

KINETICS AND MECHANISM OF HEXACHLOROIRIDATE(IV) OXIDATION OF ARSENIC(III) IN ACIDIC PERCHLORATE SOLUTIONS

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The kinetics of oxidation of arsenic(III) by hexachloroiridate(IV) at lower acid concentrations and at constant ionic strength of 1.0 mol dm^{-3} have been investigated spectrophotometrically. A first-order reaction in $[\text{IrCl}_6^{2-}]$ and fractional order with respect to arsenic(III) have been observed. A kinetic evidence for the formation of an intermediate complex between the hydrolyzed arsenic(III) species and the oxidant was presented. The results showed that decreasing the $[\text{H}^+]$ is accompanied by an appreciable acceleration of the rate of oxidation. The activation parameters have been evaluated and a mechanism consistent with the kinetic results was suggested.

We have been interested in the oxidation of two-equivalent reductants by hexachloroiridate(IV) in aqueous perchloric acid¹⁻³. This interest has now been extended to the use of arsenic(III) ion since the survey of the literature indicated that such a study had not been attempted.

In analogous kinetic studies performed previously on the oxidation of uranium(IV) (refs^{1,2}) and tin(II) (ref.³) we had been able to conclude that the reaction mechanism in these redox systems takes place by either outer-³ or inner-sphere^{1,2} mechanisms for electron-transfer. The later mechanism proceeds via intermediate complex formation. Therefore, the present study is of great importance and has been undertaken in an attempt to elucidate a suitable reaction mechanism for the oxidation of two equivalent reductants by this oxidant since hexachloroiridate(IV) is known to supply a bridging ligand if the reducing agent is substitution-labile or it expands its coordination sphere upon oxidation.

EXPERIMENTAL

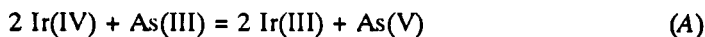
All materials used were of analytical grade. Doubly distilled water was used in all preparations. Solutions of sodium hexachloroiridate(IV) (Ventron Corp) were freshly prepared before each experiment by dissolving the appropriate amount of the reagent in perchloric-perchlorate solutions to minimize the rate of aquation^{4,5}. Optical density vs concentration plots for acidified hexachloroiridate(IV) showed that Beer's law is obeyed at wavelengths of 418 and 489 nm and the molar extinction coefficients were found to be $3\,320 \pm 16$ and $4\,070 \pm 20 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively in good agreement with previous results⁶. Sodium arsenite NaAsO_2 (Merck) was used without further purification. Sodium perchlorate was prepared by

neutralization of sodium carbonate (AnalaR) with 60% perchloric acid (BDH). Solid sodium perchlorate was obtained by partial crystallization, followed by three recrystallizations.

Kinetic measurements. The reaction was carried out under pseudofirst-order conditions in the presence of a large excess of arsenic(III) over the IrCl_6^{2-} concentration. The course of the reaction was followed by recording the decrease in absorbance of IrCl_6^{2-} at wavelength of 489 nm, its absorption maximum, on a Shimadzu UV-double beam spectrophotometer using cells of pathlength 1 cm. The cell compartment of the spectrophotometer was thermostated to within ± 0.1 °C. The procedure for the kinetic measurements was as described earlier³. No interference has been found from other reagents at this wavelength. The spectral changes during the reaction are shown in Fig. 1. The ionic strength of the reaction mixture was maintained constant by adding sodium perchlorate.

RESULTS

The estimated reduction potential for $\text{Ir}^{\text{IV}}/\text{Ir}^{\text{III}}$ (+0.87 V) and $\text{As}^{\text{V}}/\text{As}^{\text{III}}$ (-0.56 V) couples⁷ provides assurance that the reaction (A) is more favourable thermodynamically.



Preliminary experiments indicated that the reaction was relatively slow at higher acidic concentrations, and, hence the kinetics were performed at lower $[\text{H}^+]$.

Stoichiometry. Hexachloroiridate(IV) and arsenic(III) at different concentrations in the presence of $0.3 \text{ mol dm}^{-3} \text{ HClO}_4$ adjusted to constant ionic strength were kept for 24 h at room temperature. Excess $[\text{IrCl}_6^{2-}]$ was estimated periodically until it reached a constant value. It has been found that two moles of IrCl_6^{2-} are consumed by each mol of As(III) indicating that Eq. (A) is more suitable to express the reaction stoichiometry.

Dependence of reaction rate on $[\text{IrCl}_6^{2-}]$ and $[\text{As(III)}]$. The reaction order with respect to IrCl_6^{2-} concentration was determined by studying the oxidation reaction at the conditions; $[\text{As(III)}] = 1 \cdot 10^{-2} \text{ mol dm}^{-3}$, $[\text{IrCl}_6^{2-}] = 2.0 \cdot 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$ and 25 °C. Plots of $\ln(\text{absorbance})$ versus time were linear for three half-lives of the reaction. This linearity shows that the reaction is first order in $[\text{IrCl}_6^{2-}]$. The first-order dependence was indicated not only by the linearity of the pseudofirst-order plots, but also by the independence of the observed first-order rate constants, k_{obs} , on initial $[\text{IrCl}_6^{2-}]$ values from $1 \cdot 10^{-4}$ to $4 \cdot 10^{-4} \text{ mol dm}^{-3}$ at a number of different constant concentrations of all other reagents. The dependence of k_{obs} values on $[\text{As(III)}]$ was found to follow Michaelis-Menten kinetics⁸. This means that a plot of $(k_{\text{obs}})^{-1}$ against $[\text{As(III)}]^{-1}$ should be linear as is observed experimentally (Fig. 2). The good linearity obtained in addition to the positive intercept on the $(k_{\text{obs}})^{-1}$ axis indicates the formation of intermediate complex in the oxidation of As(III) by IrCl_6^{2-} ion.

Dependence of reaction rate on $[\text{H}^+]$. To clarify the effect of $[\text{H}^+]$ on the reaction rate to elucidate the reaction mechanism, kinetic measurements were performed in $\text{HClO}_4\text{-NaClO}_4$ of different $[\text{H}^+]$ at constant ionic strength and temperature. The decrease in the acid concentration was found to accelerate the reaction rate. When the

observed first-order rate constants were plotted against $[\text{H}^+]^{-1}$, the curved lines were obtained as shown in Fig. 3.

Dependence of reaction rate on ionic strength. In order to investigate the effect of ionic strength on the rate of reaction with the aim to shed some light on the reactive species in the rate-determining step, kinetic runs were performed at constant H^+ concentration with changing the ionic strength. The values of k_{obs} at $I = 1.0, 0.5$ and 0.25 mol dm^{-3} and fixed $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$, $[\text{As(III)}] = 5 \cdot 10^{-3} \text{ mol dm}^{-3}$, $[\text{IrCl}_6^{2-}] = 2 \cdot 10^{-4} \text{ mol dm}^{-3}$ and $25 \text{ }^\circ\text{C}$, were found to be $1.4 \cdot 10^{-4}$, $3.1 \cdot 10^{-4}$ and $6.9 \cdot 10^{-4} \text{ s}^{-1}$, respectively. A plot of $\log k_{\text{obs}}$ against $I^{0.5}$ according to the Debye-Hückel equation was fairly linear with a negative slope.

Dependence of reaction rate on temperature. To determine the activation parameters, the reaction was carried out at four temperatures between 25 and $40 \text{ }^\circ\text{C}$ and at constant ionic strength and $[\text{H}^+]$. A plot of data in accordance to the Eyring's equation gave good straight line from which the slope and intercept, the enthalpy and entropy of acti-

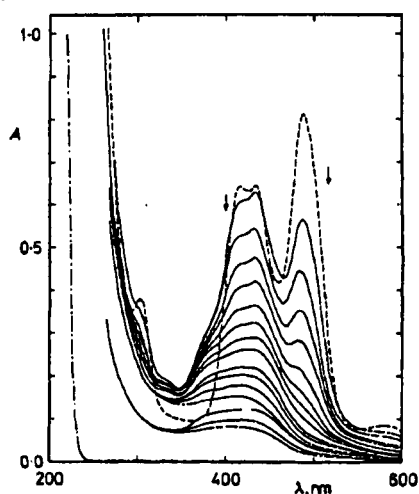


FIG. 1

Spectral changes during oxidation of As(III) by hexachloroiridate(IV) at $[\text{IrCl}_6^{2-}] = 1.99 \cdot 10^{-4} \text{ mol dm}^{-3}$, $[\text{As(III)}] = 5 \cdot 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 2.5 \cdot 10^{-2} \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$; time scanning intervals 8 min, temperature $40 \text{ }^\circ\text{C}$. IrCl_6^{2-} (broken line), As(III) (dashed line), mixture (solid line)

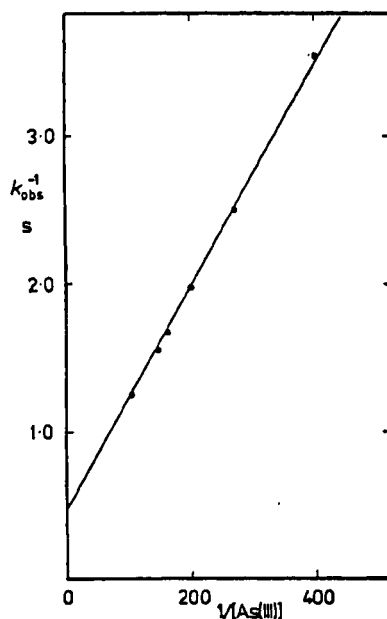


FIG. 2

Representative Michaelis-Menten plot at $[\text{IrCl}_6^{2-}] = 2.0 \cdot 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$ at $25 \text{ }^\circ\text{C}$

vation were determined ($\Delta H^\ddagger = 51.5 \pm 0.8 \text{ kJ mol}^{-1}$, $\Delta G^\ddagger = 93.5 \pm 1.8 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -141.0 \pm 3.5 \text{ J mol}^{-1} \text{ K}^{-1}$).

DISCUSSION

The paths by which arsenic(III) is oxidized by one- and two-equivalent oxidants, have been the subject of much discussions⁹⁻¹³. Two possible reaction mechanisms were suggested; one being a successive one-electron transfer mechanism, $\text{As(III)} \rightarrow \text{As(IV)} \rightarrow \text{As(V)}$ with formation of arsenic(IV) as an intermediate¹⁴⁻¹⁶. The other mechanism corresponds to a simultaneous two-electron transfer in a single step, $\text{As(III)} \rightarrow \text{As(V)}$ (refs^{17,18}). It depends on the nature of the oxidant and reaction conditions whether we deal with one- or two-equivalent changes.

The formation of an intermediate complex in the present reaction was supported not only by the kinetic evidence of the Michaelis-Menten plot but also by the change observed for the IrCl_6^{2-} spectrum in the UV-VIS region on mixing the ion with arsenic(III) (Fig. 1). The increase of k_{obs} values with decreasing $[\text{H}^+]$ suggests that the hydrolyzed species of As(III) may be the reactive species. It has been proposed that arsenic(III) tends to exist as monomeric species in aqueous solutions¹⁹⁻²¹, thus

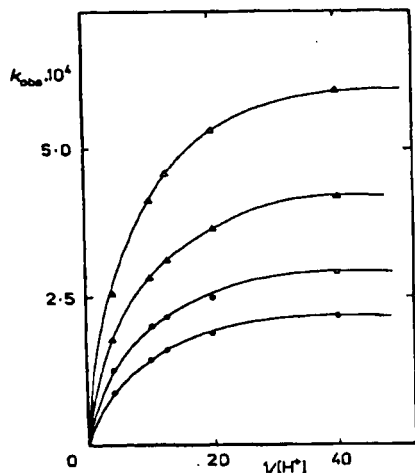


FIG. 3
Hydrogen-ion dependence of the pseudofirst-order rate constant k_{obs} (in s^{-1}). Conditions: $[\text{IrCl}_6^{2-}] = 2.0 \cdot 10^{-4} \text{ mol dm}^{-3}$, $[\text{As(III)}] = 5 \cdot 10^{-3} \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$. Temperature, °C: 25 (●), 30 (○), 35 (▲), 40 (Δ)

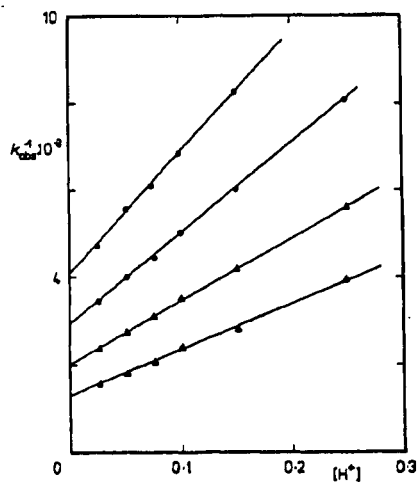
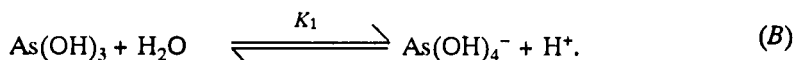
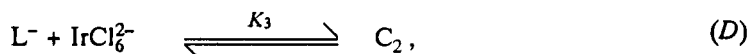
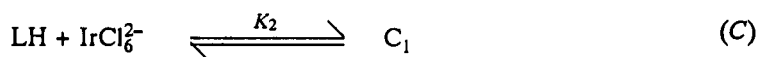


FIG. 4
Plots of $1/k_{\text{obs}}$ (in s) vs $[\text{H}^+]$ (in mol dm^{-3}) at $[\text{IrCl}_6^{2-}]$, $[\text{As(III)}]$, and I as in Fig. 3. Temperature, °C: 25 (●), 30 (○), 35 (▲), 40 (Δ)

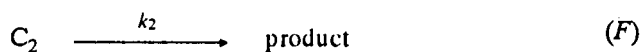
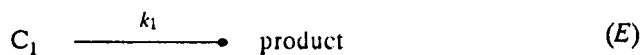


Again, the negative slope observed for the $\log k_{\text{obs}}$ vs $I^{0.5}$ plot indicates that the rate-determining step may be reaction between two anions or between a negative ion and neutral molecule.

In view of these facts, the most likely reaction mechanism involves two competitive reactions (C) and (D),



where LH and L^- denote the non-hydrolyzed and hydrolyzed As(III) species, respectively. The intermediates C_1 and C_2 are formed and subsequently undergo further dissociation to give the products in the rate-determining steps (Eqs (E) and (F)).



The change in the rate constant with change in the hydrogen ion concentration may be expressed by Eq. (1)

$$-d[\text{IrCl}_6^{2-}]/dt = ((k_1K_2 + k_2K_1K_3[\text{H}^+]^{-1})[\text{LH}][\text{IrCl}_6^{2-}]_{\text{T}})/(1 + (k_2 + k_1K_3[\text{H}^+]^{-1})[\text{LH}]), \quad (1)$$

where $[\text{IrCl}_6^{2-}]_{\text{T}}$ is the total concentration of hexachloroiridate(IV). In the presence of a large excess of arsenic(III) over the IrCl_6^{2-} concentration, the rate law is as in Eq. (2).

$$-d[\text{IrCl}_6^{2-}]/dt = k_{\text{obs}} [\text{IrCl}_6^{2-}]_{\text{T}} \quad (2)$$

Comparison of Eqs (1) and (2) thus yields the following relationship

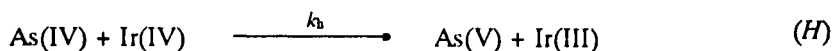
$$k_{\text{obs}} = ((k_1K_2 + k_2K_1K_3[\text{H}^+]^{-1}) [\text{LH}]) / (1 + K_2 [\text{LH}] + K_1K_3 [\text{H}^+]^{-1}[\text{LH}]). \quad (3)$$

The experimental results described here are not in agreement with the rate equation (3) since the plots of k_{obs} against $[\text{H}^+]^{-1}$ gave curved lines (Fig. 3). This means that the first term corresponding to the unhydrolyzed species of Eq. (E) is relatively small and may be neglected. Hence, reaction (F) may be considered as the sole path and the rate equation (3) can now be rewritten to Eq. (4))

$$1/k_{\text{obs}} = [H^+] / k_2' [LH] + 1/k_2, \quad (4)$$

where $k_2' = k_2 K_1 K_3$. According to Eq. (4), at constant $[H^+]$, a plot of $1/k_{\text{obs}}$ versus $1/[LH]$ should be linear as is observed experimentally (Fig. 2). Again, a plot of $1/k_{\text{obs}}$ against $[H^+]$ at constant $[LH]$ gave good straight lines from whose slopes and intercepts the values of k_2' and k_2 can be calculated. Typical plots are shown in Fig. 4. Hence, Eq. (4) is considered as the appropriate rate equation for the oxidation of As(III) by IrCl_6^{2-} ion. The values of k_2 and k_2' listed in Table I were calculated by the least-squares method ($[\text{As(III)}] = 5 \cdot 10^{-3} \text{ mol dm}^{-3}$, $[\text{IrCl}_6^{2-}] = 2 \cdot 10^{-4} \text{ mol dm}^{-3}$ and $I = 1.0 \text{ mol dm}^{-3}$).

The oxidation of arsenic(III) by IrCl_6^{2-} ion may proceed through successive one-electron changes or a simultaneous two-electron transfer mechanism. The former mechanism can be represented by the sequence reactions (G) and (H).



Assuming a steady-state approximation of As(IV) intermediate, the following relationship is obtained

$$-d[\text{Ir(IV)}] / dt = 2 k_g [\text{As(III)}] [\text{Ir(IV)}]. \quad (6)$$

It has been emphasized by Waters et al.¹⁸ that arsenic(III) is not oxidized by one-equivalent oxidants without the addition of a catalyst, but it is readily oxidized by two-equivalent oxidants. This suggestion leads us to take into consideration the latter mechanism because of the absence of catalysts in the present study, i.e., simultaneous two-electron-transfer changes,

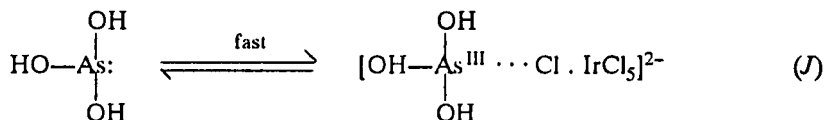


TABLE I
Temperature dependence of k_2 and k_2' constants

Temperature, °C	$k_2 \cdot 10^4, \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$	$k_2' \cdot 10^3, \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
25	2.46	7.02
30	3.41	9.81
35	4.93	11.37
40	7.19	19.92

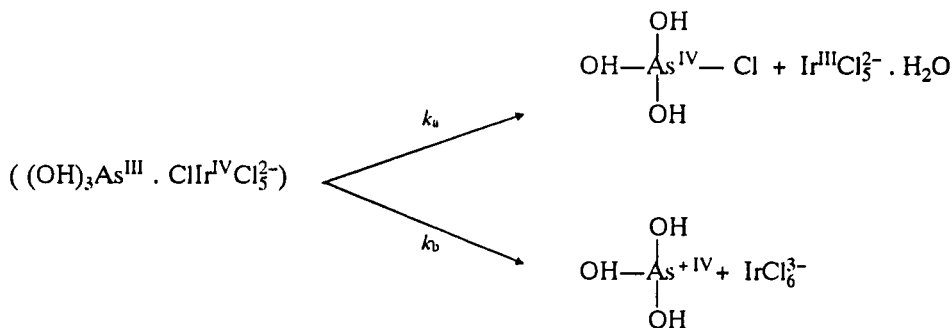
However, such a mechanism is not favoured kinetically as it disagrees with the observed stoichiometry and well known one-equivalent nature of Ir(IV). Again, the formed Ir(II) is unstable and should react in some way to form stable Ir(III) product.

In view of these facts and experimental observations, it is more reasonable to suggest a successive one electron-transfer mechanism with formation of an intermediate complex in which chloride ion from the inert IrCl_6^{2-} acts as a bridging ligand in the labile arsenic(III) coordination-sphere (Eq. (J)) for the oxidation of As(III) by IrCl_6^{2-} .



The formation of this 1 : 1 complex with chloride bridge will facilitate the transfer of electrons from As^{III} to Ir^{IV} in the subsequent rate-determining step. Since hexachloroiridate(IV) is known to be extremely inert, whereas arsenic(III) on the other hand is labile, the reaction mechanism is consistent with either inner- or outer-sphere type for electron-transfer.

It has been reported previously²²⁻²⁶ that the entropy of activation tends to be more negative for reactions of inner-sphere type, whereas the reactions of positive ΔS^\ddagger values proceed via outer-sphere mechanism. In view of this argument, the outer-sphere mechanism may be excluded (see data on p. 1454). Hence, the more favourable mechanism is that corresponding to inner-sphere type in which decomposition of the formed complex in the rate determining step takes place through two paths (k_a) and (k_b), respectively.



Our experimental results based on the spectrophotometric and ion exchange techniques^{3,4,27} indicated that the final species of reduced Ir(IV) were IrCl_6^{3-} and not $\text{IrCl}_5^{2-} \cdot \text{H}_2\text{O}$. Hence, it seems likely that k_b is the more reasonable path for the decomposition of the intermediate complex to give reaction products.

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