

Oxidation of benzhydrols by *N*-bromophthalimide : A kinetic and mechanistic study

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Abstract : Kinetic Investigations of oxidation of benzhydrol and *p*-substituted benzhydrols by *N*-bromophthalimide (NBP) in aqueous acetic acid medium in presence of mercuric(II) acetate as a scavenger have been studied. In absence of mineral acids, the oxidation kinetics of benzhydrols by NBP shows a first order dependence on NBP and fractional order on benzhydrols. The variation of ionic strength, $\text{Hg}(\text{OAc})_2$, H^+ and phthalimide (reaction product) have insignificant effect on reaction rate. Activation parameters for the reaction have been evaluated from Arrhenius plot by studying the reaction at different temperatures. A mechanism involving transfer of hydride ion in rate determining step is suggested.

Keywords : Kinetics, oxidation, benzhydrol, *N*-bromophthalimide.

Introduction

The kinetics of oxidation of substituted benzhydrols by organic halochromates such as benzyl triethylammonium chlorochromate¹, quinoxalinium bromochromate², quinolinium bromochromate³, pyridinium bromochromate⁴, tetrabutylammonium tribromide⁵, etc. have been studied earlier. A number of reports on kinetic studies of oxidation of benzhydrols with variety of *N*-halo compounds such as *N*-bromosuccinimide⁶, *N*-bromosaccharin⁷, *N*-bromoacetamide⁸ and chloramine-T⁹ as oxidants have also been made.

N-Bromophthalimide (NBP) is a potential oxidizing agent¹⁰ and has some definite advantages over other *N*-halogeno oxidants¹¹, which has been extensively used in the estimation of organic substrates¹². It seems that there are no reports about the kinetics of oxidation of benzhydrols by NBP. The present work reports kinetics and mechanism of oxidation of benzhydrols by *N*-bromophthalimide in 30% acetic acid.

Results and discussion

The kinetics of oxidation of benzhydrol by NBP in

30% acetic acid was carried at 303 K under pseudo-first order conditions. The concentration of $\text{Hg}(\text{OAc})_2$ was kept higher than NBP. The plot of $\log [\text{NBP}]$ vs time was found to be linear indicating first order dependence of the reaction rate and from the slopes of such plots pseudo-first order rate was evaluated. The rate constant (k') has been found to increase with increase in the concentration of benzhydrol and plot of $\log k'$ vs $\log [\text{benzhydrol}]$ was linear ($r^2 = 0.9987$) with slope less than unity for all the benzhydrols indicating a fractional order dependence of rate (Table 1).

The dependence of the reaction rate on hydrogen ion concentration has been investigated at different initial concentrations of H_2SO_4 keeping the concentration of the other reactants constant. There was no significant change in rate constant was observed with variation of H^+ ion.

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 the

Table 1. Effect of variation of oxidant and substrate on pseudo-first order rate constant k' at 303 K

$\text{Hg}(\text{OAc})_2 = 2.00 \times 10^3 \text{ (mol dm}^{-3}\text{)}, 30\% \text{ AcOH-H}_2\text{O (v/v) medium}$

$10^2 [\text{Benzhydryl}]$ (mol dm ⁻³)	$10^3 [\text{NBP}]$ (mol dm ⁻³)	$k' \times 10^4$ (s ⁻¹)
1.00	1.00	3.32
2.00	1.00	4.57
3.00	1.00	5.46
4.00	1.00	6.05
5.00	1.00	6.71
6.00	1.00	7.20
1.00	1.00	3.32
1.00	2.00	6.75
1.00	3.00	10.94
1.00	4.00	14.56
1.00	5.00	17.62
1.00	6.00	20.48

attack of an ion on a neutral molecule in the rate determining step¹³.

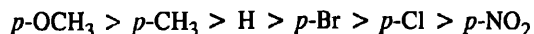
The concentration effect of mercury(II) acetate in our present study showed negligible effect on the reaction rate but found its utility to fix bromide ion during the course of reaction and avoiding the oxidation of the latter to bromine. Variation of phthalimide, one of the products of oxidation, had negligible effect on the rate of reaction. The oxidation reactions of benzhydryl with NBP 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.

The effect of solvent composition on the reaction rate was studied by varying concentration of acetic acid from 20–70%. The rate constants suggest that the rate of reaction decreases with increasing acetic acid content of the solvent mixture. In the absence of mineral acid, the probable oxidizing species is free NBP under the present experimental condition¹⁴.

Effect of substituents :

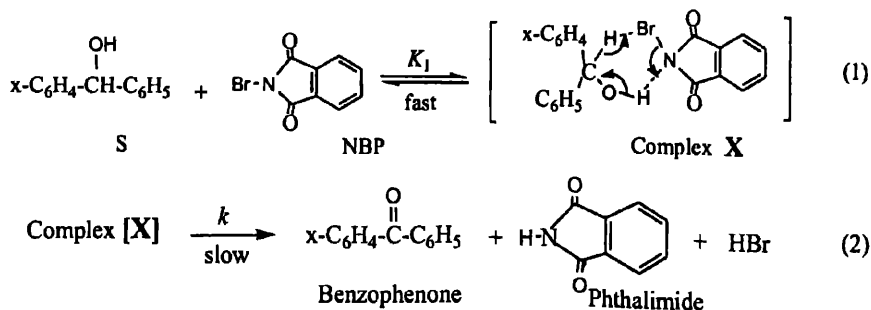
The oxidation of benzhydryl and substituted benzhydryl by NBP were carried out at the temperature range of 30–45 °C. The observed rate constants were found to increase with temperature for all the compounds. Electron donating groups increase the rate while electron withdrawing groups decrease the rate of oxidation. The order of reactivity of different benzhydrols with NBP is,



The Hammett's plot of $\log k'$ vs σ is linear with a reaction constant $\rho = -0.24$ and correlation coefficient $r^2 = 0.8503$. The negative reaction constant ρ indicates the formation of carbonium ion in the transition state, which is in agreement with the finding of Sadagopa Ramanujam¹⁵. The negative reaction constant ρ also supports the loss of secondary hydrogen atom as 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.



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

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

Reciprocal of eq. (4) gives,

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

The kinetic results suggest the possibility of formation of binary complex involving oxidant and substrate. However, such a binary complex undergoes redox decomposition. Such complex formation was also proved kinetically by the non-zero intercept of the double reciprocal plot of $1/k'$ vs $1/[\text{S}]$ (Fig. 1). Evidence is also provided by the fractional order found in substrate. The spectral

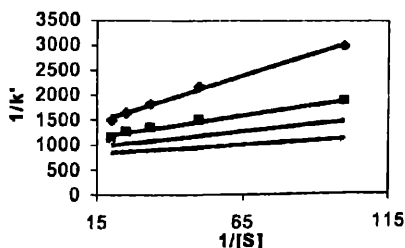


Fig. 1. Double reciprocal plot of benzhydrol.

evidence for complex formation between oxidant and substrate was obtained from UV-Vis spectra of the mixture. One sharp intense peak for mixture indicates the formation of complex. As per double reciprocal plot of $1/k'$ vs $1/[\text{S}]$ eq. (5), the decomposition rate constant k and formation constant K_1 were determined (Table 2).

The rate of oxidation was determined at different temperatures and the Arrhenius plots of $\log k$ versus $1/T$ were linear. From these plots, the activation and thermodynamic parameters for equilibrium and rate determining

steps of the scheme were evaluated (Table 2). The observed ΔS^\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. ΔH^\ddagger indicates that the reactions are enthalpy controlled. The validity of the isokinetic relation can be tested graphically by plotting $\log k$ (303) vs $\log k$ (313). The isokinetic temperature β evaluated from Exner¹⁶ criterion was found to be 357.03 K (slope = 0.7889 and $r^2 = 0.9648$), which is above the experimental temperature and implies that all the compounds are oxidized by the same mechanism¹⁷. Further the constancy in the calculated values of ΔG^\ddagger for this oxidation reaction indicates that the same type of the reaction mechanism could be operative for the reaction.

Experimental

Materials : Substituted benzhydrols were prepared by the sodium borohydride reduction of corresponding benzophenones¹⁸. Purity of benzhydrols was checked by TLC and m.p. The oxidant NBP (Aldrich sample) was used as received. Acetic acid (A.R. grade) was purified by the literature procedure. The standard solutions of substituted benzhydrols 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 iodometrically¹⁹ 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 benzhydrols over oxidant NBP. Mixture containing requisite amounts of solutions of benzhydrol, $\text{Hg}(\text{OAc})_2$ in 30% acetic acid were equilibrated at 303 K. To this mixture a measured amount of pre-equilibrated (303 K) standard solution of NBP was added. 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 iodometrically

Table 2. Decomposition rate constant (k), formation constant (K_1) and activation parameters of substituted benzhydrols at 303 K

Substituent	$k \times 10^4$ (s^{-1})	K_1 ($\text{dm}^3 \text{mol}^{-1}$)	E_a (kJ mol^{-1})	ΔH^\ddagger (kJ mol^{-1})	ΔG^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{JK}^{-1} \text{mol}^{-1}$)
X						
4-OCH ₃	11.35	82.20	22.39	19.87	75.18	-248.07
4-CH ₃	8.74	80.80	22.42	19.90	75.22	-248.18
H	8.42	63.95	23.55	21.03	75.22	-248.20
4-Br	7.37	55.70	24.93	22.41	75.24	-248.25
4-Cl	6.20	48.92	31.48	28.96	75.27	-248.33
4-NO ₂	5.64	31.68	31.44	28.92	75.34	-248.33

by withdrawing aliquots of the reaction mixture at regular time of intervals. The pseudo-first order rate constants k' were computed from linear least squares plot $-\log [a - x]$ vs time. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 4\%$.

Stoichiometry and product analysis : Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of NBP over benzhydrol and mercuric acetate in 30% acetic acid for 24 h at 30 °C. The unreacted oxidant (NBP) was determined iodometrically. The estimated amount of unreacted NBP showed that one mole of benzhydrol consumes one mole of NBP.

Benzhydrol (0.2 mol) and NBP (0.4 mol) were mixed together with mercuric acetate (0.5 mol) in 30% aqueous acetic acid (total volume 100 ml). The reaction mixture was set aside for about 24 h 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 benzophenone by m.p., TLC, HPLC and also from the formation of 2,4-DNP derivative. Analysis confirmed the formation of benzophenone in quantitative yield.

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