

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.

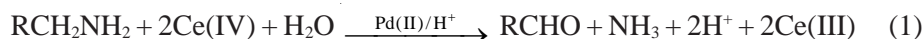
INTRODUCTION

The kinetics of oxidation of amines by chloramine-T^{1,2}, Ce(IV)³⁻⁵ and N-bromo-succinimide⁶ 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 °C 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.



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 k₁ vs. log [amine] was found to be fractional. (0.76 for methyl amine and 0.68 for ethyl amine). At low concentration of amine, k₁ (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 k₁ increases in direct

TABLE-1
EFFECT OF VARIATION OF [Ce(IV)], [AMINE] AND [PdCl₂]
ON RATE CONSTANT AT 35 °C
[HClO₄] = 1 M, [KCl] = 1.00 × 10⁻² M, μ = 4.05 M

[Ce(IV)] × 10 ³ M	[Amine] × 10 ² M	[PdCl ₂] × 10 ⁵ M	k ₁ × 10 ⁴ (s ⁻¹)	
			Methyl amine (a)	Ethyl amine (b)
0.50	2.00	4.64	4.00	7.78
0.80	2.00	4.64	4.12	7.64
1.00	2.00	4.64	3.98	7.80
1.25	2.00	4.64	4.06	7.60
1.67	2.00	4.64	4.08	7.76
2.00	2.00	4.64	3.96	7.68
1.00	0.50	4.64	1.02	2.06
1.00	1.00	4.64	2.06	3.92
1.00	2.50	4.64	4.76	8.96
1.00	3.00	4.64	5.40	10.06
1.00	5.00	4.64	7.56	15.60
1.00	2.00	1.16	1.04	1.96
1.00	2.00	2.32	2.10	3.86
1.00	2.00	3.48	3.18	5.80
1.00	2.00	5.80	5.62	9.78
1.00	2.00	6.96	6.42	12.02

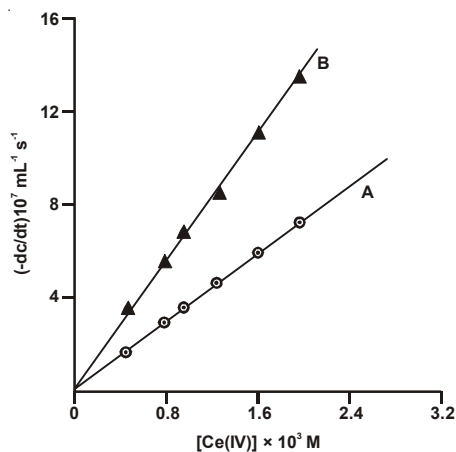


Fig. 1. Plot of $(-dc/dt)$ vs. $[Ce(IV)]$ at $35\text{ }^{\circ}C$
(A = methyl amine and B = ethyl amine)
(conditions mentioned in Table-1)

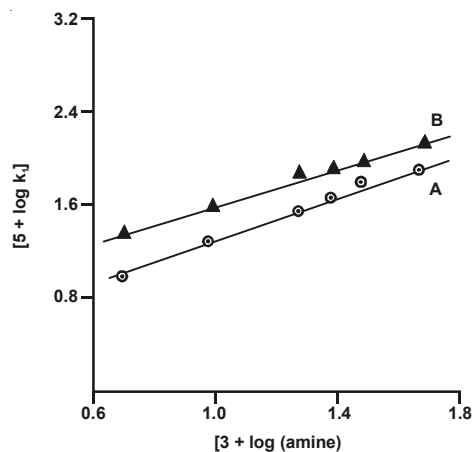


Fig. 2. Plot of $\log k_1$ vs. $\log [Amine]$ at $35\text{ }^{\circ}C$
(A = methyl amine and B = ethyl amine)
(conditions mentioned in Table-1)

TABLE-2
EFFECT OF VARIATION OF $[HClO_4]$, $[KCl]$ AND IONIC STRENGTH $[\mu]$
OF THE MEDIUM ON THE RATE CONSTANT AT 35, 40, 45 AND $50\text{ }^{\circ}C$
 $[Ce(IV)] = 1.00 \times 10^{-3}\text{ M}$, $[Amine] = 2.00 \times 10^{-2}\text{ M}$, $[PdCl_2] = 4.64 \times 10^{-5}\text{ M}$

Temperature ($^{\circ}C$)	$[HClO_4]\text{ M}$	$[KCl] \times 10^2\text{ M}$	Ionic strength (μ)	$k_1 \times 10^4\text{ (s}^{-1}\text{)}$	
				Methyl amine	Ethyl amine
35	0.75	1.00	4.05	4.68	8.36
35	1.50	1.00	4.05	3.62	7.48
35	2.00	1.00	4.05	3.24	7.02
35	3.00	1.00	4.05	2.78	6.42
35	4.00	1.00	4.05	2.36	5.92
35	1.00	0.50	4.05	4.38	8.32
35	1.00	1.50	4.05	3.74	7.56
35	1.00	2.00	4.05	3.38	7.12
35	1.00	3.00	4.05	3.00	6.64
35	1.00	4.00	4.05	2.64	6.08
40	1.00	1.00	4.05	5.48	11.72
45	1.00	1.00	4.05	8.06	16.04
50	1.00	1.00	4.05	11.08	23.86
35	1.00	1.00	1.05	5.56	10.08
35	1.00	1.00	2.05	4.98	9.16
35	1.00	1.00	3.05	4.42	8.28

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

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