Kinetics of oxidation of amino acids by hexachloroiridate(IV) in aqueous acid medium

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The title reaction studied in the pH range of 2.5 to 3.5 is pseudo-first order in [Ir(IV)] in the presence of excess [substrate]. The rate increases with increase in [substrate] and the order in [Ir(IV)] is irrational. The rate also increases with increase in [H⁺] and the order in [H⁺] is unity. Added salts and change in dielectric constant of the medium do not affect the rate appreciably. However, added acrylamide induces polymerisation. A suitable mechanism has been proposed.

In our earlier communications¹,² we have reported kinetics of oxidation of aliphatic amines and amino alcohols by hexachloroiridate (HCl). The title investigation is an extension of our earlier work on the use of HCl as an oxidant.

Experimental

Reactant solutions were always prepared fresh in doubly distilled water. Stock solution of hexachloroiridate(IV) was prepared by dissolving it (Johnson-Mathey) in perchloric acid (1 mol dm⁻³) and standardized spectrophotometrically. All amino acids used viz. glycine, valine, alanine, leucine and isoleucine were Fluka puriss grade and were used as such. Other chemicals such as sulphuric acid, acetic acid, sodium chloride and sodium perchlorate were of accepted grade. Acetic acid was distilled before use.

Kinetic run—The kinetics was followed by monitoring the disappearance of HCl at regular time intervals spectrophotometrically at 487 nm (ε = 4060 dm³ mol⁻¹ cm⁻¹) using a cuvette of 1 cm path length and a double beam UV-Vis spectrophotometer (Shimadzu model 140.02 Japan). The reaction was initiated by adding a calculated volume of thermally equilibrated HCl to a mixture of amino acid and aqueous acetic acid kept at the same temperature. Salts such as sodium chloride and sodium perchlorate were used to maintain constant ionic strength. The reaction obeyed a first order rate equation log A₀/A = 0.434 k't till 80% completion. All the computations were performed programming CASIO Data Bank Computer PB-110.

Results and discussion

All amino acids exhibited similar kinetic features. As a typical one the results of oxidation of glycine (Gly) are presented here unless otherwise mentioned.

(i) Stoichiometric experiments (24 hr) using known excess of Ir(IV) indicated that 1 mole of glycine consumed 2 mole of Ir(IV) in accordance with Eq. (1).

\[ \text{NH}_2\text{CH(R)COOH} + 2\text{Ir(IV)} \rightarrow \text{RCOCOOH} + 2\text{Ir(III)} + \text{NH}_3 \quad \ldots (1) \]

(ii) Products of oxidation under kinetic conditions were identified as corresponding keto acids which were characterised by the spot tests³.

(iii) Under the conditions [Ir(IV)] ≪ [Gly] the plot of log (absorbance) versus time was linear with no change in slope at varying [Ir(IV)] indicating first order in [Ir(IV)]. Pseudo-first order rate constant (k') was calculated from the slope and it was found to be equal to 0.4342.

(iv) At fixed [Ir(IV)], [H⁺], [NaClO₄] and temperature the rate of reaction was linearly dependent on [Gly]. The order in [Gly] from the plot of log k' versus log [Gly] was found to be fractional (Table 1).

(v) Michaelis-Menton plot of \( \frac{k'}{u} \) versus \( \frac{1}{[\text{substrate}]} \) was linear with positive intercept on Y-axis indicating probable complex formation in the reaction path (Table 1).

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<th>( [\text{HCl}] ) (mol dm⁻³)</th>
<th>( [\text{AA}] ) (mol dm⁻³)</th>
<th>( [\text{H}^+] ) (mol dm⁻³)</th>
<th>( u ) (mol dm⁻³)</th>
<th>( 10^4 k' ) (s⁻¹)</th>
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Table 1—Effect of various reactants on k' at 35°C
NOTES

Table 2—Bimolecular rate constants and activation parameters at 308 K

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<th>Temp (K)</th>
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<th>328</th>
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</table>

\[ k'(\text{dm}^3\text{mol}^{-1}\text{sec}^{-1}) \]

\[ E_a, \Delta H^\circ, \Delta G^\circ, -\Delta S^\circ \]

\[ (\text{kJ mol}^{-1}) \quad (\text{J mol}^{-1}\text{K}^{-1}) \]

\[ (\text{vii}) \] At fixed \([\text{Ir(IV)}], [\text{Gly}], \text{ionic strength and temperature the rate of oxidation increased with increase in } [\text{H}^+].\) The order in \([\text{H}^+]\) from the plot of log \(k'\) versus log \([\text{H}^+]\) was found to be one (Table 1).

\[ (\text{viii}) \] Added salts such as KCl, NaClO₄, and change in dielectric constant of the medium did not affect the rate of oxidation.

\[ (\text{ix}) \] Added acrylamide produced polymerisation.

\[ (x) \] The reactions were conducted in the temperature range 308-328 K and the calculated activation parameters are listed in Table 2.

Earlier studies⁴⁻⁶ on the oxidation of some organic compounds by hexachloroiridate(IV) in acid medium indicate that HCl is substitution inert. Photochemical behaviour of \(\text{IrCl}_6^{2-}\) in the UV region indicates that aquation of \(\text{IrCl}_6^{2-}\) leading to formation of \(\text{IrCl}_5(\text{H}_2\text{O})^-\) occurs at higher acidities (≥ 6.0 mol dm⁻³) and high Ir(IV) concentration (0.5-2.0 mol dm⁻³). Since in the present study the reactions were studied in lower acidity range, it may be assumed that \(\text{IrCl}_5(\text{H}_2\text{O})^-\) is the reactive species.

Amino acids are known to exist as zwitterions in aqueous medium. In acid medium these zwitterions get protonated to become protonated amino acid. Hence, the observed \([\text{H}^+]\) can be explained by the interaction of zwitterion and proton. The plot of \(1/k'\) versus \(1/\text{[substrate]}\) was linear with positive intercept indicating complex formation. Based on above observation the mechanism in Scheme 1 can be written for electron transfer from amino acid and HCl.

\[ \text{H}_3\text{N}^-\text{CH}(\text{R})-\text{COO}^- + \text{H}^+ \rightleftharpoons \text{H}_3\text{NCH}(\text{R})\text{COOH} \]

\[ \text{[AA]} \]

\[ \text{AAH} + \text{Ir(IV)} \rightleftharpoons \text{complex (C)} \]

\[ \text{C} \rightarrow \text{free radical + Ir(III)} \]

Free radical + Ir(IV) \(\rightarrow\) product + Ir(III) \(\Rightarrow\) fast

Step (4) must be a slow step involving the formation of free radicals by the transfer of electron from substrate to oxidant. Steps (2) and (3) will not be slow as these cannot explain observed salt effect. The absence of Ir(III) effect on rate of reaction rules out the possibility of formation of Ir(III) in step (3). Step (5) involves free radical and hence the chances are remote for it being slow. Therefore step (4) may be the rate-determining step.

From step (4) the rate of reaction in terms of disappearance of HCl can be written as

\[ \frac{d[\text{HCl}]}{dt} = k_3[\text{C}] \]

Applying steady state principle to \([\text{C}]\) we get

\[ [\text{C}] = \frac{k_2[\text{AAH}^+][\text{Ir(IV)}]}{k_{-2} + k_3} \]

Substituting Eq. (7) in Eq. (6) we get

\[ \frac{d[\text{HCl}]}{dt} = \frac{k_3k_2[\text{AAH}^+][\text{Ir(IV)}]}{(k_{-2} + k_3)} \]

\[ [\text{AAH}^+]' \text{from step (2) comes out to be} \]

\[ [\text{AAH}^+] = \frac{K_1[\text{AA}][\text{H}^+]}{1 + K_1[\text{AA}]}, \quad [\text{AA}] \gg [\text{H}^+] \]

Substituting for \([\text{AAH}^+]\) in Eq. 8 we get Eq. 9

\[ \frac{d[\text{HCl}]}{dt} = \frac{k_3K_1k_2[\text{AA}][\text{H}^+][\text{Ir(IV)}]}{(k_{-2} + k_3)(1 + K_1[\text{AA}])} \]
As $k_3 \ll k_{-2}$, $k_3$ can be neglected compared to $k_{-2}$. Hence the rate law reads as
\[ \frac{d[HCl]}{dt} = \frac{K_1k_2k_3[AA][H^+][Ir(IV)]}{1 + K_1[AA]} k_{-2} \tag{10} \]
\[ \frac{d[HCl]}{dt} = k' = \frac{K_1k_2k_3[AA][H^+]}{(1 + K_1[AA])k_{-2}} \]
\[ k' = \frac{K_1k_2k_3[AA][H^+]}{1 + K_1[AA]} \tag{11} \]

The above rate law explains all experimental observations. The substituent effects in the present study appear to be negligible as can be seen from the data given in Table 2. However the magnitude of rate of oxidation decreases from glycine to isoleucine. This indicates that the presence of electron donating groups decrease the rate of oxidation.

The bimolecular rate constants ($k^*$, at three different temperatures) and activation parameters are listed in Table 2. The data reveal that the reactions are enthalpy-controlled as the substrate with highest rate is having lowest enthalpy. The slope ($\beta = 362 \text{ K}$) of the plot of $\Delta H^+$ versus $\Delta S^+$ also indicates enthalpy-controlled nature of reaction. The constancy in $\Delta G^+$ indicate similar mechanism to be operative in all the substrates.

A good correlation was observed between rate of oxidation and structure of amino acid as seen from linear plot of log $k^*$ versus $\sigma^*$. The slope of above plot ($\rho^*$) was found to be 0.36 ($r = 0.82$) which is in agreement with the $\rho^*$ values obtained in oxidations by one electron oxidants. Low value of $\rho^*$ further indicates free radical formation in the mechanism.

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**References**