



Kinetic Study of Oxidation of Substituted Benzyl Alcohols by N-Bromophthalimide in Aqueous Acetic acid

Jagdish Bharad^{*}, Balaji Madje and Milind Ubale

Department of Chemistry, Vasant Rao Naik Mahavidyalaya, Aurangabad. 431003(M.S.), India.

Abstract: Kinetic investigations of oxidation of *p*-substituted benzyl alcohols by *N*-bromophthalimide (NBP) in aqueous acetic acid medium in presence of mercuric acetate as a scavenger have been studied. The oxidation kinetics of benzyl alcohols by NBP shows a first order dependence on NBP and fractional order on benzyl alcohols. The variation of ionic strength, $\text{Hg}(\text{OAc})_2$, H^+ and phthalimide (reaction product) have no significant effect on reaction rate. Effect of varying dielectric constant of medium on the rate has been studied. Activation parameters for the reaction have been evaluated from Arrhenius plot by studying the reaction at different temperature.

Key Words: Kinetics, Oxidation, Benzyl alcohol, *N*-bromophthalimide.

I. Introduction

The kinetics of oxidation of substituted benzyl alcohols by organic halo chromates such as Quinolinium dichromate[1], Imidazolium Dichromate[2], Benzyl triethylammonium Chlorochromate[3], Quinoxalinium bromochromate[4], Benzimidazolium Fluorochromate[5], Pyridinium bromochromate[6], Tetrabutyl ammonium tribromide[7], etc. have been studied earlier. A number of reports on kinetic studies of oxidation of benzyl alcohols with variety of *N*-halo compounds such as *N*-bromosuccinimide[8], *N*-bromosaccharin[9], *N*-bromoacetamide[10] and Chloramine-T[11] as oxidants have been reported.

N-bromophthalimide (NBP) is a potential oxidizing agent[12-14] and it seems that there are no reports about the kinetics of oxidation of benzyl alcohols by NBP. The present work reports kinetics and mechanism of oxidation of benzyl alcohols by *N*-bromophthalimide in 50% acetic acid.

II. Experimental Section

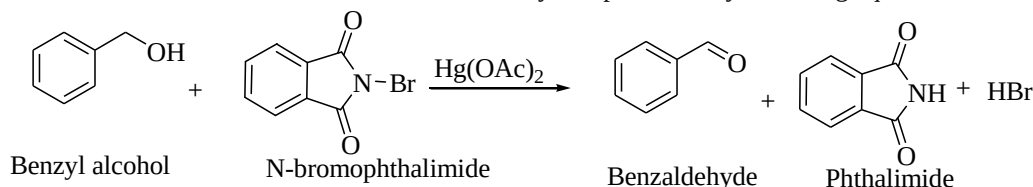
Materials: The oxidant NBP (Aldrich sample) was used. Acetic acid (A.R. grade) was purified by the literature procedure. The standard solutions of substituted benzyl alcohols were prepared in acetic acid. Double distilled water was employed in all kinetic runs. To prevent photochemical effect, the freshly prepared solution of NBP was stored in an amber colored bottle and its strength was checked iodometrically[15] using 1% solution of freshly prepared starch as an indicator.

Kinetic measurements:

All kinetic measurements were made under pseudo first order conditions, by keeping large excess of benzyl alcohols over oxidant NBP. Mixture containing requisite amounts of solutions of benzyl alcohol, $\text{Hg}(\text{OAc})_2$ in 50% acetic acid were equilibrated at 303K. To this mixture was added a measured amount of pre-equilibrated (303K) standard solution of NBP. To maintain the desired temperature (within $\pm 0.1^\circ\text{C}$) the reaction mixture was kept in a thermostated water bath and the progress of the reaction was monitored spectrophotometrically by withdrawing aliquots of the reaction mixture at regular time of intervals. The reaction rate was monitored at λ_{max} of NBP by measuring the absorbance of the unreacted NBP at the respective time. All reactions were carried out in flask blackened outside to prevent any photochemical reaction.

Stoichiometry and Product Analysis:

Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of NBP over benzyl alcohol and mercuric acetate in 50% acetic acid for 24 hrs. at 30°C . The unreacted oxidant (NBP) was determined by iodometrically. The estimated amount of unreacted NBP showed that one mole of benzyl alcohol consumes one mole of NBP. The 1:1 stoichiometry is represented by following equation.



Benzyl alcohol (0.2 Mole) and NBP (0.4 Mole) were mixed together with mercuric acetate (0.5 Mole) in 50 % aqueous acetic acid (total volume 100 ml). The reaction mixture was set aside for about 24 hrs. to ensure completion of the reaction. It was then evaporated and extracted with ether. The layer was separated and dried. The residue was confirmed as benzaldehyde by B.P., TLC, HPLC and 2, 4-DNP derivative. Analysis confirmed the formation of benzaldehyde in quantitative yield.

III. Result and Discussion

The kinetics of oxidation of benzyl alcohol by NBP in 50% acetic acid was carried at 303 K under pseudo first order conditions. The reactions were carried out under pseudo first order conditions of [Benzyl alcohol] >> [NBP]. The Plot of log [NBP] Vs time found to be linear ($r^2 > 0.995$) (plot not shown) indicating first order dependence of the reaction rate and from the slopes of such plots pseudo first order rate evaluated. Plot of log k' Vs log [Benzyl alcohol] was linear ($r^2 = 0.995$) with slope less than unity for all the benzyl alcohols indicating a fractional order ($n = 0.47$) dependence on rate of benzyl alcohol.

Effect of Hydrogen ion:

When the dependence of the reaction rate on hydrogen ion concentration was carried at different initial concentrations of H_2SO_4 , no significant change in rate constant was observed. There was marginal change in rate constant with variation of hydrogen ion concentration. Protonated NBP is not involved in reaction mechanism which may be attributed to the negligible effect of variation of H_2SO_4 on the reaction rate.

Table 1: Effect of variation of substrate and oxidant concentration on pseudo order rate constant k' at 303K

$Hg(OAc)_2 = 2.00 \times 10^3 \text{ (mol dm}^{-3}\text{)}$ 50% AcOH medium

$10^2 \times [\text{Benzyl alcohol}]$ (mol dm ⁻³)	$10^3 \times [\text{NBP}]$ (mol dm ⁻³)	$k' \times 10^4$ (s ⁻¹)
1.00	1.00	3.04
2.00	1.00	4.28
3.00	1.00	5.40
4.00	1.00	6.02
5.00	1.00	6.60
6.00	1.00	7.16
1.00	1.00	3.04
1.00	2.00	6.75
1.00	3.00	10.20
1.00	4.00	14.30
1.00	5.00	17.00
1.00	6.00	20.10

Effect of Ionic Strength:

The ionic strength of the reaction was varied by the addition of $NaClO_4$ and the influence of ionic strength on the reaction rate was studied. It was found that the ionic strength of the reaction medium has negligible effect on the reaction rate. This may presumably be due to attack of an ion on a neutral molecule in the rate determining step[16].

Effect of Mercury (II) Acetate:

The concentration effect of mercury (II) acetate in our present study showed negligible effect on the reaction rate but found its utility to fix bromide ion during the course of reaction and avoiding the oxidation of the latter to molecule bromine. It is not involve in NBP oxidation, but only act as a scavenger.

Effect of Product:

Variation of Phthalimide, one of the products of oxidation, had negligible effect on the rate of reaction.

Effect of Free Radical Inhibitor:

The oxidation reactions of benzyl alcohol with at different initial concentrations of acrylonitrile have been investigated. The reaction neither induces polymerization nor retards the reaction rate which may be attributed to the inertness shown by free radicals.

Effect of Solvent Composition:

The effect of changing solvent composition on the reaction rate was studied by varying concentration of acetic acid from 20-70 %. In the present study, the effect of solvent composition on the reaction rate suggests that the rate of reaction decreases with increasing acetic acid content of the solvent mixture. The formation of a charge separated complex in the rate-limiting step. Amis plot of log k' versus $1/D$ is linear with a negative slope and

plot of $\log k'$ versus $(D-1/2D+1)$ has been found to be linear with positive slope in accordance with Kirkwood theory[17]. It indicates that the involvement of two dipoles or a negative ion-dipole reaction.

Figure 1: Amis Plot

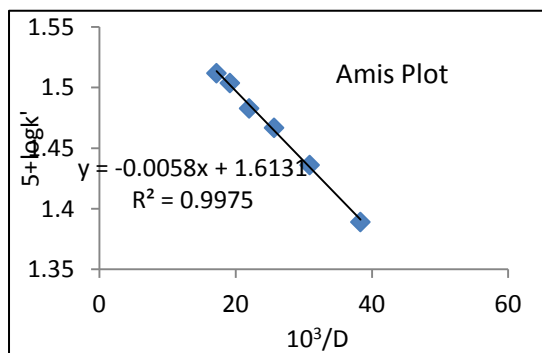
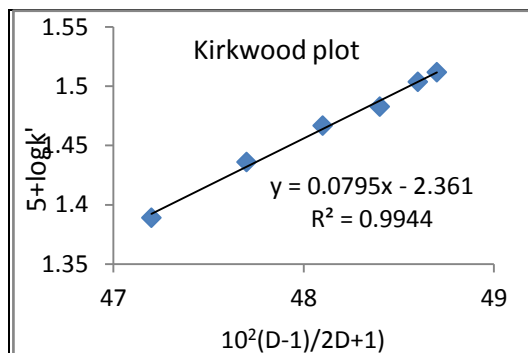


Figure 2: Kirkwood Plot



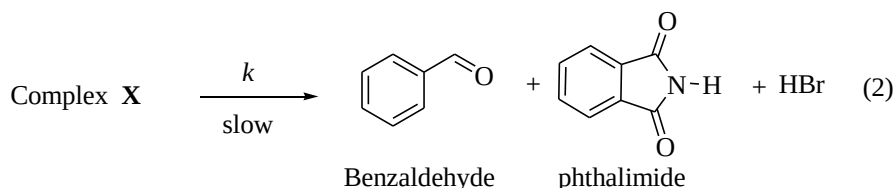
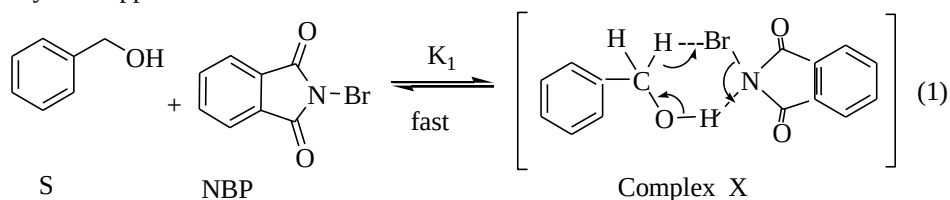
Effect of Substituent:

The oxidation of benzyl alcohol and substituted benzyl alcohols by [NBP] were carried out in the temperature range 30–45° C. The observed rate constants found to be increase with temperature for all the compounds. All the substrates obey the same rate law as the parent substrate. Electron donating groups increase the rate while electron withdrawing groups decreases the rate of oxidation. The order of reactivity of different benzyl alcohols with [NBP] is $p\text{-OCH}_3 > p\text{-CH}_3 > \text{H} > p\text{-Br} > p\text{-Cl} > p\text{-NO}_2$

The Hammett's plot of $\log k'$ Vs σ is linear with a reaction constant $\rho = -0.27$ and correlation coefficient $r^2 = 0.8593$. The negative reaction constant ρ indicates the creation of carbonium ion in the transition state; this is in agreement with finding of Sadagopa Ramanujam[18]. The negative reaction constant ρ also supports the loss of hydrogen atom as a hydride in the slow step.

Mechanism and derivation of rate law:

Based upon the experimental observations, the most probable mechanism and rate expression can be derived applying steady state approximation.



$$\frac{-d[\text{NBP}]}{dt} = \text{rate} = \frac{kK_1[\text{S}][\text{NBP}]}{1+K_1[\text{S}]} \quad (3)$$

$$k' = \frac{kK_1[\text{S}]}{1+K_1[\text{S}]} \quad (4)$$

Reciprocal of eqⁿ (4) gives,

$$\frac{1}{k'} = \frac{1}{kK_1[\text{S}]} + \frac{1}{k} \quad (5)$$

The kinetics results suggest the possibility of formation of binary complex involving oxidant and substrate is strongly favored. However, such a binary complex is undergoes redox decomposition to the end of products intramolecularly. Such complex formation was also proved kinetically by the non-zero intercept of the double reciprocal plot of $1/k'$ Vs $1/[\text{S}]$. Evidence is also provided by the fractional order found in substrate. The spectral evidence for complex formation between oxidant and substrate was obtained from UV-vis spectra of the

mixture. One sharp intense peak for mixture indicates formation of complex. As per double reciprocal plot of $1/k'$ Vs $1/[S]$ eqⁿ (5), the decomposition rate constant k and formation constant K_1 was find out (Table 2).

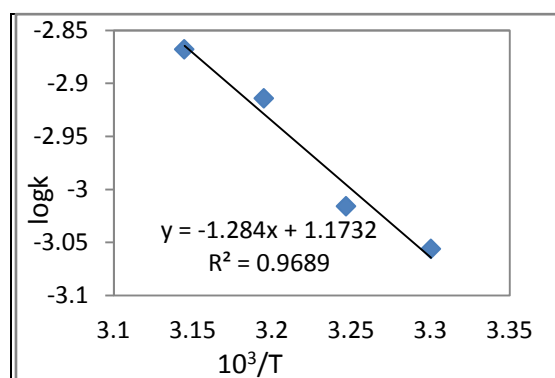
Table 2: Decomposition rate constant (k), formation constant (K_1) and Activation parameters of substituted benzyl alcohols at 303K.

Substituent x	$k \times 10^4$ (s ⁻¹)	K_1 (dm ³ mol ⁻¹)	Ea KJmol ⁻¹	$\Delta H^\ddagger$ KJmol ⁻¹	$\Delta G^\ddagger$ KJmol ⁻¹	$\Delta S^\ddagger$ JK ⁻¹ mol ⁻¹
4-OCH ₃	10.45	79.50	22.75	20.31	75.18	-248.05
4-CH ₃	9.64	68.40	23.48	20.96	75.22	-248.12
H	8.79	52.66	24.59	22.06	75.21	-248.17
4-Br	8.54	49.80	26.52	24.00	75.24	-248.24
4-Cl	6.95	46.71	30.10	27.58	75.27	-248.31
4-NO ₂	5.88	34.32	31.50	28.92	75.34	-248.36

Effect of temperature:

The rate of oxidation was determined at different temperatures and the Arrhenius plots of $\log k$ versus $1/T$ were all linear (fig.3). From these plots, the activation and thermodynamic parameter for equilibrium step and rate determining step of the scheme was evaluated (Table 2). The observed $\Delta S^\ddagger$ values are large and negative. It may be interpreted that the fraction of collisions become more stringent and decomposition of activation complex is a quite slow process. $\Delta H^\ddagger$ indicates that the reactions are enthalpy controlled. Further the constancy in the calculated values of $\Delta G^\ddagger$ for this oxidation reaction indicates that the same type of the reaction mechanism could be operative for the reaction[18].

Figure 3: Arrhenius Plot for Benzyl alcohol



IV. References

- [1] S. R. Joshi, K. L. Kataria, S. B. Sawant and J. B. Joshi, Ind. Eng. Chem. Res., 2005, 44, 325-333.
- [2] K. G. Sekar and C. L. Edison raj, J. Chem. Pharm. Res., 2011, 3(4), 596-601.
- [3] R. Kaur, N. Soni and V. Sharma, Indian J. Chem., 2006, 45A, 2441-2445.
- [4] N. Degirmenbasi and B. Ozgun, G. U. J. Sci., 2006, 19(1), 9-13.
- [5] J. Dharmaraja, K. Krishnasamy and M. Shanmugam, E-J.Chem., 2008, 5(4), 754-760.
- [6] N. Narayanan and R. Balasubramanian, J. Chem. Res. (S), 1991, 12, 336.
- [7] J. Gosain and P. K. Sharma, J. Indian Chem. Soc., 2002, 79, 815-818.
- [8] B. L. Hiran, R. K. Malkani and N. Rathore, Kinet and Catal., 2005, 46, 360-365.
- [9] V. Manoharan and N. Venkatasubramanian, Indian J. Chem., 1984, 23A, 389-391.
- [10] S. C. Pati, A. K. Sahu and Y. Sriramulu, Indian Natl. Sci. Acad., 1986, 52(5), 1205-1213.
- [11] H. Ramchandra, D. S. Mahadevappa, K. S. Rangappa and N. M. Made Gowda, Int. J. Chem. Kinet., 1999, 29(10), 773-780.
- [12] N. M. I. Alhaji, A. M. Uduman Mohideen and K. Kalamathi, E-J. Chem., 2011, 8(1), 1-8.
- [13] C. Mohan Das and P. Indrasenan, J. Indian Chem. Soc., 1987, 44, 382-384.
- [14] J. Bharad, B. Madje and M. Ubale, Proceed. Nat. Acad. Sci. Lett., 2011, 81 Part III, 211-216.
- [15] D. K. Bhat, B. S. Sherigar and B. T. Gowda, Bull. Chem. Soc. Jpn., 1996, 69, 41-45.
- [16] E. S. Amis, Solvent Effect on Reaction Rates and Mechanism, Academic Press: New York, 1967, 42.
- [17] J. G. Kirkwood, J. Chem. Phys., 1934, 2, 351-361.
- [18] V. M. Sadagopa Ramanujam, N. Venkatasubramanian and S. Sundaram, Aust. J. Chem., 1977, 30, 325-334.

V. Acknowledgement

The authors gratefully acknowledge financial support from UGC (WRO) Pune for minor research project and Principal, Vasantrao Naik Mahavidyalaya Aurangabad for providing the laboratory facilities.