Kinetics of the reduction of hexachloroiridate (IV) by L-methionine in aqueous solutions

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The kinetics of the reduction of hexachloroiridate (IV) by L-methionine in aqueous solution has been studied. The data are consistent with the rate law:

$$- \frac{d[\text{oxidant}]}{dt} = k_3 [\text{oxidant}] [\text{reductant}] [H^+]$$

with $k_3 = 1.58 \pm 0.06 \text{ mol}^{-2} \text{dm}^6 \text{s}^{-1}$, $\Delta H^* = 31.3 \pm 2.1 \text{ kJ mol}^{-1}$, $\Delta S^* = 210 \pm 11.6 \text{ JK}^{-1} \text{mol}^{-1}$ at $I = 1.0 \text{ mol dm}^{-3}$ (NaCl) and $T = 25.5^\circ \text{C}$. Free radicals are unimportant in the reaction and the reduction is rationalised in terms of an outer-sphere mechanism.

The reduction of hexachloroiridate (IV), $\text{IrCl}_6^{2-}$, by thiourea, $\text{CS(NH}_2)_2$, and substituted thioureas, as well as amino acids of the type $\text{NH}_2\text{CH(R)COOH}$ (ref. 2) have been studied. Reaction occurs at the sulphur end of the former substrates and at the nitrogen in the latter. We herein report the reduction of $\text{IrCl}_6^{2-}$ with methionine. This substrate has three possible reaction sites viz O, N and S and its reactions with $\text{HCrO}_4^-$ (ref. 3) and $\text{AuCl}_4^-$ (ref. 4) have suggested that in spite of the presence of a methyl group on the sulphur site, the formation of sulphur-bonded inner sphere complexes are feasible. In the event that intermediate complex formation is important in the present study, the choice of the thiol should reveal the effectiveness of O, N, and S as binding sites.

Experimental

Stock solutions of $\text{IrCl}_6^{2-}$ were prepared by dissolving $\text{Na}_2\text{IrCl}_6$ (Aldrich) in HCl (1 mol dm$^{-3}$) and standardized spectrophotometrically$^2$ at 487 nm using $\varepsilon = 4060 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$. L-methionine (BDH reagent) was used without further purification. HCl was used to investigate the $[H^+]$ dependence while NaCl was the supporting electrolyte.

Using varied amounts of methionine in the range $(0.8-8.0) \times 10^{-5} \text{ mol dm}^{-3}$ and $[\text{IrCl}_6^{2-}] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$ at $[\text{H}^+] = 0.5 \text{ mol dm}^{-3}$ and $I = 1.0 \text{ mol dm}^{-3}$ (NaCl), the stoichiometry was determined spectrophotometrically at 487 nm, as described elsewhere$^5,6$.

The electronic spectra of solutions containing $\text{IrCl}_6^{2-} (1.0-5.0) \times 10^{-5} \text{ mol dm}^{-3}$ in $[\text{H}^+] = 0.01-0.2 \text{ mol dm}^{-3}$ and those containing mixtures of $\text{IrCl}_6^{2-} (2 \times 10^{-5} \text{ mol dm}^{-3})$, [methionine] = (0.2-2.0) $\times 10^{-2}$ mol dm$^{-3}$ were compared between 400 and 700 nm. No clear shift in $\lambda_{\max}$ or change in $\varepsilon$ value of $\text{IrCl}_6^{2-}$ was observed.

The rates of reaction were followed by monitoring changes in absorbance due to $\text{IrCl}_6^{2-}$ at 487 nm. Pseudo-first order plots were linear to greater than 80% reaction. The strict linearity of these plots suggests that the rate is first order in $\text{IrCl}_6^{2-}$. Pseudo-first order rate constants, $k_{obs}$, obtained from the slopes of these plots under various conditions are presented in Table 1.

<table>
<thead>
<tr>
<th>$10^4 [\text{RSCH}_3]$ (mol dm$^{-3}$)</th>
<th>$[\text{H}^+]$ (mol dm$^{-3}$)</th>
<th>$I$ (mol dm$^{-3}$)</th>
<th>$10^4 k_{obs}$ (s$^{-1}$)</th>
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$[\text{IrCl}_6^{2-}] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$ throughout.
Data at other temperatures are available on request.

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Results and discussion

The salient features of the results are summarized below:

i) Spectrophotometric titration results and product analyses are consistent with Eq. (1)

\[
\text{IrCl}_6^{2-} + \text{R(HS)}^+ \text{CH}_3 + \text{H}_2\text{O} \rightarrow \text{IrCl}_6^{2-} + \text{R(CH}_3)\text{S} = \text{O} + 2\text{H}^+ \quad \ldots (1)
\]

Table 2—Kinetic and thermodynamic parameters for the oxidation of methionine by some oxidants at 25°C

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>(E^o) (volts)</th>
<th>(\log a) (mol (^{-2}) dm (^6) s (^{-1}))</th>
<th>Ref.</th>
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<tr>
<td>(\text{IrCl}_6^{2-})</td>
<td>0.87</td>
<td>0.197</td>
<td>This work</td>
</tr>
<tr>
<td>(\text{Fe(phen)}^2+)</td>
<td>0.92</td>
<td>-0.754</td>
<td>5</td>
</tr>
<tr>
<td>(\text{Fe(bipy)}^2+)</td>
<td>1.00</td>
<td>-1.00</td>
<td>5</td>
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</table>

where \(\text{R(HS)}^+ \text{CH}_3\) is the protonated methionine, \(\text{CH}_3(\text{HS})^+ \text{CH}_2\text{CHNH}_2\text{CO}_2\text{H}\). Methionine sulfoxide was confirmed as the reaction product as described previously\(^3\) while \(\text{IrCl}_6^{2-}\) was characterized as the sole metallic product by oxidizing the reaction product with \(\text{S}_2\text{O}_8^{2-}\) followed by spectrophotometric determination of \(\text{IrCl}_6^{2-}\) \((\lambda_{\text{max}} = 487 \text{ nm})\). (ref. 2). The formation of \(\text{RCH}_3 = \text{O}\) suggests that reaction occurred at the sulphur.

ii) Plots of \(k_{\text{obs}}\) versus [methionine] were linear with positive slopes at a constant temperature, showing that the reaction is first order with respect to methionine. Thus

\[
- \frac{d[\text{IrCl}_6^{2-}]}{dt} = k_2 [\text{IrCl}_6^{2-}][\text{methionine}] \quad \ldots (2)
\]

iii) A plot of \(k_2\) versus [\(\text{H}^+\)] at fixed [methionine] and temperature was linear passing through the origin. Hence the overall rate law is

\[
- \frac{d[\text{IrCl}_6^{2-}]}{dt} = k_3 [\text{IrCl}_6^{2-}][\text{methionine}][\text{H}^+] \quad \ldots (3)
\]

iv) The values of \(k_3\) at 15, 20, 25.5 and 30.0°C were 0.94 ± 0.02, 1.24 ± 0.05, 1.58 ± 0.06, and 1.86 ± 0.12 mol \(^{-2}\) dm \(^6\) s \(^{-1}\) respectively, which yielded \(\Delta H = 31.3 ± 2.1\) kJ mol \(^{-1}\) and \(\Delta S = -210 ± 11\) JK \(^{-1}\) mol \(^{-1}\).

v) Tests for polymerization of acrylamide or acrylonitrile, performed as described earlier\(^6\) did not yield the required polymers, suggesting that free radicals are unimportant in this reaction in contrast to the corresponding reactions of \(\text{IrCl}_6^{2-}\) with \(\text{NH}_2\text{CH(R)}\text{COOH}\) (ref. 2).

vi) Michaelis-Menton plot of \(1/k_{\text{obs}}\) versus \(1/[\text{methionine}]\), as applied by Kumar et al.\(^2\) was linear without an appreciable intercept at each temperature, indicating the absence of intermediates with significant formation constants.

In line with arguments presented earlier\(^2,3\), protonated methionine \(\text{R(HS)}^+ \text{CH}_3\), is the principal reductant. Since \(\text{IrCl}_6^{2-}\) does not enter into deprotonation-protonation equilibria over the acid range employed\(^2\), the observed [\(\text{H}^+\)] dependence almost certainly arose from the interaction between the Zwitterion of the substrate and the proton. Further support for reaction between \(\text{IrCl}_6^{2-}\) and \(\text{R(HS)}^+ \text{CH}_3\) is gained from the dependence of the rate on the ionic strength (Table 1), which suggests a negative Bronsted-Debye salt effect reminiscent of reaction between oppositely charged species\(^7\).

A reaction sequence consistent with the results is presented in Scheme 1.

\[
\text{RSCH}_3 + \text{H}^+ \underset{K}{\rightarrow} \text{R(HS)}^+ \text{CH}_3 \quad \ldots (4)
\]

\[
\text{R(HS)}^+ \text{CH}_3 + \text{IrCl}_6^{2-} \rightarrow \text{IrCl}_6^{2-}.\text{R(HS)}^+ \text{CH}_3 \quad \ldots (5)
\]

\[
[\text{IrCl}_6^{2-}.\text{R(HS)}^+ \text{CH}_3] + \text{H}_2\text{O} \rightarrow [\text{IrCl}_6^{2-} + \text{R(CH}_3)\text{S} = \text{O} + 2\text{H}^+] \quad \ldots (6)
\]

Scheme 1

This Scheme leads to Eq. (7)

\[
- \frac{d[\text{IrCl}_6^{2-}]}{dt} = KKak_0 [\text{IrCl}_6^{2-}][\text{RSCH}_3][\text{H}^+]/(1 + K_a[\text{H}^+] + KKak_0 [\text{IrCl}_6^{2-}][\text{H}^+]) \quad \ldots (7)
\]

where

\[
[\text{RSCH}_3] = [\text{RSCH}_3]/(1 + K_a[\text{H}^+] + KKak_0 [\text{IrCl}_6^{2-}][\text{H}^+])\]

If \(1 >> (K_a[\text{H}^+] + KK_k_0 [\text{IrCl}_6^{2-}][\text{H}^+])\), Eq. (7) reduces to the observed rate equation (3) with \(k_3 = KK_k_0\).

The rate of aquation of the first chloride in \(\text{IrCl}_6^{2-}\) \((10^{-6} \text{s}^{-1})\) depicts its substitution inertness\(^8\). When this is judged along with the fact that the most susceptible reaction site on methionine is blocked by a methyl group, the species \(\text{IrCl}_6^{2-}, \text{R(HS)}^+ \text{CH}_3\) may be regarded as an ion-pair. Although it may be argued that a binuclear intermediate as in the corresponding reactions with amino acids\(^2\) and uranium (IV)\(^9\) could not be excluded, we found no kinetic or spectrophotometric evidence in its favour.

As a further test of the outer sphere nature of the title reaction, we interpreted our data in terms
of Marcus theory\(^9\). A plot of \(\log a\) (\(a\) is rate constant for the redox reaction of \(R(HS^+)CH_3\) with \(IrCl_6^{2-}\), \(Fe(phen)_3^{3+}\) and \(Fe(bipy)_3^{3+}\) (Table 2)) versus \(E^0\) of the oxidants was linear (\(r=0.92\)) with a slope of 8.2 \(v^{-1}\), in excellent agreement with predicted value of 8.5 \(v^{-1}\) for reactions occurring by the outer sphere mechanism.

References