A reinvestigation of hexachloroiridate (IV) oxidation of arsenous acid in acid medium: Intra-contradictions in the earlier study

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In the oxidation of arsenious acid, As(III), by [IrCl₆]²⁻ ion in perchloric acid (µ = 1 mol dm⁻³, NaClO₄), Δ[As(OH)₃]/Δ[As(III)] = 1.99 ± 0.07. The reaction is first order both with respect to [As(III)] and [Ir(IV)] ions. The kₜₚₑₙ, the pseudo-first order rate constant ([As(III)]ₚₑₙ·[Ir(IV)]), is independent of ionic strength (µ), [H⁺], [Ir(III)] and [As(V)]. A rapid scan spectra of the reaction mixture indicates the formation of a weak intermediate which is probably a chlorine-bridged complex between [Ir(IV)] and As(III). The kinetic viability of such an intermediate is also indicated by the change in the absorbance of the reaction mixture compared to that of Ir(IV) solution of the same concentration as noted from stopped-flow measurements. The rate determining step is the disproportionation of the weak complex which is followed by the rapid oxidation of H₂AsO₃ radical intermediate by a second Ir(IV) ion. The hydrolysis of [IrCl₆]³⁻ over the period of time (the reaction mixture was left overnight for completion) resulted in the formation of [IrCl₆(OH)₄]²⁻ which was spectrophotometrically detected in quantitative yield.

The contradictory results of an earlier study are discussed and rationalised by suggesting an alternate mechanism in which [IrCl₆(OH)₂]²⁻ and As(OH)₃ are the reactive Ir(IV) and As(III) species respectively.

Materials and Methods
The freshly prepared solutions of [IrCl₆]³⁻ and [IrCl₆]²⁻ (Johnson Matthey) in HClO₄ were standardised spectrophotometrically and used immediately though such acidic solutions are stated to be stable. NaClO₄ used to adjust the ionic strength, was prepared by neutralising Na₂CO₃ (Sarabhai-M, GR) by HClO₄ (Merck, GR), LiClO₄ solution was prepared by weighing the sample (G.F. Smith). The solutions of As₂O₅ (May & Baker, AR), and Na₃H₂AsO₄ (Merck, GR) were standardised as described in the literature. Doubly distilled water was used throughout the experiment.

Standardisation of [IrCl₆]³⁻
Two identical solutions from the same source [IrCl₆]³⁻ (0.003 mol dm⁻³) were prepared in 2.5 mol dm⁻³ (i) HClO₄ and (ii) Cl₂ saturated HClO₄. The later oxidises [IrCl₆]³⁻ to [IrCl₆]²⁻ (ref. 9). The respective HClO₄ was used as the reference. The [IrCl₆]²⁻ in solution (i) and (ii), calculated from the respective absorbance at 488 nm (ε₄₈₈ (ref. 9) = 4050 dm³ mol⁻¹ cm⁻¹), was 2.63 x 10⁻³ and 2.97 x 10⁻³ mol dm⁻³ respectively. The sample, thus, had some [IrCl₆]³⁻ as impurity.

Detection of [IrCl₆(OH)₂]²⁻
The spectral characters of [IrCl₆]³⁻ and [IrCl₆(OH)₂]²⁻ are very similar making it difficult to identify one from the other. These Ir(III) complexes are rapidly and quantitatively oxidised by chlorine to corresponding Ir(IV) complexes which
have different spectra. The reaction mixture, 
\(10^{4}[\text{IrCl}_6^{3-}] = 3.10, \ 10^{4}[\text{As(OH)}_2] = 2.0 \) and 
\([\text{HClO}_4] = 1 \text{ mol dm}^{-3}\), left overnight for completion, was diluted by a factor of two with Cl_2 saturated HClO_4 ([HClO_4] = 2.5 mol dm^{-3}). The absorbance of the resulting solution was 0.516 at 448 nm in agreement with known \(A_{\text{max}}\) for \([\text{IrCl}_5(\text{OH}_2)_2]^{-}\) at 450 nm \((\varepsilon_{450} = 3320 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1})\). Thus in the diluted solution \([\text{IrCl}_5(\text{OH}_2)_2]^{-}\) is \(1.55 \times 10^{-4} \text{ mol dm}^{-3}\) which is about the same as the initial \([\text{IrCl}_6]^{3-}\) which on reduction was quantitatively aquated to \([\text{IrCl}_5(\text{OH}_2)_2]^{-}\) in the overnight period.

**Test for the intermediate complex**

The rapid scan spectra of the reaction mixture, covering 48 nm on either side of 488 nm, the \(\lambda_{\text{max}}\) of \([\text{IrCl}_6]^{3-}\) ion, were recorded on a Union-Giken RA-401 stopped-flow spectrophotometer fitted with RA-415 rapid scan attachment which replaces photomultiplier tube with a multichannel photodetector head (MCPD). The MCPD measures the change of spectrum instead of the change in absorbance at a fixed wavelength. The photodetector itself is a photodiode array. Spectral resolution is 256 points per 96 nm. A 3.5 mm slit and water was used as reference. A total of 16 spectra could be recorded at predetermined intervals of time. In Fig. 1 are shown the even numbered spectra (interval = 0.2 s) for greater clarity. The reproducibility of the spectra was ascertained by recording the spectra thrice.

A study of the spectra shows that there was an initial increase in the absorbance (spectrum 6 > spectrum 4 > spectrum 2) followed by the decrease in the absorbance of the subsequent spectra (12-16 (almost constant) < spectrum 10 < spectrum 8 < spectrum 6).

**Stopped-flow measurements**

The absorbencies of the reaction mixture and \([\text{Ir(IV)}]\) solution of the same concentration were measured over 440 to 540 nm at intervals of 10 nm by the stopped-flow immediately after the respective solutions were pushed into the reaction cell. A perceptible, though not significant, change was noted in the two absorbencies.

**Kinetic measurements**

The kinetics was studied under pseudo-first order conditions ([As(III)] \(\geq 10 [\text{Ir(IV)}]\)) at constant ionic strength (1.0 mol dm^{-3}, NaClO_4) in the presence of HClO_4. The absorbance of the unreacted \([\text{Ir(IV)}]\) at any given time was measured at 488 nm using a SFA-11 colorimeter (Photoelectric Instruments, Jodhpur), modelled on the line of stopped-flow spectrophotometer. The solutions of H_2AsO_3, H_3AsO_4 and Ir(III) were transparent at this wavelength. The temperature of the reactant solutions and the mixing cell was maintained \((\pm 0.1^\circ\text{C})\) by circulating water from a Haake D8G circulatory water bath. The plots between \(\log(A_t - A_\infty)\) versus \(t\), where \(A_t\) and \(A_\infty\) are the absorbencies at time \(t\) and at the end of the reaction respectively, were linear for more than three half-lives. The mean value of \(k_{\text{obs}}\) was reproducible within 3-5%. The use of LiClO_4 in place of NaClO_4 indicated no significant change in the \(k_{\text{obs}}\) values indicating the absence of medium effect. Hence, NaClO_4 was used throughout the study.

**Stoichiometry**

The stoichiometry of the reaction was studied...
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by using an excess concentration of either HAsO₃ or H₃AsO₄ over the other. In each case H₃AsO₄ was estimated at the completion of the reaction. The stoichiometry is given by Eq. (1).

**Results**

Figure 2 shows that kₐ decreases linearly with [As(III)] at all temperatures and the plots passed through the origin indicating a first order dependence in [As(III)]. Hassan, however, reported a fractional order dependence in [As(III)] as the plots of kₐ against [As(III)] were independent of [H⁺] in the range 0.01-1.0 mol dm⁻³.

A decrease in the kₐ with increasing [H⁺] to 0.3 mol dm⁻³ was reported in the previous study. The invariance of the kₐ with the ionic strength (NaClO₄) indicated that one of the reactants carried no charge. Further, the kₐ was unaffected by the added [Ir(III)], [As(V)] and [O⁻] indicating that none of these ions appeared in any equilibrium prior to the rate determining step.

**Discussion**

The spectral changes in the reaction mixture are not indicative of the formation of an intermediate which, at best, represented the decay in the absorbance of the reacting Ir(IV). The formation of a weak intermediate is indicated by the rapid scan spectra of the reaction mixture. The weak intermediate is most likely a chlorine-bridged complex for such chlorine-bridged complexes have been proposed between active H₃PO₄ and As(III) in the presence of HCl. The kinetic viability of the formation of an intermediate is also supported by a perceptible though not significant change in the absorbance of the As(OH₃) atom which has 4p₃ and 4s² electrons in the chlorine-bridged complex. The 4p₃ configuration is also supported by the absence of any perceptible chlorine atom in the coordination number of As(OH₃), which suggests that the chlorine atom is in a chlorine-bridged complex.

The distribution curve of H₃AsO₄ at different pH indicated that H₃AsO₄ is not protonated in the pH range used in the study. Similarly, [IrCl₄]²⁻, having a negligible base strength, cannot be protonated. Hence H⁺ is unlikely to influence the rate which affects the geometry of As(OH₃). However, a speculation about the change in the geometry of As(OH₃) due to the change in the coordination number of the oxygen atom in arsenic acid cannot be provided by Ir(IV) which has to come through the solvent.

**Figure 2**

- Linear plots of kₐ against [As(III)] passing through the origin at 35°C (I), 40°C (II), 45°C (III) and 50°C (IV). The distributions of H₃AsO₄ are shown in Table 1. [2H⁺ + H₃AsO₄ + H₂O → 2H⁺ + H₃AsO₄] (2)

†...
is confirmed from the fact that \( k_{\text{obs}} \) is unaffected by \([H^+]\). The reactive entities are therefore \( \text{H}_3\text{AsO}_3 \) and \([\text{IrCl}_6]^2-\). The predicted effect of the charges on these two reactants is consistent with the observed effect of ionic strength. We, therefore, propose the reaction mechanism given in Eqs (3)-(5) and the nature of electron transfer is shown in Eq. (4A). The formation of intermediate \( \text{H}_2\text{AsO}_3 \) radical is indicated by the induced polymerisation of acrylonitrile which is a good scavenger of the \( \text{As}^{\text{IV}} \) radical\(^8\) which has been reported in several \( \text{As}(\text{III}) \) oxidations\(^3-4\).

\[
[\text{IrCl}_6]^2- + \text{As(OH)}_3 \xrightarrow{K} [\text{Complex}]^2- \quad \cdots (3)
\]

\[
[\text{Complex}]^2- \xrightarrow{k} \text{H}_2\text{AsO}_3 + [\text{Ir(Cl)}_6]^2- + \text{H}^+ \quad \cdots (4)
\]

\[
[\text{IrCl}_6]^2- + \text{H}_2\text{AsO}_3 ^{\text{fast}} \xrightarrow{k} [\text{IrCl}_6]^2- + \text{HAsO}_4 + \text{H}^+ \quad \cdots (5)
\]

Eq. 4A, is an amplification of Eq. 4 emphasising the fact that \( \text{Cl}^- \) ion is bridging the binuclear inner-sphere complex between \([\text{IrCl}_6]^2-\) and \( \text{As(OH)}_3 \). It might be of interest to know whether the \( \text{Cl}^- \) is retained by reduced \( \text{Ir(III)} \) or becomes a part of oxidised \( \text{As(IV)} \) in the successor complex. The detection of \( \text{Cl}^- \) with \( \text{As(IV)} \) may not be easy considering the very short life of \( \text{As(IV)} \) which is immediately oxidised to \( \text{As(V)} \) as shown in Eq. (5). Although \( \text{AsCl}_3 \) has been prepared at low temperature, it is known\(^12\) to decompose above \( \approx -50^\circ\text{C} \) indicating that \( \text{As(V)}-\text{Cl} \) bonds are very weak. Hence, it might be surmised that \( \text{Cl}^- \) is retained by reduced \( \text{Ir(III)} \).

Since \( \text{H}_2\text{AsO}_3 \) is oxidised to \( \text{H}_3\text{AsO}_4 \) it is imperative to know the pathway for \( \text{O} \) transfer to arsenic centre. It is felt that the additional \( \text{O} \) atom in \( \text{As(V)} \) comes from the solvent for \( \text{H}_3\text{AsO}_4 \) is the hydrated form of \( \text{HAsO}_3 \) as shown in Eq. (5A).

\[
\text{HAsO}_3 + \text{H}_2\text{O} ^{\text{fast}} \xrightarrow{k} \text{H}_2\text{AsO}_4 \quad \cdots (5A)
\]

The rate of disappearance of \([\text{IrCl}_6]^2-\) is therefore given by Eq. (6).

\[
-\frac{d[\text{IrCl}_6]^2-}{dt} = 2kK[\text{IrCl}_6]^2-[\text{As(OH)}_3] \quad \cdots (6)
\]

Since \( 1 > K[\text{As(OH)}_3] \) because the order with respect to \([\text{As(III)}] \) is one, Eq. (6) reduces to Eq. (7) where \( k_2 \) (\( = kK \)) is the second order rate constant and the parameters \( k \) and \( K \) are kinetically inseparable. The activation parameters associated with \( k_2 \) where \( k_{\text{obs}} = 2k_2[\text{As(OH)}_3] \) are \( \Delta H^\circ = 40 \pm 3 \) \( \text{kJ mol}^{-1} \) and \( \Delta S^\circ = -192 \pm 9 \) \( \text{JK}^{-1}\text{mol}^{-1} \).

The present values of \( \Delta H^\circ \) and \( \Delta S^\circ \) are distinctly different from the values \( 55 \text{kJ mol}^{-1} \) and \( -135 \text{JK}^{-1}\text{mol}^{-1} \) respectively reported by Hassan\(^3\) and correspond to the rate determining decomposition of the complex formed between \([\text{IrCl}_6]^2-\) and \([\text{As(OH)}_3]^2-\). It is felt that this difference in the activation parameters is indicative of a different rate determining step and this aspect is discussed at a later stage of discussion.

Hassan\(^3\) did not report the value of the formation constant of the intermediate complex. An analysis of his data provided a value \( \approx 10^{10} \text{dm}^3\text{mol}^{-1} \) which is highly unlikely for a bridged-complex involving substitutionally inert \([\text{IrCl}_6\text{F}^-] \). It is essential to peruse the mechanism given in reactions (8)-(10), proposed by Hassan\(^3\), before contradictions are discussed, and the deducted rate law is in Eq. (11).

\[
\text{As(OH)}_3 \xrightarrow{K_4} \text{H}_2\text{AsO}_3 + \text{H}^+ \quad \cdots (8)
\]

\[
\text{H}_2\text{AsO}_3 + [\text{IrCl}_6]^2- \xrightarrow{K_4} \text{Complex} \quad \cdots (9)
\]

\[
\text{Complex} \xrightarrow{k_3} \text{products} \quad \cdots (10)
\]

\[
\text{HAsO}_3 + \text{H}_2\text{O} \xrightarrow{k_2} \text{H}_3\text{AsO}_4 \quad \cdots (11)
\]

The inverted form of Eq. (11) suggests linear plots between \( k_{\text{obs}}^{-1} \) and \( [\text{H}^+] \) and, \( k_{\text{obs}}^{-1} \) and \( [\text{H}_2\text{AsO}_3]^{-1} \) with a common intercept value \( (= k_5^{-1}) \). Although the linearity of these plots was demonstrated, the intercept value in the plot between \( k_{\text{obs}}^{-1} \) and \( [\text{H}^+] \) plot was nearly eight times more than intercept value in the plot between \( k_{\text{obs}}^{-1} \) and \( [\text{H}_2\text{AsO}_3]^{-1} \). Thus there is very little agreement between the predicted rate law and the observed results rendering the mechanism unacceptable. The other weaknesses were referred to earlier in the introduction.

Hassan’s results could be explained by a mechanism in reactions (12)-(15) where \([\text{IrCl}_5\text{(OH)}]^-\) and \( \text{As(OH)}_3 \) as the reactive species.

\[
[\text{Cl}_5\text{Ir(OH)}_2]^- \xrightarrow{K_4} [\text{Cl}_5\text{Ir(OH)}]^- + \text{H}^+ \quad \cdots (12)
\]

\[
\text{As(OH)}_3 + [\text{Cl}_5\text{Ir(OH)}]^- \xrightarrow{K_4} [\text{Cl}_5\text{IrOAs(OH)}]^- + \text{H}_2\text{O} \quad \cdots (13)
\]
\[
[\text{Cl}_3\text{IrOAs(OH)}_2]^2^- \xrightarrow{k_d} [\text{IrCl}_3]^2^- + \text{H}_2\text{AsO}_3
\]

\[
[\text{Ir(IV)}] + \text{H}_2\text{AsO}_3 \xrightarrow{\text{fast}} [\text{Ir(III)}] + \text{HAsO}_3 + \text{H}^+
\]

The ionisation of \([\text{IrCl}_3(\text{OH}_2)]^-\) is due to the increased acidity of the coordinated water molecule and is similar to the deprotonation equilibrium of the increased acidity of the coordinated water molecule. To the best of our knowledge, the value of \(K_d\) has not been, perhaps, reported. Nevertheless, it is obvious that the value of \(K_d\) may be several orders higher than the dissociation constant \(K_a\) of arsenous acid. Hence, the preferential ionisation of \([\text{IrCl}_3(\text{OH}_2)]^-\) over that of \(\text{As(OH)}_3^-\) is obvious.

The levelling of the \(k_{\text{obs}}\) at low \([\text{H}^+]\) and becoming immeasurably slow at high \([\text{H}^+]\) indicated \([\text{IrCl}_3(\text{OH}_2)]^-\) to be the reactive \(\text{Ir(IV)}\) species. The assumption is based on the fact that any substitution on \([\text{IrCl}_3(\text{OH}_2)]^-\) compared to \([\text{IrCl}_3(\text{OH}_2)]^-\) would be easier and faster because \(\text{H}_2\text{O}\) is a stronger nucleophile than \(\text{OH}^-\) ion. Further, for a weak acid like \(\text{H}_2\text{AsO}_3\) it is easier to react with \([\text{IrCl}_3(\text{OH}_2)]^-\) compared to \([\text{IrCl}_3(\text{OH}_2)]^-\) because the difference in the basicity of \(\text{OH}^-\) ion and \(\text{H}_2\text{O}\) is 17 \(pK\) units. In either case the dinuclear \([\text{Cl}_3\text{IrOAs(OH)}_2]^2^-\) complex is an innersphere complex in which the \(\text{O}\) atom belongs to \(\text{As(III)}\).

The rate law, based on the reactions (12)-(15), is expressed by Eq. (16).

\[
k_{\text{obs}} = \frac{2k_2K_dK_s[H^+][\text{As(OH)}_3]}{1 + k_d[H^+]+(1 + K_d[\text{As(OH)}_3])}
\]

At low \([\text{H}^+]\), \(K_d[H^+]+(1 + K_d[\text{As(OH)}_3]) > 1\) and therefore Eq. (16) changes to Eq. (17) which is independent of \([\text{H}^+]\) and is consistent with the saturation of the rate constant observed by Hassan at low \([\text{H}^+]\). At other \([\text{H}^+]\), Eq. (16) holds good and its inverted forms in Eqs (18) and (19) explain the linearity of the plots between \(k_{\text{obs}}^{-1}\) and \([\text{H}^+]\) and \(k_{\text{obs}}^{-1}\) and \([\text{As(OH)}_3]^{-1}\) with different intercept values as observed by Hassan:

\[
k_{\text{obs}} = \frac{2k_2K_s[\text{As(OH)}_3]}{1 + K_d[\text{As(OH)}_3]}
\]

\[
\frac{1}{k_{\text{obs}}} = \frac{[\text{H}^+]}{2k_2K_sK_d[\text{As(OH)}_3]} + \frac{1}{2k_2K_sK_d[\text{As(OH)}_3]}
\]

Therefore in a sample where both \([\text{IrCl}_3]^2^-\) and \([\text{IrCl}_3(\text{OH}_2)]^-\) are present, \([\text{IrCl}_3(\text{OH}_2)]^-\) can preferably initiate the oxidation because \([\text{IrCl}_3(\text{OH}_2)]^-/2^-\) couple has a higher redox potential; 1.1 V compared to 0.96 V for \([\text{IrCl}_3]^2/-3^-\) couple. Except for its source as an initial impurity in the sample of \([\text{IrCl}_3]^2^-\) used, there is no way to visualise the availability of \([\text{IrCl}_3(\text{OH}_2)]^-\) to initiate the reaction with results reported by Hassan.

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