Mechanism of Pd(II) Catalysis in Ce(IV) Oxidation of Amines in Acidic Medium

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Palladium(II) catalyzed oxidation of methyl amine and ethyl amine by Ce(IV) in perchloric acid has been found to be acid dependent. The reaction exhibited first-order kinetics in each of Ce(IV) and Pd(II). First order kinetics in amines in lower concentration range shifts to zero order at their higher concentrations. Negative effects of [H⁺], [Cl⁻] and µ (ionic strength) variations on the rate of reaction were observed. Pd(II), catalysis of Ce(IV)-amine reaction is explained in terms of a 1:1 complex formation between Pd(II) species and amine. The complex formed is hydrolyzed and the hydrolyzed species later reacts with Ce(IV) to give the products, namely, ammonia and the corresponding aldehyde.

Key Words: Kinetics, Pd(II), Oxidation, Ce(IV), Amines, Perchloric acid.

INTRODUCTION

The kinetics of oxidation of amines by chloramine-T1,2, Ce(IV)3-5 and N-bromosuccinimide6 in acidic medium and by hexacyanoferrate(III)7 in alkaline medium-incorporating certain transition metal ions viz. osmium(VIII), ruthenium(III) and palladium(II)8,9 as homogeneous catalysts have been investigated from a mechanistic point of view. However, the palladous ion as homogeneous catalyst in Ce(IV)-amine redox reaction has not been studied mechanistically. Therefore, it was thought worthwhile that the studies in this direction may be useful in understanding the catalytic activity of palladous ion. The present communication reports the kinetics and mechanism of Pd(II) catalyzed oxidation of methyl amine and ethyl amine by Ce(IV) in perchloric acid medium.

EXPERIMENTAL

The reagents employed were methyl amine and ethyl amine (AR quality), PdCl₂ (AR, Ranbaxy) and perchloric acid (E. Merck). All other chemicals used were of AR quality and their solutions were prepared in doubly distilled water. A stock solution of PdCl₂ (0.0225 mol dm⁻³) were prepared by dissolving the sample in dil. HCl (0.01 mol dm⁻³) solution and stored in black bottle to prevent photochemical decomposition. The kinetics was followed by estimating unreacted Ce(IV) at definite time intervals volumetrically.
Stoichiometry and product analysis: A reaction mixture containing a known excess of [Ce(IV)] over [amine] were kept in the presence of HClO₄ and PdCl₂ at 35 ºC for 72 h. After completion of the reaction, the remaining Ce(IV) was estimated in different sets of the experiment. The results showed that one mole of amine consumed two moles of Ce(IV) according to the stoichiometry eqn. 1.

\[
\text{RCH}_2\text{NH}_2 + 2\text{Ce(IV)} + \text{H}_2\text{O} \xrightarrow{\text{Pd(II)/H}^+} \text{RCHO} + \text{NH}_3 + 2\text{H}^+ + 2\text{Ce(III)} \quad (1)
\]

where R stands for H and CH₃ is methyl amine and ethyl amine, respectively.

The presence of corresponding aldehyde and ammonia as end products was detected by spot test⁶ and the presence of aldehyde was confirmed by converting it into 2,4-dinitrophenyl hydrazine and comparing it with an authentic sample (CO-TLC). The results are in agreement with earlier works.

RESULTS AND DISCUSSION

The reaction were studied at various initial [reactants]. At fixed [Pd(II)], the order in [Ce(IV)] was found to be unity as observed from linear plot of \((-dc/dt)\) vs. [Ce(IV)] (Fig. 1). The order in [amine] obtained from the plot (Fig. 2) of log \(k_1\) vs. log [amine] was found to be fractional. (0.76 for methyl amine and 0.68 for ethyl amine). At low concentration of amine, \(k_1\) (first-order rate constant) increases linearly but it increases non-linearly at high concentration of amine, showing thus shifting first order in amine to zero order (Table-1). The value of \(k_1\) increases in direct

<table>
<thead>
<tr>
<th>[Ce(IV)] × 10³ M</th>
<th>[Amine] × 10² M</th>
<th>[PdCl₂] × 10⁵ M</th>
<th>(k_1) × 10³ (s⁻¹)</th>
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proportionality with [Pd(II)], indicating first-order kinetics in Pd(II). Increase in [H+] or [Cl–] decreased the rate of oxidation. Increase in ionic strength of the medium showed negative effect on the rate of reaction, indicating interaction of dissimilar changed species in the rate determining step. Induced polymerization was observed when acrylamide was added to the reaction mixture. Corresponding aldehydes were
identified as oxidation product by TLC analysis of their 2,4-dinitrophenyl hydrazone derivatives and further confirmed by melting points of these derivatives.

The kinetic runs were also made at 35, 40, 45 and 50 °C and the energies of activation obtained from Arrhenius plots were 68.92 and 58.40 kJ mol⁻¹ for the oxidation of methyl amine and ethyl amine, respectively (Table-2).

Palladium(II) chloride is quite soluble in HCl and exists primarily as [PdCl₄]²⁻. The formation of 1:1 complex of palladium(II) chloride species with amines has already been reported. The oxidation kinetics of both amines by Ce(IV) in presence of palladium(II) chloride are similar and therefore, a common mechanism is proposed (Scheme-I). The fast equilibria steps (i)-(iii) are already reported in earlier studies. Considering above statements and other kinetic data, the reaction mechanism can be written as in Scheme-I.

\[
[PdCl_4]^{2-} + RCH_2NH_2 \xrightarrow{k_1} [PdCl_4(NH_2CH_2R)]^{1-} + Cl^- \quad \text{(i)}
\]

\[
[PdCl_4(NH_2CH_2R)]^{1-} + H_2O \xrightarrow{k_2} [Pd(NH_2CH_2R)(H_2O)Cl_2] + Cl^- \quad \text{(ii)}
\]

\[
[Pd(NH_2CH_2R)(H_2O)Cl_2] + H_2O \xrightarrow{k_3} [Pd(NH_2CH_2R)(OH)Cl_2]^- + H_3O^+ \quad \text{(iii)}
\]

\[
[Pd(NH_2CH_2R)(OH)Cl_2]^- + Ce(IV) \xrightarrow{k_{slow}} [Ce(III)] + R-CH‧NH_2 + H_2O + PdCl_2 \quad \text{(iv)}
\]

\[
R-CH-NH_2 + Ce(IV) \xrightarrow{\text{fast}} Ce(III) + R‧CHNH_2 \quad \text{(v)}
\]

\[
RCHNH_2 + H_2O \xrightarrow{\text{fast}} R\xrightarrow{\text{fast}} H\xrightarrow{\text{fast}} C\xrightarrow{\text{fast}} \text{NH}_2 + \text{H}^+ \quad \text{(vi)}
\]

\[
R\xrightarrow{\text{fast}} C\xrightarrow{\text{fast}} \text{NH}_2 \xrightarrow{\text{fast}} \text{RCHO} + \text{NH}_3 \quad \text{(vii)}
\]

\[
PdCl_2 + 2 \text{Cl}^- \xrightarrow{\text{fast}} [PdCl_4]^{2-} \quad \text{(viii)}
\]

**Scheme-I**

**Scheme-I** leads to the rate law (1).

\[
-\frac{d[\text{Ce(IV)}]}{dt} = \frac{k_k K_{1} K_{4} [Pd(II)] [\text{Ce(IV)}] [RCH_2NH_2]}{k_1 [H^+] [Cl^-] + k_1 K_{2} [A] [H^+] + K_3} \quad \text{(1)}
\]

The rate law (1) clearly explains all the observed kinetics.
REFERENCES


(Received: 21 May 2007; Accepted: 9 September 2008)  AJC-6846

INTERNATIONAL CONFERENCE ON HYDROGEN AND HYDROGEN STORAGE - METHODS AND MATERIALS

3 — 6 JANUARY 2009

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