Kinetics and mechanism of palladium(II) catalysed oxidation of some α-aminoacids by chloramine-T in perchloric acid

Necil Grover, Neelu Kambo & Santosh K Upadhyay
Department of Chemistry, H B Technological Institute, Kanpur 208 002

Received 6 March 2002; revised 26 September 2002

The catalytic as well as inhibition action of Pd\(^{II}\) in various redox reactions is reported\(^{1,2}\). Over the past decade there has been considerable interest on the speciation of the aqueous PdCl\(_2\) solutions and complexes\(^{3-7}\) of Pd\(^{II}\) with Cl\(^{-}\). The complexes of palladium with amines and aminoacids and related molecules have also received the attention of various workers\(^{8,10}\). Recently, the formation of 1:1 and 1:2 complexes between aliphatic amine and Pd\(^{II}\) in the absence of Cl\(^{-}\) and HClO\(_4\) and formation of only 1:1 complex i.e.(amine-Pd\(^{II}\)) in the presence of Cl\(^{-}\) and HClO\(_4\) has been observed\(^{11}\).

Kinetics of oxidation of α-aminoacids(AA) by sodium N-chloro-p-toluene sulphonamide generally known as chloramine-T (CAT) in acidic medium has been studied extensively and reviewed\(^{12,13}\). The reactions have been found to follow a complex kinetics due to the formation of various reactive species of CAT depending upon [H\(^{+}\)]. In order to observe the nature of Pd\(^{II}\) towards aminos acids and to examine the reactivity the complexes formed between Pd\(^{II}\) and AA towards CAT, the title reaction has been studied in detail and the results are reported in the present paper.

Materials and Methods

Stock solution of chloramine-T [LOBA, AR] was prepared in doubly distilled water, standardized iodometrically and stored in dark coloured bottle. Aqueous solutions of glycine, alanine, phenylalanine and valine were prepared from samples (Thomas Baker, AR). All other reagents viz. NaCl, HClO\(_4\), NaClO\(_4\) used were of analar grade and their solutions were prepared in doubly distilled water.

The stock solution of palladous chloride (22.5×10\(^{-3}\) mol dm\(^{-3}\)) was prepared by dissolving the sample (SDS) in dilute HCl (1.0×10\(^{-3}\) mol dm\(^{-3}\)) and was stored in black coated bottles to prevent photochemical decomposition. The reaction vessels were also coated with black varnish to avoid any photochemical effect.

Appropriate quantities of solutions of CAT, HClO\(_4\) and PdCl\(_2\) were placed in a 100 cm\(^3\) Jena glass vessel. The requisite amount of doubly distilled water was added so that the total volume of the reaction mixture was 50 cm\(^3\) after adding the substrate. The reaction mixture was then placed in a thermostatic bath maintained at the desired temperature ± 0.1°C. The mixture was allowed to attain the bath temperature and reaction was then initiated by adding the requisite amount of AA solution, placed separately in same bath. The progress of the reaction was followed by determining CAT iodometrically in aliquots, withdrawn after regular time intervals.

Product analysis and stoichiometry

The products were identified under the kinetic conditions i.e. in the conditions of [AA] >> [CAT].
Several reaction mixtures with [AA] >> [CAT] were prepared keeping [PdCl₂] and [HClO₄] fixed. After the complete reaction, the reaction mixtures were treated with 2,4-dinitrophenyl-hydrazine. The formation of hydrazones indicated the presence of aldehydes as the oxidation products of aminoacids under the kinetic condition. The presence of aldehyde was confirmed by converting it into 2,4-dinitrophenylhydrazone and comparing it with an authentic sample (m.p. and TLC). The amount of aldehyde was calculated from the weight of hydrazone formed and the yield of the corresponding aldehyde from aminoacid was obtained as 52 to 56% under the kinetic conditions.

Evidence for complex between Pd²⁺ and AA

The ability of platinum metal ions to form complexes with organic substances is well reported in the literature. During the present investigations, the spectrophotometric evidence for the formation of complex between Pd²⁺ and AA has been observed. The λₘₐₓ of PdCl₂ solution has been observed at 400 nm. The absorbance of AA(s) at 400 nm was negligible. A series of solutions were prepared containing a fixed amount of PdCl₂ and a varying amount of AA. The solutions were allowed to stand for 30 min at 35°C and the absorbance of the solutions were measured at 400 nm. It was observed that addition of increasing amount of AA decreases the absorbance due to PdCl₂ until [AA]:[PdCl₂] ratio becomes nearly unity, thereafter, there was no further decrease in the absorbance (Fig. 1). These results indicate the formation of a 1:1 complex between PdCl₂ and AA.

The experiments were also repeated in the presence of HClO₄ and Cl⁻. It was observed that addition of HClO₄ in the solution containing PdCl₂ and AA, resulted in decrease in the absorbance of the solution while addition of NaCl in the solution resulted in an increase in the absorbance of the solutions. The decrease or increase in the absorbance of the solution on addition of HClO₄ or Cl⁻ may be due to the formation of different species of PdCl₂ in the presence of HClO₄ or Cl⁻. However, there was no change in the nature of the complex i.e. a 1:1 complex between Pd²⁺ and AA was also observed in presence of HClO₄ or Cl⁻.

Results

All the kinetic runs were carried out with [AA], always at least six times, in excess of [CAT]. In the case of Ala, Ph-Ala and Val, the log [CAT] versus time plots at various initial concentrations of reactants, were linear up to 70-80% of the reactions in both the conditions i.e. in the absence and presence of the catalyst. Therefore, the pseudo-first order rate constants in CAT (kₐ₀) were evaluated from the slopes of these plots. The uncatalysed oxidation of aminoacids by CAT has been well studied and has also been reviewed. Therefore, in the present paper, only the results of catalysed reactions are reported. Identical value of kₐ₀ at various [CAT] confirmed the first order dependence of rate with respect to CAT in case of Ala, Ph-Ala and Val (Table 1).

The effect of [H⁺] on the reaction rate was studied at fixed ionic strength maintained by addition of sodium perchlorate. The amount of acid already present in the catalyst was taken into account. The effect of variation in [H⁺] and [AA] on the rate of reaction was similar. In the presence of the catalyst, the plots of (1/kₐ₀) versus 1[HClO₄] and (1/kₐ₀) versus 1[AA] were linear with intercepts, suggesting that the order of reaction in H⁺ and AA in the presence of catalyst decreases from unity to zero at higher [H⁺] and [AA] respectively.

The plots of (kₐ₀) versus [PdCl₂] were linear with intercepts suggesting that the rate r = [kₐ + kₐ[PdCl₂]] where kₐ and kₐ are rate constants for uncatalysed and catalysed path respectively. The rate constants kₐ₀ obtained experimentally in the absence of the catalyst i.e. at [PdCl₂] = 0 were matching with the intercepts of the plots of (kₐ₀) versus [PdCl₂].
Table 1—Effect of reactants on the rate constant at 35°C; [PdCl₂] = 2.25×10⁻³ mol dm⁻³

*The effect of acid was studied at a fixed ionic strength μ = 0.004 mol dm⁻³ maintained by sodium perchlorate.

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<tr>
<th>10⁻³[CAT] (mol dm⁻³)</th>
<th>10⁻²[AA] (mol dm⁻³)</th>
<th>10⁻⁰[HClO₄] (mol dm⁻³)</th>
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The effect of Cl⁻ on the rate of oxidation was studied by adding different amounts of NaCl in the reaction mixture. It was observed that an increase in [Cl⁻] in the reaction mixture resulted in an increase in the rate constants kobs. However, a plot of [Cl⁻]/(kobs) versus [Cl⁻] was linear with an intercept. Therefore, pseudo-second order rate constants in CAT were evaluated from the slopes of these plots. The effect of [Reactants] on the pseudo-second order rate constants k'obs in case of Gly are summarised in Table 2. The plots of (1/k'obs) versus 1/[H⁺] or 1/[Gly] and (k'obs) versus [PdCl₂] were linear with intercepts suggesting that the other results are similar.
Addition of $p$-tolylenesulphonamide (RNH$_2$, the reaction product of CAT) had no effect on the reaction rate. The effect of ionic strength was studied by carrying out investigations in the presence of different amounts of NaClO$_4$, which had a negligible effect on the rate of oxidation.

The reactions were also studied at 35, 40, 45 and 50°C and activation parameters for catalysed paths have been evaluated (Table 3).

**Discussion**

In acidic solutions RNHCl, RNCl$_2$, HOCl and chloramine-T itself have been considered as the reactive species of chloramine-T. In higher acid concentrations H$_2$OCl$^-$ or RN$^+$H$_2$Cl have also been considered as the reactive species in some cases.

RNCl$_2$ is a strong base and, therefore, likely to be fully prototated even if only an equivalent amount of acid is present and will exist as RNHCl. Further, addition of the acid will not result in a linear increase in the concentration of RNHCl. Therefore, the increase in the rate at lower acid concentration cannot be due to formation of RNHCl.

In acid solutions, amino acid exists in protonated form as,

$$
RCH(NH)_3^+COO^- + H^+ \rightleftharpoons RCH(NH)_3^+COOH
$$

The complex formation between AA and palladium(II) was suppressed by addition of H$^+$ and, therefore, zwitter-ion of AA has been considered as the reactive species of AA during the present investigations. However, by considering the zwitter-ion of AA as reactive species, the above equilibrium will result in retardation of rate on increasing $[H^+]$ even at low concentration which has not been observed experimentally.

The catalysis of $H^+$ at low acid concentrations may be possible by further protonation of RNHCl as,

$$
RNHCl + H^+ \rightleftharpoons (RNH_2Cl)^+; K'' = 1.03 \times 10^2
$$

The existence of different species of palladium chloride viz. Pd$^{3+}$, PdCl$^+$, PdCl$_2$, PdCl$_3^-$ and PdCl$_4^{2-}$ in HClO$_4$ medium depending upon [Cl$^-$/[Pd]$^+$ has been observed. It has been found that species Pd$^{3+}$, PdOH$^+$ and PdCl$^+$ were present when [Cl$^-$/[Pd]$^+$ was up to 0.8; PdCl$^+$ and PdCl$_2$ were present when [Cl$^-$/[Pd]$^+$ was 2.2 to 2.8 and only PdCl$_2$, PdCl$_3^-$ and PdCl$_4^{2-}$ were present when [Cl$^-$/[Pd]$^+$ was 4.0 to 4.8. Therefore, it may be considered that Pd$^{3+}$, PdCl$^+$ and PdCl$_2$ are reactive species of the catalyst in the absence of Cl$^-$ when [Cl$^-$/[Pd]$^+$ is low. While, in the presence of Cl$^-$ when [Cl$^-$/[Pd]$^+$ is high, the reactive species of palladium(II) are PdCl$_2$, PdCl$_3^-$ and PdCl$_4^{2-}$.

The hydrolysis of palladium(II) chloride species in aqueous medium has received the attention of many investigators and the formation constants for the mixed i.e. hydroxy-chloride palladium species formed due to hydrolysis of palladium chloride complexes are reported. The dominance of $\delta_2$Pd(OH)Cl and PdCl$_3$(OH)$_2$ species among various species in aqueous medium depending upon Cl$^-$ concentration in solution has also been observed. The formation of these species may be considered as follows,

$$
PdCl_2 + H_2O \rightleftharpoons PdCl(OH) + H^+ + Cl^-(c)
$$

$$
PdCl_3^{2-} + H_2O \rightleftharpoons PdCl_3(OH)_{2-} + H^+ + Cl^-(d)
$$

It has been observed that complex formation between AA and palladium(II) get suppressed on increasing $[H^+]$ in the reaction mixture. Therefore, the complex formation may be proposed between AA and PdCl$_2$(OH) (in the absence of Cl$^-$) and between AA and PdCl$_3$(OH)$_2$ (in the presence of Cl$^-$).

On the basis of above facts and experimental results the mechanism for the oxidation of Ala, Phe-Ala and Val by CAT in presence of Pd$^0$ may be proposed as given in Scheme 1.

Table 3—Activation parameters for catalysed oxidation of amino acids in presence of palladium chloride

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\Delta E^a$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^a$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^a$ (JK$^{-1}$ mol$^{-1}$)</th>
<th>$\Delta G^a$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alanine</td>
<td>53.56</td>
<td>50.96</td>
<td>-130.21</td>
<td>91.67</td>
</tr>
<tr>
<td>Valine</td>
<td>49.91</td>
<td>43.31</td>
<td>-150.86</td>
<td>91.19</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>49.75</td>
<td>47.14</td>
<td>-139.75</td>
<td>90.66</td>
</tr>
<tr>
<td>Glycine</td>
<td>32.5</td>
<td>29.90</td>
<td>-142.0</td>
<td>74.00</td>
</tr>
</tbody>
</table>
According to Scheme 1, the rate of disappearance of CAT may be given as,

$$ \frac{d[CAT]}{dt} = k_0 [X][RN^+H_2Cl] $$  \hspace{1cm} (1)$$

Considering the equilibria (i) to (vi), we get,

$$ [PdCl^+] = K_1[Pd^{++}][Cl^-] $$ \hspace{1cm} (2)

$$ [PdCl_2] = K_1K_2[Pd^{++}][Cl^-]^2 $$ \hspace{1cm} (3)

$$ [PdCl(OH)] = K_1K_2K_3[Pd^{++}][Cl^-] $$ \hspace{1cm} (4)

$$ [X] = K_1K_2K_3K_4[Pd^{++}][Cl^-][AA] $$ \hspace{1cm} (5)

and

$$ [RN^+H_2Cl] = K_3[H^+][CAT] $$ \hspace{1cm} (6)

where $K_1$ and $K_3$ also involve water molecule. Under the kinetic conditions, the HClO$_4$ concentration is about fifty times the total palladium concentration, so that any contribution to overall acidity of the solutions by the hydrolysis of palladium (step (iii)) is negligible. Therefore, the involvement of $H^+$ (retarding effect) in the determination of [PdCl(OH)] (Eq.4) has not been considered.

Again by considering the total concentration of catalyst and CAT at any time as,

$$ [\text{Catalyst}]_T = [Pd^{++}] + [PdCl^+] + [PdCl_2] + [PdCl(OH)] + [X] $$ \hspace{1cm} (7)$$

and

$$ [\text{CAT}]_T = [RNHCl] + [RN^+H_2Cl] $$ \hspace{1cm} (8)$$

[X] and [RN$^+$H$_2$Cl] in terms of $[\text{Catalyst}]_T$ and $[\text{CAT}]_T$ respectively have been obtain as,

$$ [X] = \frac{K_1K_2K_3[\text{Catalyst}]_T[Cl^-][AA]}{1 + K_1[Cl^-] + K_2[Cl^-]} + K_3K_3 + K_2K_4[AA]) $$ \hspace{1cm} (9)$$

and

$$ [RN^+H_2Cl] = \frac{K_3[\text{CAT}]_T[H^+]}{1 + K_3[H^+]} $$ \hspace{1cm} (10)$$

Substituting the values of [X] and [RN$^+$H$_2$Cl], the rate law (1) becomes,

$$ \frac{d[CAT]}{dt} = k_0 \times [AA][Cl^-][\text{Catalyst}]_T[H^+] $$ \hspace{1cm} (11)$$

where, $K_3[Cl^-]$ has been neglected in comparison to $1 + K_5[Cl^-]$ at higher [H$^+$] and [AA] respectively and effect of Cl$^-$ on the rate of oxidation. However, rate law (11) does not reflect the intercept obtained in the plot of $(k_{obs})$ versus $[\text{PdCl}_2]$, because the steps responsible for uncatalysed path have not been included in the proposed mechanism.

In the presence of Cl$^-$, mechanism may be proposed by considering PdCl$_2$, PdCl$_3^-$ and PdCl$_4^{2-}$ as the reacting species of the catalyst as given in Scheme 2, which would result in similar rate law as given in equation (11).
(Y) + (RNH₂Cl)⁺ \overset{k_5}{\longrightarrow} \text{products} \quad \text{(vii)}

By including these steps in the case of Gly and applying the steady state conditions with respect to [Y], the rate of disappearance of CAT will be obtained as,

\[
\frac{d[CAT]}{dt} = k_6k_1[X][\text{RNH}_2\text{Cl}]^+ - k_6[H^+] + k_1[\text{RNH}_2\text{Cl}]^+ \quad \text{(12)}
\]

Rate law (12) will explain the observed second order dependence of rate with respect to CAT under the conditions when \(k_6[H^+] \gg k_1[\text{RNH}_2\text{Cl}]\) i.e. at higher acid concentration or at low CAT concentration. However, at very low \([H^+]\) or at very high \([\text{CAT}]\), when \(k_6[H^+] \gg k_1[\text{RNH}_2\text{Cl}]\) would not be valid, the reaction will not be exactly second order with respect to \([\text{CAT}]\), rather the order in \([\text{CAT}]\) will be between 1 and 2. This is supported by the experimental observed fact that at very high \([\text{CAT}]\), the second order plots in CAT initially were curve up to 10-20% of the reaction then became linear. The effect of other reagents on rate can be explained by substituting the value of \([X]\) from Eq. (9) in rate law (12).

An insignificant effect of ionic strength, observed in the absence of CI, is in the support of rate determining step (vi) of Scheme 1.

The reaction mechanism is multistep and observed values of activation parameters do not have much importance. However, the negative entropy of activation suggests the compactness of the transition state as compared to the ground state. Nearly same value of \(\Delta G^\ddagger\) in the case of Ala, Ph-Ala and Val is in favour of a common mechanism for oxidation in the case of these three amino acids. In case of Gly, the different value of \(\Delta G^\ddagger\) suggests the involvement of a different rate determining step.

Acknowledgement

Thanks are due to Director and Head of Chemistry Department, HBTI, Kanpur, for their interest in the work. One of us (NK) is thankful to the CSIR, New Delhi for award of SRF.

References

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