the pseudo-first order rate constant is independent of $[\text{Pt(IV)}]$.

The effect of variation of $[\text{OH}^-]$ on the pseudo-first order rate constant was studied at constant $[\text{Pt(IV)}]$ of $1.3 \times 10^{-3} \text{ mol dm}^{-3}$ but at different temperatures in the range 308–323 K (Table-1). The plots of k_{obs} vs. $[\text{OH}^-]$ are linear passing through the origin indicating that the reaction is first order with respect to $[\text{OH}^-]$.

The influence of ionic strength on the pseudo-first order rate constant was studied at $[\text{Pt(IV)}]$, $[\text{OH}^-]$ and temperature of $1.3 \times 10^{-3} \text{ mol dm}^{-3}$, $2.0 \times 10^{-1} \text{ mol dm}^{-3}$ and 308 K respectively. The values of pseudo-first order rate constants are 0.85×10^{-4} , 1.05×10^{-4} , 1.54×10^{-4} , 1.65×10^{-4} and $2.09 \times 10^{-4} \text{ s}^{-1}$ at ionic strength of 0.2, 0.3, 0.4, 0.5 and 0.6 mol dm^{-3} respectively. The fact that rate increases with the increase in ionic strength indicates that the reaction takes place between ions of similar charge.

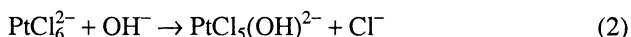
The influence of dielectric constant was studied at $[\text{Pt(IV)}]$, $[\text{OH}^-]$ and temperature of $1.3 \times 10^{-3} \text{ mol dm}^{-3}$, $6 \times 10^{-1} \text{ mol dm}^{-3}$ and 308 K respectively. Dielectric constant was varied by the addition of dioxane (% v/v). The values of pseudo-first order rate constants are 2.56×10^{-4} , 2.19×10^{-4} , 1.92×10^{-4} , 1.70×10^{-4} , $1.40 \times 10^{-4} \text{ s}^{-1}$ at 0, 10, 20, 30 and 40% (v/v) respectively. The rate decreases with the increase in solvent composition. The plot of $\log k_{\text{obs}}$ against $1/\epsilon$ ($\epsilon = \text{dielectric constant}$) yields a good straight line with negative slope. The values of dielectric constant (ϵ) at 308 K are taken from the work of Akerlof and Short.⁶ Theoretical considerations would suggest a reaction between two similarly charged ions.

The values of $k_2(k_{\text{obs}}/[\text{OH}^-])$ are 4.25×10^{-4} , 5.3×10^{-4} , 6.8×10^{-4} and $8.5 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, at 308, 313, 318 and 323 K respectively. Activation parameters were calculated using the equation

$$k_2 = \frac{RT}{Nh} \exp\left(\frac{-\Delta H^\ddagger}{RT}\right) \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (1)$$

The plot of $\log k_2/T$ ($k_2 = k_{\text{obs}}/[\text{OH}^-]$) against $1/T$ is linear. A least square treatment of the $\log k_2/T$ against $1/T$ plot 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 $35 \pm 4 \text{ kJ mol}^{-1}$ and $-195 \pm 14 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. The large negative entropy of activation confirms that the reaction takes place between ions of similar charge.⁷

There is literature evidence⁸ to indicate that in alkaline medium ($\text{pH} > 8$) PtCl_6^{2-} changes to $\text{PtCl}_5(\text{OH})^{2-}$ as shown below.



The addition of Cl^- to the reaction mixture failed to inhibit the reaction indicating that the step (2) is not reversible. On standing the reaction mixture for 25 h, successive replacement of $\text{PtCl}_5(\text{OH})^{2-}$ occurs leading to the formation⁴ of $\text{Pt}(\text{OH})_6^{2-}$.

TABLE-1
REACTIVITY OF Pt(IV) AT DIFFERENT $[\text{OH}^-]$ AND TEMPERATURES AT $[\text{Pt(IV)}]$
OF $1.3 \times 10^{-3} \text{ mol dm}^{-3}$

$[\text{OH}^-] \times 10$ mol dm^{-3}	$k_{\text{obs}} \times 10^4 \text{ s}^{-1}$			
	308 K	313 K	318 K	323 K
2	0.85	1.06	1.36	1.70
4	1.71	2.13	2.73	3.39
6	2.56	3.20	4.09	5.15
8	3.41	4.25	5.45	6.80
9	3.84	4.80	6.14	7.65

ACKNOWLEDGEMENT

Thanks are due to Indian Government for an ICCR fellowship to Bilkis A.B. and to the authorities of Bangladesh Atomic Energy Commission for granting her leave.

REFERENCES

1. D.A. Fine, *Inorg. Chem.*, **8**, 1014 (1969).
2. K.K. Sen Gupta, Bilkis A.B. and N. Bhattacharjee, *Asian J. Chem.* **10**, 169 (1998).
3. J.W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. XVI, Longman (London), p. 245 (1972).
4. E. Blasius, W. Preetz and R. Schmitt, *J. Inorg. Nucl. Chem.*, **19**, 115 (1961).
5. G. Svehla, *Vogel's Text Book of Macro and Semimicro Qualitative Inorganic Analysis*, 5th Edn., Orient Longmans, p. 517 (1985).
6. G. Akerlof and O.A. Short, *J. Am. Chem. Soc.*, **58**, 1241 (1936).
7. A.A. Frost and R.G. Pearson, *Kinetics and Mechanism*, 2nd Edn., Wiley Eastern (New Delhi), p.144 (1970).
8. K.K. Sen Gupta and P.K. Sen, *J. Inorg. Nucl. Chem.*, **39**, 165, (1977).

(Received: 16 January 1998; Accepted: 27 April 1998)

AJC-1483