



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

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The kinetics of Pd(II) catalyzed oxidation of methyl amine by alkaline solution of *N*-bromosuccinimide (NBS) in the presence of mercuric acetate as scavenger is investigated in the temperature range 30-45 °C. First order kinetics in the lower concentration range of *N*-bromosuccinimide was observed to tend to zero order at its higher concentrations. The reaction follow identical kinetics, being zero order in substrate and [OH<sup>-</sup>]. A positive effect of variation of palladous chloride was observed while addition of succinimide and mercuric acetate did not affect the rate constant of reaction. The variation of ionic strength of the medium and [Cl<sup>-</sup>] showed zero effect on the reaction rate. The oxidation product formaldehyde formed was detected by spot test and 2,4-dinitrophenyl hydrazine test. Various thermodynamic parameters have been computed. A suitable mechanism, consistent with the kinetic observation has been proposed.

**Key Words:** Methyl amine, *N*-bromosuccinimide, Palladous chloride, Oxidation, Kinetics.

### INTRODUCTION

Recently considerable attention has been focused on *N*-halogeno compounds<sup>1-7</sup>. The diverse nature of these compounds is due to their ability to acts as a source of halogenium cation hypohalite species and nitrogen anions. Although the oxidative capacity of *N*-bromosuccinimide has been examined in several uncatalyzed<sup>8,9</sup> and catalyzed<sup>10-12</sup> reactions in acidic media. However it appears from the literature that no attempt has so far been made to determine the catalytic potential of Pd(II) in *N*-bromosuccinimide oxidation. So the aim of the present paper is to investigate the kinetics and mechanism of Pd(II) catalysis in *N*-bromosuccinimide oxidation of methyl amine in alkaline media.

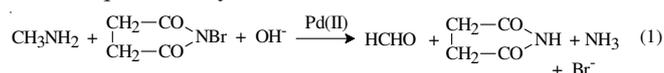
### EXPERIMENTAL

*N*-boromosuccinimide (G.R.S. Merck) solution was always prepared afresh and its strength was checked by iodimetric titration of active bromine. Solution of methyl amine (BDH, AR) sodium hydroxide, Hg(OAc)<sub>2</sub> and KCl were prepared by weighing and dissolving their sample in double distilled water. Sodium perchlorate (E. Merck) was used to maintain the ionic strength of the medium. Pd(II) chloride solution was prepared by dissolving 1.0 gm of the sample (Johnson & Mathey) in 500 mL of 0.1 M HCl and then diluted it hundred times. All other reagents were of analytical grade. Jena glass still were employed. Black coated reaction vessel were used to avoid any photochemical effects.

A thermostated water bath was used to maintain the desired temperature to within ± 0.1 °C. The reactions were initiated by the addition of *N*-bromosuccinimide solution to the other reagents equilibrated separately at 30 °C. The progress of the reaction was monitored by determining unconsumed *N*-bromosuccinimide iodometrically at regular time intervals. The course of the reaction was studied for over 75 % of the reaction.

### Stoichiometry

**Various ratios of [NBS] : [CH<sub>3</sub>NH<sub>2</sub>]** under the experimental conditions [NBS] >> [CH<sub>3</sub>NH<sub>2</sub>] were taken in different reaction vessels and were allowed to stand for 72 h. Estimation of unreacted [NBS] revealed that 1 mole of methyl amine consumed 1 mole of NBS and accordingly stoichiometric equation may be written as :



The presence of HCHO as products was confirmed by spot test<sup>13</sup> and 2,4-dinitrophenyl hydrazine test.

### RESULTS AND DISCUSSION

The kinetics of Pd(II) catalyzed oxidation of methyl amine by *N*-bromosuccinimide was investigated at several initial concentration of the reactant (Table -1). First order kinetics in *N*-bromosuccinimide at low concentration tended to zero order at higher concentration, which is clear from the plot of (-

$dc/dt$  versus  $[NBS^*]$  (Fig. 1) (\*indicates  $[NBS]$  at which  $-dc/dt$  value was determined). The reaction was observed to be independent of  $[substrate]$ , *i.e.* zero order kinetics with respect of methyl amine. A positive fractional order in Pd(II) is also obvious from slope (0.54) of the plot of  $\log k$  versus  $\log [Pd(II)]$  (Fig. 2). Constant values of  $k_1$  with increase in the  $[NaOH]$  indicates that reaction follows zero order dependence.

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

$[NBS] \times 10^3 M$	$[Methyl Amine] \times 10^2 M$	$[Pd(II)] \times 10^6 M$	$[OH^-] \times 10^3 M$	$k_1 \times 10^4 S^{-1}$
0.50	1.66	2.26	1.66	5.05
0.66	1.66	2.26	1.66	4.53
0.80	1.66	2.26	1.66	4.18
1.00	1.66	2.26	1.66	3.87
1.66	1.66	2.26	1.66	3.15
2.50	1.66	2.26	1.66	2.65
1.00	0.83	2.26	1.66	2.68
1.00	1.00	2.26	1.66	2.77
1.00	1.25	2.26	1.66	2.77
1.00	1.66	2.26	1.66	2.64
1.00	2.50	2.26	1.66	2.62
1.00	5.00	2.26	1.66	2.77
1.00	1.66	0.56	1.66	2.97
1.00	1.66	1.13	1.66	2.11
1.00	1.66	2.26	1.66	2.46
1.00	1.66	4.53	1.66	2.90
1.00	1.66	6.80	1.66	4.62
1.00	1.66	9.06	1.66	5.50
1.00	1.66	2.26	0.83	3.43
1.00	1.66	2.26	1.00	3.46
1.00	1.66	2.26	1.25	3.33
1.00	1.66	2.26	1.66	3.38
1.00	1.66	2.26	2.50	3.33
1.00	1.66	2.26	5.00	3.33
1.00 <sup>a</sup>	1.66	2.26	1.66	4.44
1.00 <sup>b</sup>	1.66	2.26	1.66	6.78
1.00 <sup>c</sup>	1.66	2.26	1.66	10.17

a  $\rightarrow$  35 °C; b  $\rightarrow$  40 °C; c  $\rightarrow$  45 °C

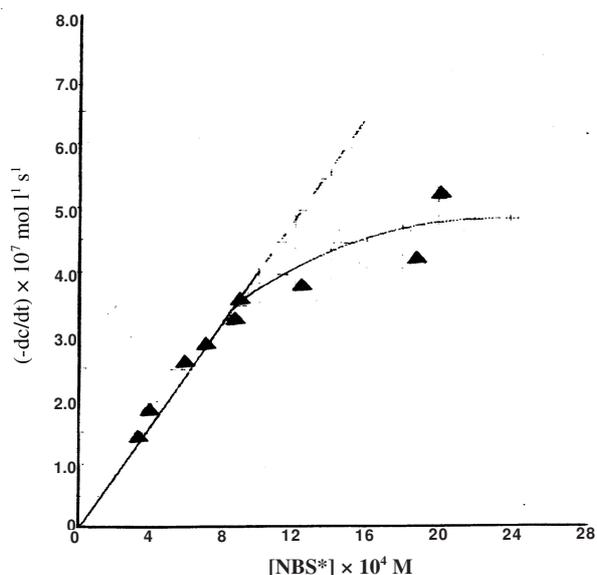


Fig. 1. Plot between  $(-dc/dt)$  and  $[NBS^*]$  at 30 °C;  $[Methyl amine] = 1.66 \times 10^{-2} M$ ;  $[NaOH] = 1.66 \times 10^{-3} M$ ;  $[Pd(II)] = 2.26 \times 10^{-6} M$ ;  $[Hg(OAc)_2] = 3.33 \times 10^{-3} M$

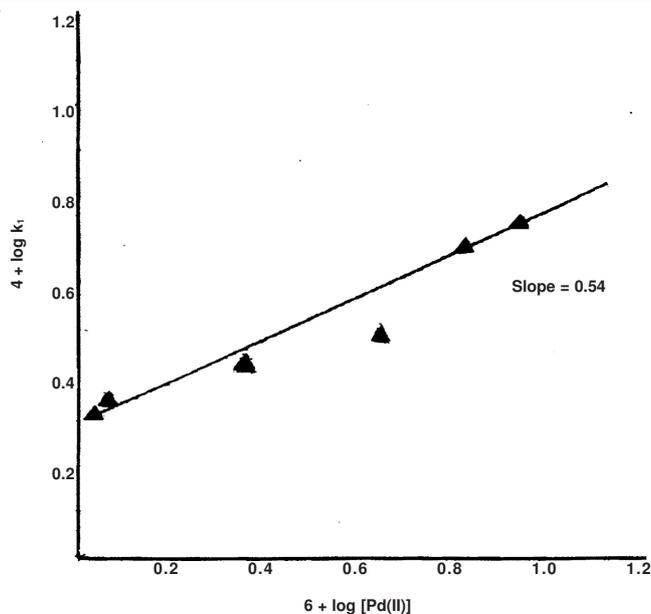


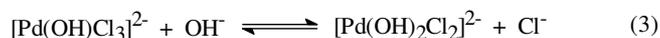
Fig. 2. Plot between  $\log k_1$  and  $\log [Pd(II)]$  at 30 °C;  $[NBS] = 10.00 \times 10^{-4} M$ ;  $[Methyl amine] = 1.66 \times 10^{-2} M$ ;  $[NaOH] = 1.66 \times 10^{-3} M$ ;  $[Hg(OAc)_2] = 1.25 \times 10^{-3} M$

Addition of chloride ion, mercuric acetate succinimide (NHS) and variation of ionic strength of the medium had an insignificant effect on  $k_1$  values observed in each case (Table -2). Kinetic measurements at 30-45 °C led us to compute the value of energy activation  $\Delta E^* = 18.82 K cal mol^{-1}$ , entropy of activation  $\Delta S^* = 43.85 JK^{-1} mol^{-1}$  and free energy change  $\Delta G^* = 60.84 KJ mol^{-1}$  respectively.

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 METHYL AMINE IN AQUEOUS ALKALINE MEDIUM AT 30 °C

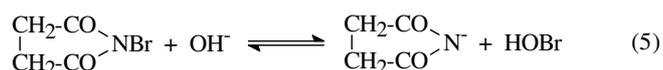
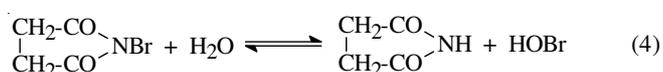
$[KCl] \times 10^3 M$	$\mu \times 10^2 M$	$[NHS] \times 10^3 M$	$[Hg(OAc)_2] \times 10^3 M$	$k_1 \times 10^4 S^{-1}$
1.66	-	-	1.25	3.14
2.00	-	-	1.25	3.00
2.50	-	-	1.25	2.07
3.00	-	-	1.25	3.95
5.00	-	-	1.25	2.90
10.00	-	-	1.25	3.07
-	3.38	-	1.25	2.64
-	4.98	-	1.25	2.57
-	7.50	-	1.25	2.66
-	10.00	-	1.25	2.71
-	12.50	-	1.25	2.55
-	15.00	-	1.25	2.77
-	-	0.83	1.25	4.62
-	-	1.00	1.25	4.62
-	-	1.25	1.25	4.31
-	-	1.66	1.25	4.44
-	-	2.50	1.25	4.44
-	-	5.00	1.25	4.62
-	-	-	0.71	3.33
-	-	-	0.33	3.35
-	-	-	1.00	3.53
-	-	-	1.25	3.70
-	-	-	2.00	3.33
-	-	-	3.33	3.38

Zero effect of mercuric acetate eliminates the possibility of its involvement of *N*-boromosuccinimide oxidation and thus it only acts as scavenger<sup>7,8</sup>, for any Br<sup>-</sup> formed and rules out any possibility of parallel oxidation by Br<sub>2</sub>. In alkaline medium the following equilibria has been reported to exist in Palladous chloride-



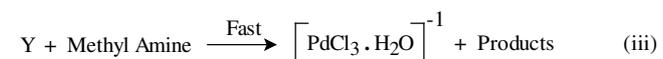
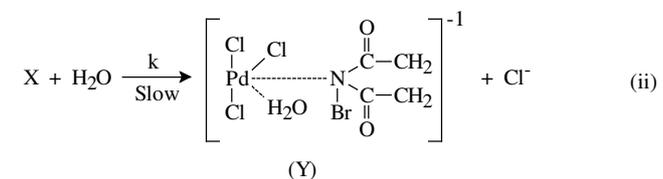
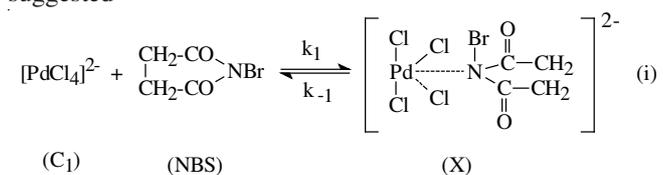
From above equilibria it is clear that in alkaline medium either [PdCl<sub>4</sub>]<sup>2-</sup> or [Pd(OH)Cl<sub>3</sub>]<sup>2-</sup> or [Pd(OH)<sub>2</sub>Cl<sub>2</sub>]<sup>2-</sup> is taken as reactive species of palladous chloride. When any of [Pd(OH)Cl<sub>3</sub>]<sup>2-</sup> or [Pd(OH)<sub>2</sub>Cl<sub>2</sub>]<sup>2-</sup> is taken as reactive species, the rate law derived does not confirm to the observed kinetic data. Hence these species are ruled out as real catalytic species. In this circumstances the only choice left [PdCl<sub>4</sub>]<sup>2-</sup> is the real catalytic species in the present investigation.

In aqueous alkaline medium NBS hydrolyses according to the following equilibrium-



Thus in alkaline medium, reactive species may be either *N*-boromosuccinimide itself or HOBr formed either through equilibrium (4) or (5) or anions of *N*-boromosuccinimide. Neither HOBr nor anion of *N*-boromosuccinimide explains the results when assumed as oxidizing species. Now only choice left *N*-boromosuccinimide as such to be involved as oxidizing species as rate law derived on this explains all the results.

Considering [PdCl<sub>4</sub>]<sup>2-</sup> and *N*-boromosuccinimide as such the real reactive species of Pd(II) chloride and *N*-boromosuccinimide respectively along with other kinetic data with respect to methyl amine, NaOH, mercuric acetate, potassium chloride and succinimide (NHS) the following steps are suggested -



Application of steady state treatment with reasonable approximation yields rate law (6) in terms of rate of less of *N*-boromosuccinimide.

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

The rate law (6) explains all the observed kinetic results *i.e.* rate is independent of [NaOH], [Hg(OAc)<sub>2</sub>], [Cl<sup>-</sup>], [Methylamine] and succinimide[NHS].

It shows that reaction is first order with respect to *N*-boromosuccinimide at their low concentration and tends to zero order at the higher concentrations. A positive fractional order with respect to Pd(II) chloride. Hence the mechanism derived on the basis of kinetic results seems to be valid.

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