Kinetics of Oxidation of Hydroxylammonium Ion by Hexachloroiridate(IV) in Perchloric Acid Medium

PRATIK K. SEN, SURAJIT MAITI & KALYAN K. SEN GUPTA*

Department of Chemistry, Jadavpur University, Calcutta 700 032

The empirical rate expression of the title reaction in the perchloric acid range (1 to 15) $\times$ 10^{-2} M is

$$\frac{-d[\mathrm{IrCl_6^{2-}}]}{dt} = \frac{k_{sp}[\mathrm{IrCl_6^{2-}}]\,[\mathrm{NH_3OH^+}]}{[\mathrm{H^+}]}$$

where k_{sp} is the specific rate constant $= k_{obs}\,[\mathrm{H^+}]/[\mathrm{NH_3OH^+}]$. At 30°C, the value of k_{sp} is $(8.0 \pm 0.3) \times 10^{-3}$ (sec^{-1}). Over the temperature range 30°-50°C the values of E_a, $-\Delta S_{\ddagger}^{*}$ and $\Delta G_{\ddagger}^{*}$ are 81 ± 4kJ mol^{-1}, 17.0 ± 12 J mol^{-1}deg^{-1} and 84 ± 4 kJ mol^{-1} respectively. The reaction seems to proceed through the intermediate formation of free radicals. The addition of hexachloroiridate(III) to the reaction has no influence on the reaction rate.

THE kinetics of the oxidation of hydroxylammonium ion by some transition metal ions have been studied[1-4], though studies using Ir(IV) are lacking. We have earlier studied the kinetics and mechanism of the oxidation of hydroxylammonium ion by hexachloroplatinate(IV)[5] in the acid medium. Since both hexachloroiridate(IV) and hexachloroplatinate (IV) are isostructural, it was thought worthwhile to investigate the kinetics and mechanism of oxidation of hydroxylammonium ion by hexachloroiridate(IV).

Materials and Methods

Hydroxylamine hydrochloride and other inorganic compounds used were of AR (BDH) grade. Hydroxylamine hydrochloride was standardized bromatometrically[6]. Sodium hexachloroiridate(IV) (Na$_2$IrCl$_6$, 6H$_2$O) (Johnson-Mathey) was used as such and its solution, standardised spectrophotometrically[7], was kept in the dark and used under subdued lighting conditions generally within 5-6 hr of its preparation. Dioxane was purified first by refluxing and then distilling twice over metallic sodium, each time collecting the middle fraction.

The absorption spectrum of freshly prepared hexachloroiridate(IV) solution exhibited a maximum at 488 nm ($\epsilon = 4050M^{-1}$ cm^{-1}) and a minimum at 460 nm. Beer's law was found to be valid in the concentration range (2.83 to 24.0) $\times$ 10^{-5} M. The aquo compound, IrCl$_5$(OH$_2$)$^-$ exhibited maximum and the minimum at 450 nm and 380 nm respectively. The spectral pattern of aquo pentachloroiridate(IV) was different from that of hexachloroiridate(IV).

Kinetics measurements — The rate of decrease in Ir(IV) concentration was followed spectrophotometrically by measuring the absorbance at 488 nm. The IrCl$_6^{2-}$ or its hydrolysed product was transparent in this region. The cell compartment of the spectrophotometer (Beckman DU model) was kept at constant temperature. Pseudo-first order conditions were maintained in all the runs. The kinetic runs were thus performed with [Ir(IV)] $= 1.0 \times 10^{-4}M$ and [NH$_3$OH$^+$] in the range (0.8 to 8.0) $\times$ $10^{-3}M$. Measurements were carried out at [HClO$_4$] $= 1.0 \times 10^{-1}M$ and at different temperatures. The reaction rate was followed for at least two half-lives. Pseudo-first order rate constants (k_{obs}) were calculated from the log$A$ ($A =$ absorbance) against time plots. The rate constants were reproducible within $\pm 5\%$.

Polymerization test — The polymerization reaction was studied at room temperature with different initial concentrations of NH$_3$OH$^+$ (2×10^{-3}, 4×10^{-3} or $6 \times 10^{-3}M$) and in the presence of 16% (w/v) of the monomer, acrylamide. The initial concentrations of iridium (IV) and H$^+$ were 9.44×10^{-5} and $1.0 \times 10^{-1}M$ respectively. Acrylamide was polymerised, as revealed by the appearance of turbidity. The addition of dioxane to the reaction mixture enhanced the formation of polymer. Control experiments showed that no polymerization of acrylamide took place under the experimental conditions with either iridium(IV) or hydroxylammonium ion alone.

Results

Stoichiometry — The results of stoichiometric runs wherein the unreacted hydroxylammonium ion was estimated bromatometrically by adding an excess of standard potassium bromate and HCl and back titrating the unconsumed bromate by a standard thiosulphate, revealed that 1 mol of NH$_3$OH$^+$ reacted with 1 mol of Ir(IV) according to Eq. (1) NH$_3$OH$^+$.

$$\mathrm{Ir(IV) + NH_3OH^+ \longrightarrow Ir(III) + \tfrac{1}{2}N_2 + 2H^+ + H_2O} \quad ..(1)$$
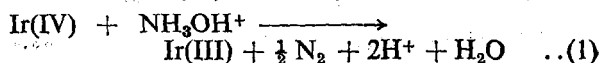
The extent of aquation of Ir(III) species under the conditions of kinetic run was determined as follows. The Ir(III) species generated was reoxidized to the corresponding Ir(IV) species by passing dry and HCl free Cl_2 gas through the solution for a long period and the concentration of $IrCl_5(H_2O)^-$ determined spectrophotometrically following the procedure of Littler et al.[8-10]. Spectrophotometric examination of the product solution showed that the Ir(III) was mostly in the form of hexachloroiridate(III) (over 90%). This suggests that the hydrolysis of hexachloroiridate(III) to give aquo pentachloroiridate(III) is not significant under this condition of study.

Effect of varying reactant concentration —The reaction was studied at constant $[NH_3OH^+]$ and $[H^+]$ of 5 × 10^{-3} and 1 × $10^{-1}M$ respectively while $[Ir(IV)]$ was varied in the range (0.5-3.0) × $10^{-4}M$. The values of $k_{obs} = (7.5 \pm 0.3) \times 10^{-4}$ (sec⁻¹) were obtained. The results indicated that the reaction was first order with respect to Ir(IV). The effect of varying $[NH_3OH^+]$ on the rate was also investigated at constant $[Ir(IV)]$ and $[H^+]$ of 1 × $10^{-4}M$ and 1 × $10^{-1}M$ respectively. The reaction rate was found to increase with increase in [substrate] (Table 1). The plots of k_{obs} against $[NH_3OH^+]$ were linear passing through the origin at each temperature.

Effect of varying pH — The influence of H^+ on the reaction rate was studied by varying acidity from (1 to 15) × 10^{-2} M while the ionic strength was maintained constant at $\mu = 0.50M$ with sodium perchlorate. Hydrogen ion has been found to inhibit the rate of reaction (Table 2). The values of $k_{obs} \times [H^+]$ were observed to be constant over a considerable range of acidities (Table 2). The reaction rate appeared to become complex at higher acidities (> $0.15M$) possibly because of the reaction of H^+ with $IrCl_6^{2-}$ to give $HIrCl_6^-$. The latter might complicate the reaction by reacting with NH_3OH^+ to give reaction products.

Effect of varying temperature — The pseudo-first order rate constants were calculated at different $[NH_3OH^+]$ and temperature, keeping $[Ir(IV)]$ and $[H^+]$ constant at 1 × 10^{-4} and 1 × $10^{-1}M$ respectively. The results are recorded in Table 1. The values of specific rate constant (k_{sp}) have been calculated from the relation $k_{sp} = k_{obs} [H^+]/[NH_3OH^+]$. From the plot of log k_{sp} against 1/T, the energy of activation (E_a) came out to be 81 ± 4 kJ mol⁻¹. The values of $-\Delta S‡$ and $\Delta G‡$ were 17.0 ± 12 J mol⁻¹ deg⁻¹ and 84 ± 4 kJ mol⁻¹ respectively.

Discussion

It has earlier been suggested[5], in connection with the oxidation of hydroxylammonium ion by hexachloroplatinate(IV) that unprotonated hydroxylamine rather than hydroxylammonium ion reacted with hexachloroplatinate(IV) in a slow and rate-determining step. This is expected since the reaction was studied at lower acidities (pH 4.6 to 5.93). However, the dissociation constant of hydroxylammonium ion (Eq. 2) is 1.09 × 10^{-6} at 25°C.
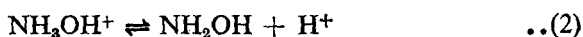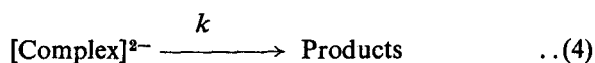
$$NH_3OH^+ \rightleftharpoons NH_2OH + H^+ \qquad ..(2)$$

Table 1 — Effect of Varying Substrate Concentration on Pseudo-first Order Rate Constants

$[Ir(IV)] = 1.00 \times 10^{-4}M$, $[H^+] = 1.0 \times 10^{-1}M$

$[NH_3OH^+] \times 10^3 M$	$k_{obs} \times 10^{+4}$ (sec⁻¹)	$k^{sp} \times 10^2$ (sec⁻¹)
Temp. = 30°C		
2	1.61	0.805
4	3.13	0.783
5	3.95	0.790
6	4.68	0.780
7	5.91	0.844
8	6.53	0.816 (0.803)*
Temp. = 35.5°C		
2	2.70	1.35
3	4.49	1.49
4	5.87	1.47
5	7.60	1.52
6	8.83	1.47
7	10.06	1.44 (1.48)*
Temp. = 40°C		
1	2.05	2.05
2	4.15	2.07
3	6.45	2.15
4	9.14	2.28
5	11.3	2.26
6	13.05	2.17 (2.17)*
Temp. = 45°		
1	3.45	3.45
2	6.99	3.49
3	11.1	3.70
4	14.1	3.60
5	18.7	3.74 (3.60)*
Temp. = 50°C		
0.8	4.76	5.95
1	5.99	5.99
2	11.82	5.91
3	17.96	5.98
4	23.64	5.91 (5.95)*

* Average of several determinations

In the present study the reaction was carried out at much higher acidities (1 to 15) × $10^{-2}M$ and since $[H^+] >> K_a$, the substrate remained exclusively as NH_3OH^+. Few kinetics runs were also carried out in the presence of ten-fold excess of hexachloroiridate(III) over Ir(IV). No kinetic effect was observed, indicating that any reverse effect was insignificant. Again, hexachloroiridate(IV) is known to be stable[8,9,11] towards substitution or hydrolysis over wide range of acidities. It has been shown by Moggi et al[12]. that $IrCl_6^{2-}$ is photo-sensitive in the UV region (~ 254 nm) whereas at 433 or 495 nm, the complex is a photosensitive. Hence photochemically induced reaction of $IrCl_6^{2-}$ is not expected to be significant under the present reaction conditions.

Mechanism and rate law — It is suggested that $IrCl_6^{2-}$ reacts with NH_3OH^+ to form an unstable intermediate (Eq. 3) with the release of a proton. It is already known that unprotonated hydroxylamine forms complexes with metal ions[1,4]. Complex compounds with second and third transition series metals having coordination number of seven are also known[13,14]. This is attributable in part of the larger size of these ions and also to the availability of orbitals[15,16]. The intermediate then decomposes in the rate-determining step(4) to give reaction products.

$$IrCl_6^{2-} + NH_3OH^+ \overset{K}{\rightleftharpoons} [Complex]^{2-} + H^+ \quad ..(3)$$

$$[Complex]^{2-} \overset{k}{\longrightarrow} Products \quad ..(4)$$

The rate expression would then be given by expression (5) or (6)

$$-\frac{d[IrCl_6^{2-}]}{dt} = \frac{kK[IrCl_6^{2-}][NH_3OH^+]}{[H^+] + K[NH_3OH^+]} \quad ..(5)$$

$$k_{obs} = \frac{kK[NH_3OH^+]}{[H^+] + K[NH_3OH^+]} \quad ..(6)$$

Since K is insignificant and $[H^+] >> K[NH_3OH^+]$, Eq. (6) reduces to a much simpler form (7)

$$k_{obs} = \frac{k_{sp}[NH_3OH^+]}{[H^+]} \quad ..(7)$$

Equation (7) explains the observed orders with respect to each reactant in the acid range (1 to 15) $\times 10^{-2}M$. The inverse dependence on $[H^+]$ may also be explained if it is assumed that $IrCl_5(OH)^{2-}$ reacts with hydroxylammonium ion (Eqs. 8 and 9).

$$IrCl_5(H_2O)^- \rightleftharpoons IrCl_5(OH)^{2-} + H^+ \quad ..(8)$$

$$IrCl_5(OH)^{2-} + NH_3OH^+ \longrightarrow Product \quad ..(9)$$
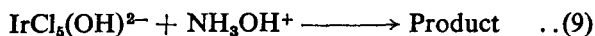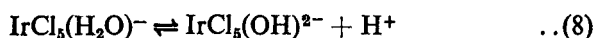
Since a fresh solution of hexachloroiridate(IV) is always used and the solution is stable[17] for 24 hr, it is unlikely that $IrCl_5(OH)^{2-}$ oxidizes NH_3OH^+.

The electron transfer from substrate to oxidant takes place by the breakdown of the complex to give free radical of the type, $:\dot{N}HOH$ and hexachloroiridate(III). The formation of free radical is supported by the polymerisation of the monomer, acrylamide. The free radical, $:\dot{N}HOH$ probably remains in tautomeric equilibrium[17] with $NH_2O\cdot$ (Eq. 10). The existence of $NH_2O\cdot$ radical has been demonstrated by ESR studies of Gutch and Waters[17].
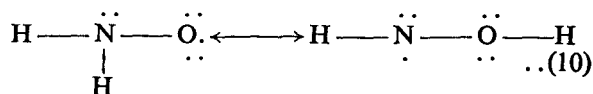
However, the formation of nitrogen as the reaction product can better be explained through the formation of $:\dot{N}HOH$ radical, which dimerises and then decomposes to give nitrogen.

Hydroxylammonium ion can be oxidized to short-lived free radicals by one-equivalent oxidants[17] whereas HNO is formed when it is oxidized by two-equivalent oxidants[18,19]. Had the present reaction been initiated by the intermediate formation of HNO radical, HNO_2 would have formed as one of the reaction products. Moreover, dimerization of HNO followed by the decomposition of the dimerized products has been reported[19] to give N_2O. The absence of HNO_2 in the reaction mixture and the observed stoichiometry indicates that the intermediate HNO does not intervene in the reaction. The activation energies in the oxidations of some inorganic[16] as well as organic[20] compounds, by hexachloroiridate(IV), known to proceed by free radical mechanism have been found to be very high (> 80 kJ mol^{-1}). The high activation energy of 81 kJ mol^{-1} obtained in this study also coroborates the fact that hexachloroiridate(IV) behaves as one-equivalent oxidant in the present study.

Acknowledgement

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TABLE 2 — EFFECT OF [H$^+$] ON THE PSEUDO-FIRST ORDER RATE CONSTANT

$[Ir(IV)] = 1.00 \times 10^{-4}M$, $[NH_3OH^+] = 4.0 \times 10^{-3}M$, $\mu = 0.50M$

TEMP. = 35°C

$[H^+] \times 10^2$ M	$k_{obs} \times 10^3$ (sec^{-1})	$k_{obs} \times [H^+] \times 10^{-4}$ (mol litre^{-1} sec^{-1})
1.0	10.2	1.02
3.0	3.42	1.03
5.0	1.99	0.995
7.0	1.46	1.03
10.0	1.05	1.05
15.0	0.72	1.08

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