# KINETICS AND MECHANISM OF OXIDATION OF TIN(II) BY HEXACHLOROIRIDATE(IV) IN AQUEOUS PERCHLORATE SOLUTIONS*

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The kinetics of hexachloroiridate(IV) oxidation of tin(II) in aqueous perchlorate media at a constant ionic strength of $2.0$ mol dm$^{-3}$ have been studied spectrophotometrically. The reaction was found to follow second-order overall kinetics and first order with respect to each of the reactants. The results showed hydrogen ion dependence where the reaction rate increased with increasing hydrogen ion concentration. The activation parameters were evaluated and a tentative reaction mechanism has been discussed.

There has been much discussion on whether simultaneous or near simultaneous transfer of two-electrons is possible for redox reactions between metal ions[1,2]. In this context the redox reactions of Tl(III) (ref.[3]), Sn(II) (ref.[4]) and Pt(IV) (ref.[5]) have proved most relevant.

Although considerable work has been done on the kinetics of oxidation of some organic compounds[6−8] as well as inorganic compounds[9−11] by hexachloroiridate(IV), no attempts seem to have been made of such Sn(II) by this oxidant. It was, therefore, worthwhile to investigate the present reaction, to gain some information about the nature of electron changes and to elucidate reaction mechanism.

## EXPERIMENTAL

Sodium hexachloroiridate(IV) of analar quality (Ventron Corp) was used without further purification. The preparation and analysis were described earlier[12]. Solutions of tin(II) were prepared and standardized as described elsewhere[13]. All other reagents were of analytical grade and their solutions were prepared by dissolving the requisite amounts of the samples in twice distilled water. The ionic strength of the reaction mixture was maintained constant at $2.0$ mol . . dm$^{-3}$ using NaClO$_4$ as a non-complexing agent.

*Kinetic measurements.* All the measurements were conducted under pseudo first-order conditions where Sn(II) concentrations were in great excess over IrCl$_6^{2-}$ ones. The reaction solutions were thermally equilibrated in a constant temperature water-bath maintained at the desired temperature within $\pm 0.1°$C. When the two solutions had attained the temperature of the ther-

mostat, the required volumes of the reactants were syringed out and poured in the reaction cell. The course of the reaction was followed by recording change in the absorbance of $IrCl_6^{2-}$ at wavelength of 489 nm, its absorption maximum ($\varepsilon = 4\,075$ $dm^3$ $mol^{-1}$ $cm^{-1}$), as a function of time on a Shimadzu UV double beam spectrophotometer using cells of the pathlength 1 cm. No interference has been found from the other reagents at this wavelength.

Some experiments under second-order conditions have been undertaken in which $[IrCl_6^{2-}]_0/$ $/[Sn(II)]_0 \simeq 2$. The results were found to be in good agreement with those observed for pseudo first-order reaction kinetics, indicating the reproducibility of the results obtained.

## RESULTS AND DISCUSSION

*Stoichiometry.* The stoichiometry of reaction of tin(II) with hexachloroiridate(IV) can be determined spectrophotometrically in terms of the consumption ratio (change in $[Ir(IV)]$: change in $[Sn(II)]$ at different initial concentrations of the reactants which had been allowed to react to completion at room temperature. In every case the consumption ratio was found to be $2 \cdot 1 \pm 0 \cdot 1$ for $[Ir(IV)] : [Sn(II)]$. This indicates that the stoichiometry of the overall reaction may be expressed by Eq. (A).

$$2\,IrCl_6^{2-} \;+\; Sn^{2+} \;=\; 2\,IrCl_6^{3-} \;+\; Sn^{4+} \tag{A}$$
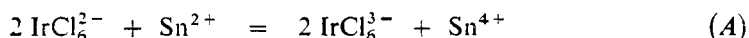
*Dependence of reaction rate on $[IrCl_6^{2-}]$ and $[Sn(II)]$ reactants.* The pseudo first-order plots were linear for three half-lives of the reaction and, hence, consistent with the first-order decrease in the concentration of $IrCl_6^{2-}$, i.e.

$$-d\,[IrCl_6^{2-}]/dt = k_{obs}[IrCl_6^{2-}] , \tag{1}$$

where $k_{obs}$ is the observed first-order rate constant,

$$k_{obs} = 2k_2[Sn(II)] \tag{2}$$

The effect of variation of Sn(II) concentration on the pseudo first-order rate constant was studied at constant $[IrCl_6^{2-}]$ and $[H^+]$. Plot of $k_{obs}$ versus $[Sn(II)]$ gave straight line passing through the origin as required by Eq. (2). This fact indicates that the reaction is also first order with respect to the reductant. Then, the rate law of the oxidation of Sn(II) by $IrCl_6^{2-}$ is

$$-d\,[IrCl_6^{2-}]/dt = k_2[IrCl_6^{2-}]\,[Sn(II)] , \tag{3}$$

where $k_2$ is the second-order rate constant. The values of $k_{obs}$ were calculated using the least-squares method and are summarized as follows ($[Sn^{2+}] = 5 \cdot 11 \cdot 10^{-4}$ mol . . $dm^{-3}$, $[IrCl_6^{2-}] = 4 \cdot 98 \cdot 10^{-5}$ mol $dm^{-3}$, $I = 2 \cdot 0$ mol $dm^{-3}$ at 25°C):

| $[H^+]$. mol $dm^{-3}$ | 2·0 | 1·5 | 1·25 | 1·0 | 0·5 |
| --- | --- | --- | --- | --- | --- |
| $k_{obs} \cdot 10^2$, $s^{-1}$ | 3·24 | 4·34 | 4·88 | 5·84 | 10·29 |

*Dependence of reaction rate on* $[H^+]$. The effect of variation of the hydrogen ion concentration on the rate of reaction at constant ionic strength of $2.0 \, \text{mol dm}^{-3}$ was studied. An increase in the observed first-order rate constant with decrease in $[H^+]$ is apparent. This observation can be explained if a hydrogen ion is released in step $(B)$ with equilibrium constant $K_1$, yielding[14] the hydrolysis species of tin(II) as follows,

$$Sn^{2+} + H_2O \overset{K_1}{\rightleftharpoons} Sn(OH)^+ + H^+ . \qquad (B)$$
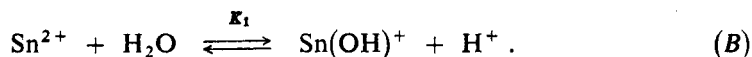
As shown in Fig. 1, plots of $k_2$ against $[H^+]^{-1}$ were fairly linear with positive intercept on $k_2$ axis indicating a rate law of the form

$$\text{rate} = a + b[H^+]^{-1} , \qquad (4)$$

where $a$ and $b$ are constants.

*Dependence of reaction on ionic strength.* The rate of reaction was found to be increased with increasing ionic strength of the medium. The ionic strength was maintained each time before mixing the two reactants, thus keeping the $[H^+]$, temperature and reactants concentrations constant during the measurements. The values of $k_{obs}$ at $I = 1.0$ and $3.0 \, \text{mol dm}^{-3}$ and fixed $[H^+] = 1.0$, $[Sn(II)]_0 =$ $= 5.11 \cdot 10^{-4} \, \text{mol dm}^{-3}$ and $[ICl_6^{2-}] = 4.98 \cdot 10^{-5} \, \text{mol dm}^{-3}$ and 30°C were 0.018 and $0.041 \, \text{s}^{-1}$, respectively. However, the present measurements, of necessity, lie far outside the Debye–Hückel region, covering a range over which the activity coefficients of many electrolytes are known to be fairly dependent on ionic strength[15].
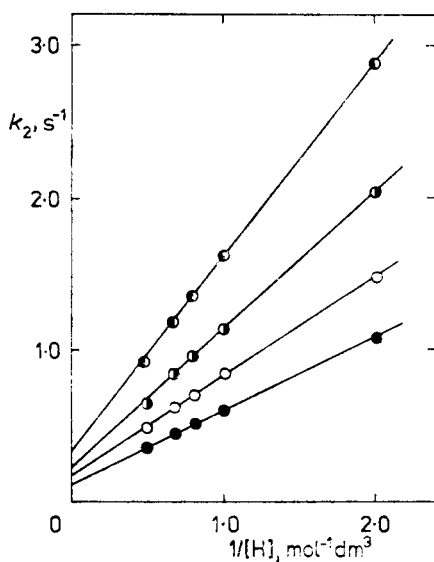


FIG. 1

Hydrogen ion dependence $[Sn(II)] = 5.11 \cdot 10^{-4} \, \text{mol dm}^{-3}$, $[IrCl_6^{2-}] = 4.98 \cdot 10^{-5} \, \text{mol dm}^{-3}$, $I = 2.0 \, \text{mol dm}^{-3}$. Temperature, °C: ● 15, ○ 20, ◑ 25, and ◐ 30

The ionic strength dependence is qualitatively expected when considering the charges involved[16].

*Dependence of reaction rate on temperature.* The temperature dependence was found to follow the Eyring equation[17] over the temperature range $15-30°C$. The activation parameters were calculated by the method of least-squares and are summarized in Table I.

A question of basic interest in connection with the oxidation of $Sn(II)$ by multicharged metal ions is whether the redox reaction proceeds via successive one--electron transfer steps

$$Sn^{2+} + M^{n+} \rightarrow Sn^{3+} + M^{(n+e)+} \tag{C}$$

$$Sn^3 + M^{n+} \rightarrow Sn^{4+} + M^{(n+e)+} \tag{D}$$
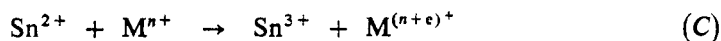
or involves a simultaneous two-electron transfer in a single step

$$Sn^{2+} + M^{n+} \rightarrow Sn^{4+} + M^{(n+2e)+}, \tag{E}$$

where M denotes the polyvalent metal ion, $n$ stands for its valency, and e is the electron transferred from the reductant to the oxidant.

Since the oxidation of $Sn(II)$ by one-electron metal ion oxidizing agent has generally been proposed to occur by two successive one-electron transfer steps involving unstable $Sn(III)$ intermediate oxidation state, the mechanism defined by Eq. $(E)$ is avoided. Hence, the most likely reaction mechanism which may be suggested is
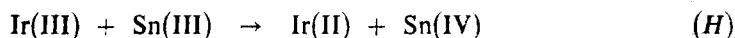
$$Ir(IV) + Sn(II) \rightarrow Ir(III) + Sn(III), \tag{F}$$

$$Ir(IV) + Sn(III) \rightarrow Ir(III) + Sn(IV). \tag{G}$$
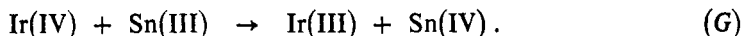
Applying the steady state approximation of $Sn(III)$, one concludes that the rate law obtained is quite similar to that defined by Eq. $(3)$.

An alternative reaction mechanism was considered to account for slight deviation of the experimental stoichiometry from the theoretical one. It may be suggested that
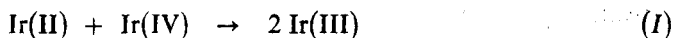
TABLE I
The activation parameters in the oxidation of $Sn(II)$ by $IrCl_6^{2-}$ ion

| Pathway | $\Delta S^{\pm}$ J mol$^{-1}$ K$^{-1}$ | $\Delta H^{\pm}$ kJ mol$^{-1}$ | $\Delta G^{\pm}$ kJ mol$^{-1}$ |
|---|---|---|---|
| $k_a$ | $-56.03 \pm 2.24$ | $48.33 \pm 1.44$ | $65.03 \pm 2.11$ |
| $k_b'$ | $-54.57 \pm 2.70$ | $45.47 \pm 1.12$ | $61.73 \pm 1.92$ |

Ir(III) is further reduced by Sn(III) to give Ir(II) species

$$Ir(III) + Sn(III) \rightarrow Ir(II) + Sn(IV) \qquad (H)$$

followed by

$$Ir(II) + Ir(IV) \rightarrow 2\,Ir(III) \qquad (I)$$

Assuming that the initial Ir(IV) is at least more than twice the concentration of Sn(II) and applying the steady state approximation for Ir(II) and Sn(III), analogous rate law similar to that defined by Eq. (3) is observed. Indeed, this mechanism is rejected since Sn(II) is present in a large excess over that of $IrCl_6^{2-}$ concentration. On the other hand, if reaction (I) is omitted, a complicated rate law in disagreement with the experimental observations is obtained. Therefore this deviation may be neglected since the stoichiometrical results have obtained after 72 h, and at the time of measurements studied, the Ir(II) could hardly be formed.

The reaction mechanism which may be suggested to account for experimental observations involves the two competitive reactions (J) and (K).

$$IrCl_6^{2-} + Sn^{2+} \xrightarrow{\;\;k_a\;\;} \qquad (J)$$

$$IrCl_6^{2-} + Sn(OH)^+ \xrightarrow{\;\;k_b\;\;} \qquad (K)$$
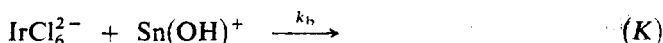
The variation of the rate constant with the change of the Sn(II) and hydrogen ion concentrations can be expressed by the following equation

$$-\frac{d\,[IrCl_6^{2-}]}{dt} = \frac{(k_a + k_b K_1 [H^+]^{-1})}{1 + K_1 [H^+]^{-1}}\,[Sn(II)]_T\,[IrCl_6^{2-}], \qquad (5)$$

where $[Sn(II)]_T$ represents the analytical total concentration of Sn(II). Comparing Eqs (3) and (5), the following relationship is obtained

$$k_2 = \frac{k_a + K_1 k_b [H^+]^{-1}}{1 + K_1 [H^+]^{-1}}. \qquad (6)$$

Assuming that $K_1 [H^+]^{-1} \ll 1$ under our experimental conditions[14], Eq. (6) becomes

$$k_2 = k_a + k_b K_1 [H^+]^{-1}. \qquad (7)$$

The activation parameters of $k_a$ and $k_b'$ (where $k_b' = k_b K_1$) are summarized in Table I. The smaller activation energies obtained in the present investigation support the fact that the reaction takes place between ions of different charges. Therefore, the electrostatic attraction between the reactants does not need much energy to bring them together in order to form the activated complexes.

Redox reactions involving $IrCl_6^{2-}$ as an oxidizing agent are usually proceeding via either or both outer-sphere and inner-sphere mechanisms. The form of the rate law (5) provides no information regarding these two mechanisms. The absorbance changes observed for the reaction were consistent with a simple one-electron transfer mechanism and no evidence could be obtained for the presence of appreciable amounts of precursor or successor binuclear complexes. However, some information may be derived by examination of the magnitude of the rate constant. Using value of $K_1 \simeq 10^{-4}$ mol dm$^{-3}$ reported elsewhere[18] ,the rate constant of the principal path, i.e. the reaction between $Sn(OH)$ and $IrCl_6^{2-}$, is $1 \cdot 3 \cdot 10^5$ mol$^{-1}$ dm$^3$ s$^{-1}$ at 25°C. This value lies in the range of outer-sphere limits for the $IrCl_6^{2-}$-metal ion redox reactions[10,19,20]. However, this suggestion is not conclusive since no information is available on the substitution reactions of Sn(II) to examine the validity of Marcus theory[21].

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