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RESEARCH ARTICLE

KINETICS AND MECHANISM OF THE OXIDATION OF AMINES BY N-BROMOPHTHALIMIDE

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ABSTRACT

N-Bromophthalimide (NBP) is reported to be a stable oxidizing agent and is used as an oxidiometric titrate for the estimation of a variety of organic, inorganic and pharmaceutical compounds. The kinetics of oxidation of primary aliphatic amines by NBS in acid solution showed first order dependence on (NBS) and (amine). An increase in $[H^+]$ increased the rate marginally. The rate of reaction increased with decrease in the dielectric constant of the medium. The observed order of reactivity of different amines towards oxidation is: methyl<ethyl<n-propyl<n-butyl<iso propyl amine. Add succinimide and salt had negligible effects on the rate stoichiometric studies revealed that one mole of amine consumed one mole of NBS to give one mole of Carboxyl compound and ammonia. Recent reports include R_4 (III)-Catalyzed oxidation of aliphatic amines by NBS in perchloric acid medium.

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INTRODUCTION

Amines find many applications in chemical industries. There have been a number of studies on the reaction between amines and halogenating agents (Uma and Mayanna, 1985). Primary aromatic amines can be oxidized to nitroso compounds (Hedaytuallah, 1972) and intrest in N-nitroso amines has considerably increased in the past few years. This is due to the realization that these compounds are carcinogenic and are present as pollutants in the atmosphere, foods, beverages (Digenis, 1979) etc. it is known that phenothiazines and certain thioxanthenes with organic brominating agents is quite specific. N-haloimides such as NBS and NBP react with tertiary amino group of the side chain of thioxanthenes to give corresponding N-bromo derivative (Walash et al., 1988). Oxidation of amines by various one and two electron oxidants have been extensively studied (Bayer, 1900; Emmons, 1957; Greenspan, 1947; Ibne, 1962; Radhakrishnamurthy, 1980; Prasad Rao, 1930; Panda, 1981 and Ogata, 1979), but such studies with N-halo compounds is sporadic in literature. N-halo compounds, particularly NBS was used to differentiate alcohols, amines (Kruse, 1954 and Barakat, 1952), etc. Dunstan and Henbest (1990) were the first to report the oxidation of amines by NBS and a systematic kinetic study of the oxidation of aliphatic amines by NBS both in acidic and alkaline solutions has been reported recently (Saroja, 1990). The reaction exhibit a first order dependence of rate both on [NBS] and (amine) in acid medium. The marginal increase of rate increase in $[H^+]$ has been attributed to the protonation of NBS in the equilibrium.

MATERIALS AND METHOD

N-Bromophthalimide: Freshly prepared N-bromophthalmide (NBP) solution was used throughout. The required amount of NBP was weighted accurately and dissolved in distilled acetic acid in a standard flask. The NBP solution was standardized by titrating a known volume of it in acidified KI solution against standard sodium thiosulphate solution using starch as indicator. The concentration of NBP was calculated stoichiometric equation.

Kinetic Parameters

Under the experimental conditions of [substrate] >> [NBP], the plots of log (a/a - x) versus time were linear (where a and (a-x) time't') indicating first order dependence of rate of [NBP].

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This has been found to be true with all the substrates studied in the present work. The pseudo-first order rate constants (k') were calculated from the slopes of these plots. The order in [substrate] was obtained from the linear plot of log k' versus log [substrate]. However, the order in certain amino acids viz., alanine, phenyl alanine serine and threonine were determined from the linear plots of log (initial rate) versus log [amino acid]. The reactions followed Michaelis-Menten type of mechanism (Mohana Das and Indrasenan, 1987), the rate law derived was

$$-\frac{d[NBP]}{dt} = \text{rate} = \frac{kK[NBP][\text{substrate}]}{1 + K[\text{substrate}]}$$

$$-\frac{2.303\, d\log[NBP]}{dt} = k' = \frac{kK[\text{substrate}]}{1 + K[\text{substrate}]}$$

Where k is the rate constant for the slow step and k formation constant of the precursor complex.
Reciprocal of the equation-2 gives

$$\frac{1}{k'} = \frac{1}{kK[\text{substrate}]} + \frac{1}{k}$$

From the intercept and slope of the reciprocal plots of 1/k versus 1/[substrate,. K and k were evaluated.

Effect of Substituents

The effect of substituents on the rate of NBP oxidation of amines and hydroxyl acids was studies to find electronics and steric effect on the rate of oxidation and also to understand the reaction side to support the proposed mechanism. In the oxidation of benzyl alcohols by NBP, the effect of substituents on reaction rates were studies to correlate the rates with Hammett's σ value, to get an insight into the type of mechanism operative in the oxidation process.

Effect of ionic strength

The effect of ionic strength (M) on rates of NBP oxidation of amines α-amino, benzyl alcohols and sugars was studies by varying [KCl] to find the general applicability of Bjerrum's equation. The effect of M-on the rate gives a clue to the nature of the reactive species involved in the oxidation process.

Activation Parameters

The activation energies (Ea) for the oxidation reaction studies were evaluated from the slope of Arrhenius plots log k *vs* 1/T in the temperature range 288-328 k. According to the theory of absolute reaction rares 11, the expression relation rate constant k and free energy of activation may be written as

$$k = \frac{kT}{h} e^{-\Delta G\#/RT}$$

ΔG# was calculated from the rearranged equation

$$\Delta G^{\#} = 2.303RT \log \frac{RT}{NhK}$$

Where R, the gas constant, h, the Planck's constant, N, the Avogadro's number and T the temperature in absolute scale. The entropy of activation and enthalpy of activation were calculated using the following equations.

$$\Delta H^{\#} = E_a - RT \text{ and}$$

$$\Delta S^{\#} = \frac{\Delta H^{\#} - \Delta G^{\#}}{T}$$

Isokinetic relationship

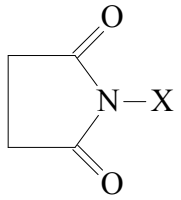
Isokinetic temperature (β) was evaluated by using Leffler'sequation (12-18).

$$\Delta H^{\#} = \Delta H_0^{\#} + \beta \Delta S^{\#}$$

RESULT AND DISCUSSION

Kinetics of oxidation of aliphatic amines by n-bromophthalimide in aqueous acetic acid medium

N-haloimides (I) have emrged as effective halogentating as well as oxidizing agents (Filler, 1963; Mathur and Narang, 1975). The upsurging interest in N-haloimides as oxidants could be attributed mainly to the fact that they function as the source of halonium cations (II) and hypohalite species (III).



(I) N-haloimide

X^+

(II) Halonium cation

HOX

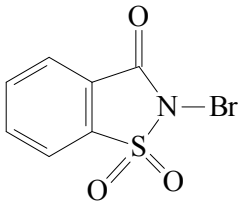
(III) Hypohalite species

Among the several N-haloimides, N-bromosuccinimide (NBS), N-iodosuccinimide (NIS), N-chlorosuccinimide (NCS) and N-bromosaccharin (NBSacc) are noteworthy and these have been employed extensively as oxidants by several groups of workers (Filler, 1963; Mathur and Narang, 1975). These N-haloimides have also been used widely in the determination of various organic, inorganic and pharmaceutical compounds. Recently it has been reported by AbouOuf et al. (1980) that N-bromophthalimide (NBP) is much more stable and better bromination and oxidizing agent compared to the other related N-halomides.

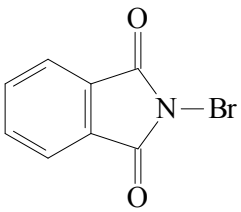
They have also reported that it is an effective oxidimertric titrant in the determination of certain pharmaceuticals.Indrasenan et al. (Mohana Das and Indraseran, 1987; Girish Kumar et al., 1988) in their search for new redox titrants found NBP as stable oxidant in acetic acid medium and it has been used by them in the determination of a wide variety of reductants. For example, NBP has been used to brominate the sulphonamides (Girish Kumar and Indrasenan, 1988) present in the sulpha drugs directly without any added bromide. The actual brominating species suggested in Br^+ (bromonium ion) produced by the heterolytic fission of N-Br bond. The N-Br bond is polar and more so it is attached to $\alpha > C= 0$ groups in NBP, therefore the heterolytic fission of the bond becomes more feasible. Here acetic acid I used as a solvent which prevents bromine from escaping during the course of reaction. In most of the potentiometric titrations the addition of auxillary reagent to the reductant is not needed when NBP (Girish Kumar et al., 1988) is employed as a titrant, whereas with other N-haloimides, in order to get a sharp end point, the auxillary reagent is required. During these titrations NBP is reported to undergo reduction to phthalimide according to the equilibrium.

$$RNBr + H^+ + 2e \rightleftharpoons RNH + Br^-$$

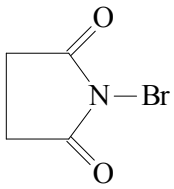
Where R represents the phthalimide part excluding nitrogen. The redox potential for the NBP/NHP couple in 50% (v/v) HOAc – H_2O was found (Mohana Das and Indrasenan, 1984) to be 1.09 V at 32°C indicating that it is a moderately strong oxidant. The reactivity of NBP could be compared to the other structurally analogous N-haloimides such as NBS and NBSacc.



N-bromosaccharin
(NBSacc)



N-bromophthalimide
(NBP)



N-bromosuccinimide
(NBS)

The reaction exhibit a first order dependence of rate both on [NBS] and (amine) in acid medium. The marginal increase of rate increase in $[H^+]$ has been attributed to the protonation of NBS in the equilibrium.

$$NBS + H^+ \rightleftharpoons (NBSH)^+$$

The solvent effect, $[H^+]$ effect and other kinetic features a involving reaction between protonated oxidant and neutral rate-determining step has been proposed. Abstraction of hydride ion from the α-carbon of amine followed by simultaneous loss of proton from the amino group proposed in the mechanism is supported by the observed order of reactivity of these substituents which is in the increasing order of +I effect of allyl group attached to nitrogen. The ρ* value was found to be -2.70.

In alkaline solutions BrO^- has been proposed as the active oxidizing species which is formed according to the equilibrium.

$$NBS + {}^-OH \rightleftharpoons BrO^- + \text{succinimide}$$

And the reaction involves the natural amine and BrO^- to give the corresponding aldehyde. The order of reactivity observed is methylamine > ethylamine >n-propylamine> n-butylamine>isobutylamine>iso-propylamine which is just the reverse of what has been observed in acid media. NBP is more stable and structurally analogous to NBS. Its redox potential is comparable with those of related N-halomides. In spite of this, very little attention has been paid towards the kinetic study involving this oxidant. To understand the nature of reactive species of NBP and to fully evaluate the oxidizing power of this reagent the author has

undertaken the study of kinetics and mechanism of oxidation of a variety of compounds, of which discussion presented here is for aliphatic amines, viz., methylamine (MA), n-propylamine (PA), n-butylamine (BA), diethylamine (DEA) and triethylamine (TEA). These oxidations have been carried out in acetic acid medium in the presence of $Hg(OAc)_2$.

Salient features of data

- All the experiments were carried out under the conditions of [NBP] << [amine] in the presence of excess of $Hg(OAc)_2$ in 10% (v/v) HOAc – H_2O. The plots of log (a/a-x) versus time (where a and (a-x) correspond to the initial concentration and concentration of NBP after time 't') were linear passing through the origin indicating a first order dependence of rate on [NP] (Table 1). from the slopes of such plots the pseudo-first-order rate constant (K') have been evaluated. The k' values were found to be independent of initial concentration of NBP, confirming the first-order dependence of reaction on [NBP].

- The rate of oxidation of amines by NBP was found to increase with increase in [amine]. In the case of primary amines, viz., methylamine, n-propylamine and n-butylamine the plots of log k' versus log [amine] were linear with slopes less than unity indicating fraction order dependence of rate on these amines (Tables 2, 4).

Table- 1 Order in (NBP) in the oxidation of methylene by NBP in aqueous acetic acid medium

[NBP] = 6.38×10^{-4}mol dm^{-3}; [methylamine] = 3.00×10^{-2}mol dm^{-3}[$Hg(OAc)_2$] = 4.00×10^{-3}moldm; [HOAc] = 10% (v/v); Temp = 305 k

Time(min)	(a-x)	log (a/a-x)
0	11.7	0.000
2	10.4	0.05
5	8.50	0.139
7	7.45	0.196
10	6.20	0.276
12	5.55	0.324
15	4.65	0.401

Table 2. Order in [methylamine] in the oxidation of methylamine by NBP in aqueous acetic acid medium

[NBP] = 6.38×10^{-4}mol dm^{-3};[HOAc] × 10% (v/v) [$Hg(OAc)_2$] = 4.00×10^{-3}mol dm^{-3}; Temp = 305 K

10^2 × [methylamine] ($moldm^{-3}$)	10^4× k' (s^{-1})	2+log [methylamine]	4+log k'
1.00	6.45	0.000	0.809
2.00	8.15	0.301	0.911
3.00	10.5	0.477	1.02
4.00	12.00	0.602	1.08
5.00	14.4	0.699	1.16

Table 3. Effect of [methylamine] on k' in NBP-methylamine (MA) reaction at different temperatures and search for complex formation

[NBP] = 6.38×10^{-4}mol dm^{-3}; [HOAc] = 10% (v/v)
[$Hg(OAc_2)$] = 4.00×10^{-3}mol dm^{-3}

Temp (k)	10^2 × [MA] (mol dm^3)	$\frac{1}{[MA]}$	10^4 × k' (s^{-1})	$\frac{10^{-3}}{k'}$ (s)
305	1.00	100	6.45	1.35
	2.00	50.0	8.15	1.32
	3.00	33.3	10.5	0.947
	4.00	25.0	12.0	0.833
	5.00	20.0	14.4	0.694
313	1.00	100	7.67	1.80
	1.50	66.7	10.0	1.00
	2.00	50.0	3.5	0.740
	2.50	40.0	14.0	0.714
	3.00	33.3	14.8	0.674
318	1.00	100	9.50	1.05
	1.50	66.7	12.5	0.800
	2.00	50.0	16.0	0.625
	2.50	40.0	18.6	0.536
	3.00	33.3	21.5	0.465

Table 4. Effect of [n-propylamine] on k' in NBP-n-propylamine (PA) reaction at different temperatures and search for complex formation

[NBP] = 6.38 × 10-4 mol dm^{-3};[HOAc] =10%(v/v)
$[Hg(OAc)_2]$ = 4.00 × 10^{-3}mol dm^{-3}

Temp (k)	10^2 × [PA] (mol dm^{-3})	$\frac{1}{[PA]}$	10^4 × k' (s^{-1})	$\frac{10^{-3}}{k'}$ (s)
304	1.00	100	9.60	1.04
	1.50	66.7	11.5	0.868
	2.00	50.0	13.4	0.744
	2.50	40.0	14.4	0.694
	3.00	33.3	15.3	0.651
313	1.00	100	14.0	0.714
	1.50	66.7	17.5	0.572
	2.00	50.0	20.5	0.488
	2.50	40.0	25.0	0.400
	3.00	33.3	28.0	0.357
318	1.00	100	16.5	0.606
	1.50	66.7	21.0	0.476
	2.00	50.0	26.0	0.385
	2.50	40.0	30.0	0.333
	3.00	33.3	32.5	0.308

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