



Mechanistic Study of *N*-Bromosuccinimide Oxidation of Ethyl Amine Catalyzed by Palladium(II) in Alkaline Medium : A Kinetic Approach

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The kinetics of oxidation of ethyl amine by *N*-bromosuccinimide in the presence of alkaline solution of palladium(II) chloride as homogeneous catalyst has been investigated at 303 K. A 1 : 1 stoichiometry has been observed. The reaction exhibits a zero order rate dependence with respect to amine and first order at low concentration of *N*-bromosuccinimide tending to zero order at high concentration of *N*-bromosuccinimide. A positive fractional order is observed in the case of Pd(II) whereas ionic strength, [OH⁻] and Hg(OAc)₂ do not influence the oxidation rate. The reaction follows negligible effect on addition succinimide and chloride ion. The activation parameters have been evaluated from the Arrhenius plot. Mechanistic steps are discussed and the rate law derived was found to confirm the observed kinetic results.

Key Words: Oxidation, Mechanism, NBS, Pd(II) chloride, Amine.

INTRODUCTION

N-haloimides have recently been used as oxidizing agents in many redox systems. *N*-bromosuccinimide is a very mild and very often selective but potent oxidant for many organic compounds. Oxidation kinetics with *N*-bromosuccinimide as oxidant and esters¹, alcohols^{2,3} and ketones⁴⁻⁶ as substrate has been discussed in acidic media. The kinetics of redox reaction incorporating certain transition metal ions *viz* Osmium(VIII)⁷⁻⁹, ruthenium(III)¹⁰⁻¹⁴ and Ir(III)^{15,16} as homogeneous catalyst has extensively investigated from mechanistic point of view. However the reaction involving Pd(II)¹⁷⁻²⁰ as homogeneous catalyst have been little investigated. This prompts us to study the kinetics and mechanism of Pd(II) catalyzed *N*-bromosuccinimide oxidation of ethyl amine in an alkaline media.

EXPERIMENTAL

All the reagents used were of highest purity available. Aqueous solution of *N*-bromosuccinimide (S. Merck, G.R.) was prepared always afresh and standardized iodometrically. The standard solution of ethyl amine (BDH A.R) was prepared by dissolving its desired weight sample in known volume of double distilled water. The stock solution of palladous chloride was prepared by dissolving 1.0 gm sample (Johnson & Mathey) in 500 mL of 0.1 M hydrochloric acid and then diluted hundred times. The other reagent *i.e.* Hg(OAc)₂, KCl,

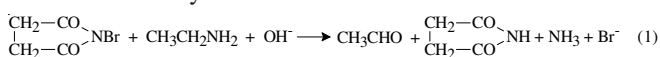
Sodium perchlorate were also prepared in double distilled water. Stock solution of NaOH (E. Merck) was standardized with standard solution of oxalic acid (E. Merck).

Kinetic study: The reaction was carried out under pseudo-first order conditions *i.e.* the concentration of ethyl amine was always about two-fold excess over [NBS] at constant temperature 30 ± 0.1 °C. The reaction was initiated by mixing the requisite volumes of thermally equilibrated solution of *N*-bromosuccinimide and solution of ethyl amine, which also contained the required volumes of solution of Pd(II), NaOH, NaClO₄, KCl and Hg(OAc)₂. The progress of the reaction was followed by iodometric determination of unreacted oxidant *i.e.*, *N*-bromosuccinimide for its active bromine in aliquots (5 mL each) of the reaction mixture withdrawn at regular time intervals. Most of the kinetic runs were followed to more than 70 % completion of the reaction and rate constant were reproducible within ± 3.5 %.

RESULTS AND DISCUSSION

Different reaction mixture containing different sets of reactant concentrations at constant alkalinity, chloride ion and ionic strength were kept to react for 24 h at 303 K and then analyzed. The unconsumed *N*-bromosuccinimide was estimated by iodometric method for active bromine. Succinimide formed was the main product as detected by the method reported. Another product formed during the course of reaction was acetaldehyde was evidenced by the spot test and 2,4

dinitrophenylhydrazine test. The result were in agreement with 1 : 1 stoichiometry.



Oxidation of ethyl amine in alkaline medium by free bromine, which results from the interaction of *N*-bromosuccinimide with bromide ions was prevented by adding mercury(II) ions²¹, which complexes with bromide ions to give $[\text{HgBr}_4]^{2-}$. The addition of mercuric(II) acetate did not interfere with kinetic results. The kinetic investigations were carried out at several initial concentrations of the reactant and the results are given in the Table-1. First order dependence in *N*-bromosuccinimide at low concentrations tended to zero order at high concentration, which is clear from the plot of $(-dc/dt)$ versus $[\text{NBS}^*]$ (Fig. 1) (* indicates $[\text{NBS}]$ at which $-dc/dt$ value was determined). The reaction was found to be independent of $[\text{OH}^-]$ and $[\text{substrate}]$; zero order kinetics with respect to ethyl amine. Catalyst Pd(II) showed fractional order as was evident from slope (0.50) (Fig. 2) obtained by plotting graph between $\log k$ versus $\log [\text{Pd(II)}]$. Table-2 contains the effect of variation of $[\text{Cl}^-]$, $[\text{Hg}(\text{OAc})_2]$, $[\text{NHS}]$ and ionic strength of the medium. Negligible effect of $[\text{Cl}^-]$, $[\text{NHS}]$, $[\text{Hg}(\text{OAc})_2]$ and ionic strength variation on the observed rate constant was obvious. The kinetic data indicates that addition of mercury(II) acetate does not interfere with the reaction. Thus oxidation is purely through *N*-bromosuccinimide. Measurements at different temperatures allowed to compute the energy of activation ΔE , the entropy of activation ΔS^* and the free energy change ΔG^* as 20.88 K cal mol⁻¹, 67.69 JK⁻¹ mol⁻¹ and 64.25 KJ mol⁻¹ respectively.

TABLE-1
EFFECT OF VARIATION OF $[\text{NBS}]$, $[\text{ETHYL AMINE}]$, $[\text{Pd(II)}]$ AND $[\text{OH}^-]$ ON THE RATE CONSTANT OF Pd(II) CATALYZED OXIDATION OF ETHYL AMINE IN AQUEOUS ALKALINE MEDIUM AT 30 °C

$[\text{NBS}] \times 10^3 \text{ M}$	$[\text{Ethyl amine}] \times 10^2 \text{ M}$	$[\text{Pd(II)}] \times 10^6 \text{ M}$	$[\text{OH}^-] \times 10^3 \text{ M}$	$k_1 \times 10^4 \text{ S}^{-1}$
0.50	1.66	2.26	1.66	5.29
0.66	1.66	2.26	1.66	5.07
0.80	1.66	2.26	1.66	5.09
1.00	1.66	2.26	1.66	3.97
1.66	1.66	2.26	1.66	3.02
2.50	1.66	2.26	1.66	2.30
1.00	0.83	2.26	1.66	2.77
1.00	1.00	2.26	1.66	2.95
1.00	1.25	2.26	1.66	2.77
1.00	1.66	2.26	1.66	2.95
1.00	2.50	2.26	1.66	2.64
1.00	5.00	2.26	1.66	2.77
1.00	1.66	0.56	1.66	2.46
1.00	1.66	1.13	1.66	2.87
1.00	1.66	2.26	1.66	3.33
1.00	1.66	4.53	1.66	3.70
1.00	1.66	6.80	1.66	5.00
1.00	1.66	9.06	1.66	7.40
1.00	1.66	2.26	0.83	2.58
1.00	1.66	2.26	1.00	2.46
1.00	1.66	2.26	1.25	2.31
1.00	1.66	2.26	1.66	2.25
1.00	1.66	2.26	2.50	2.27
1.00	1.66	2.26	5.00	2.22
1.00 ^a	1.66	2.26	1.66	2.46
1.00 ^b	1.66	2.26	1.66	3.70
1.00 ^c	1.66	2.26	1.66	6.01

a → 35 °C; b → 40 °C; c → 45 °C

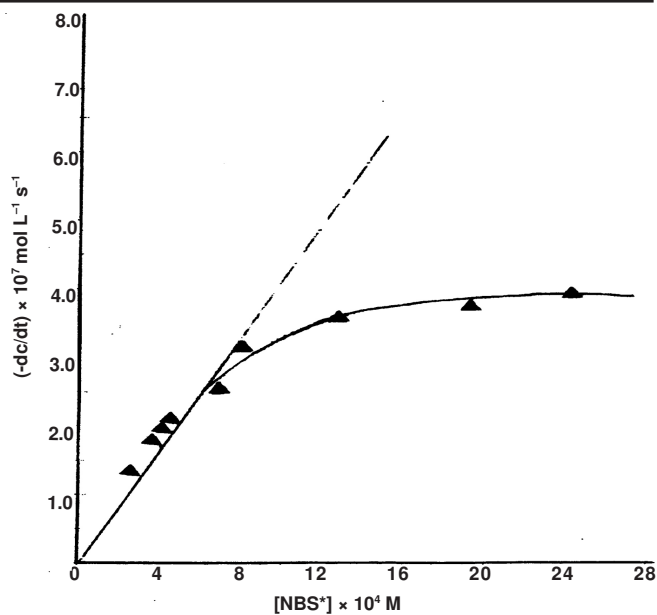


Fig. 1. Plot between $(-dc/dt)$ and $[\text{NBS}^*]$ at 30 °C; $[\text{Ethyl amine}] = 1.66 \times 10^{-2} \text{ M}$; $[\text{NaOH}] = 1.66 \times 10^{-3} \text{ M}$; $[\text{Pd(II)}] = 2.26 \times 10^{-6} \text{ M}$; $[\text{Hg}(\text{OAc})_2] = 3.33 \times 10^{-3} \text{ M}$

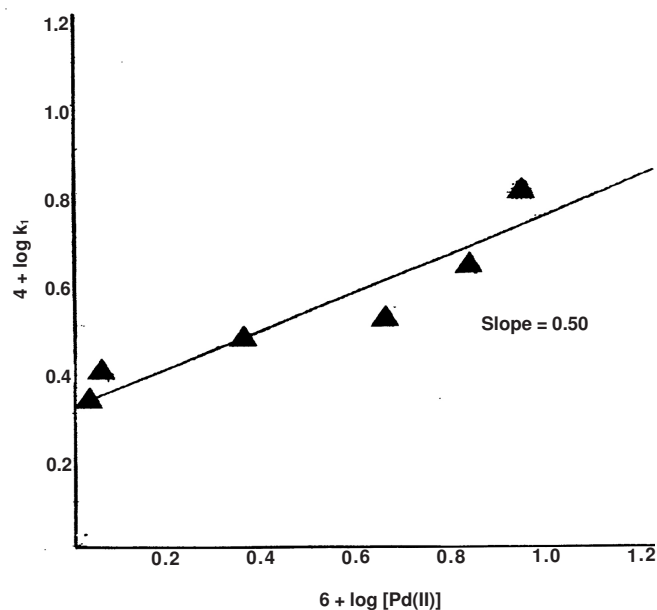
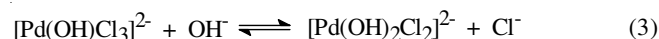


Fig. 2. Plot between $\log k_1$ and $\log [\text{Pd(II)}]$ at 30 °C; $[\text{NBS}] = 10.00 \times 10^{-4} \text{ M}$; $[\text{Ethyl amine}] = 1.66 \times 10^{-2} \text{ M}$; $[\text{NaOH}] = 1.66 \times 10^{-3} \text{ M}$; $[\text{Hg}(\text{OAc})_2] = 1.25 \times 10^{-3} \text{ M}$

Palladium chloride is quite stable in hydrochloric acid and exists as $[\text{PdCl}_4]^{2-}$. In alkaline medium palladium chloride has been reported to exist as-

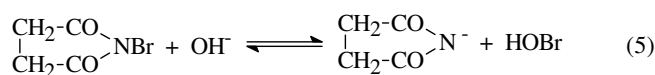
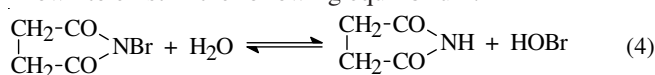


Thus from above equilibrium it is clear that in alkaline medium either $[\text{PdCl}_4]^{2-}$ or $[\text{Pd}(\text{OH})\text{Cl}_3]^{2-}$ or $[\text{Pd}(\text{OH})_2\text{Cl}_2]^{2-}$ in the reactive species. But when any of $[\text{Pd}(\text{OH})\text{Cl}_3]^{2-}$ or $[\text{Pd}(\text{OH})_2\text{Cl}_2]^{2-}$ is taken as reactive species then the rate law derived does not confirm the observed kinetics. Hence the only choice left is to assume $[\text{PdCl}_4]^{2-}$ as the real catalytic species. Therefore in present study $[\text{PdCl}_4]^{2-}$ is taken as real catalytic species.

TABLE -2
EFFECT OF VARIATION OF POTASSIUM CHLORIDE, IONIC STRENGTH OF MEDIUM, ADDITION OF SUCCINIMIDE (NHS) AND MERCURIC ACETATE ON THE RATE CONSTANT OF Pd(II) CATALYZED OXIDATION OF ETHYL AMINE IN AQUEOUS ALKALINE MEDIUM AT 30 °C

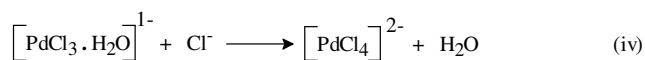
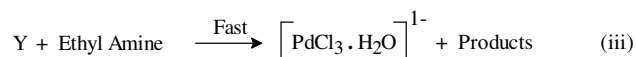
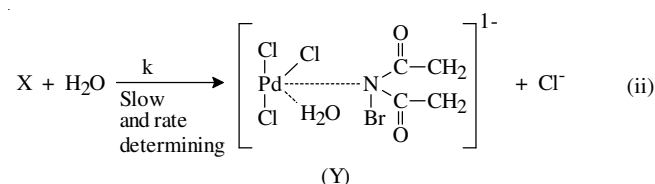
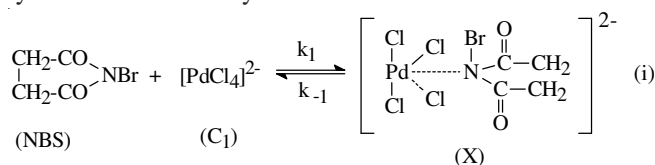
[KCl] × 10 ³ M	μ × 10 ³ M	[NHS] × 10 ³ M	[Hg(OAc) ₂] × 10 ³ M	k ₁ × 10 ⁴ S ⁻¹
1.66	-	-	1.25	1.84
2.00	-	-	1.25	1.73
2.50	-	-	1.25	1.84
3.00	-	-	1.25	1.84
5.00	-	-	1.25	1.84
10.00	-	-	1.25	1.84
-	3.38	-	1.25	3.33
-	4.98	-	1.25	3.27
-	7.50	-	1.25	3.91
-	10.00	-	1.25	3.88
-	12.50	-	1.25	3.66
-	15.00	-	1.25	3.72
-	-	0.83	1.25	3.46
-	-	1.00	1.25	3.46
-	-	1.25	1.25	3.43
-	-	1.66	1.25	3.51
-	-	2.50	1.25	3.43
-	-	5.00	1.25	3.51
-	-	-	0.71	2.46
-	-	-	0.83	2.52
-	-	-	1.00	2.64
-	-	-	1.25	2.62
-	-	-	2.00	2.68
-	-	-	3.33	2.58

In aqueous alkaline medium *N*-bromosuccinimide is known to exist in the following equilibrium.



Thus in alkaline medium it seems that either *N*-bromosuccinimide itself or HOBr or anion may be active species formed through the equilibrium (4) or (5). Neither HOBr nor anions of *N*-bromosuccinimide explains the result when assumed as oxidizing species. Hence only choice left is to assume *N*-bromosuccinimide as such which when taken as real oxidising species, leads to the rate law capable of explaining all the kinetic orders and other effects.

On the basis of above discussion and experimental results the following reaction scheme is proposed for Pd(II) catalyzed oxidation of ethyl amine in alkaline media.



The final rate law, which is obtained on applying steady state treatment with reasonable approximation can be given by the expression (6).

$$\frac{-d[\text{NBS}]}{dt} = \frac{k K_1 [\text{NBS}]_{\text{T}} [\text{Pd(II)}]_{\text{T}}}{1 + K_1 [\text{NBS}] + [\text{Pd(II)}]} \quad (6)$$

where, $K_1 = k_1/k_{-1}$.

The rate law (6) is in agreement with all the experimental observations. The proposed mechanism is also consistent with activation parameters. The high positive values of free energy of activation (ΔG^*) indicate that the transition state is highly solvated.

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