



Kinetic Study of Oxidation of Cyclohexanol by N-Bromophthalimide in Acetic Acid- Water Medium

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ABSTRACT:

Kinetic investigations of oxidation of cyclohexanol by N-bromophthalimide (NBP) in aqueous acetic acid medium have been studied. The reaction exhibits a first order rate dependence with respect to oxidant, while it is fractional order in cyclohexanol. The variation of ionic strength, $\text{Hg}(\text{OAc})_2$, H^+ have insignificant effect on reaction rate. Effect of varying dielectric constant of medium on the rate has been studied. Activation parameters have been evaluated from Arrhenius plot by studying the reaction at different temperature. The rate law has been derived on the basis of obtained data.

Key Words: Kinetics, Oxidation, Cyclic alcohols, N-bromophthalimide.

INTRODUCTION

Kinetics of oxidation of cyclic alcohols with variety of oxidants such as Cerium (IV), KBrO_3 , Quinolinium dichromate¹⁻³ etc are reported earlier. A number of reports on kinetic studies of oxidation of cyclic alcohols by N-halo compounds such as NBS, NBA, NBB, chloramine-T, Bromamine-T, CBT, NBSA⁴⁻¹⁰, as an oxidants have been reported. N-bromophthalimide (NBP) is a potential oxidizing agent¹¹ and has some definite advantages over other N-halogeno oxidants¹², which has been extensively used in the estimation of organic substrates¹³. In the present investigation oxidation of cyclohexanol by N-Bromophthalimide in 40 % acetic acid has been reported.

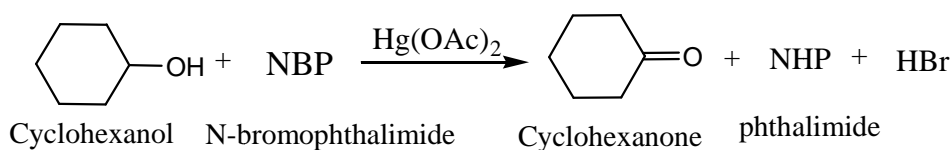


EXPERIMENTAL SECTION

Materials: All the cyclohexanol used of AR grade. The oxidant NBP (Aldrich sample) was used. Acetic acid (A.R. grade) was purified by the literature procedure. The standard solution of cyclohexanol was 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 using 1 % solution of freshly prepared starch as an indicator.

Kinetics: Kinetic measurements were made under pseudo first order conditions, by keeping large excess of cyclohexanol over oxidant. Mixture containing requisite amounts of solutions of cyclic alcohol and $\text{Hg}(\text{OAc})_2$ in 40 % acetic acid were equilibrated at 303 K. To this mixture was added a measured amount of pre-equilibrated (303 K) 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 iodometrically 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 of $-\log [a - x]$ Vs time.

Stoichiometry and Product Analysis: Stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of NBP over cyclohexanol and mercuric acetate in 40 % 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 cyclohexanol consumes one mole of NBP.



Cyclohexanol (0.2 Mole) and NBP (0.4 Mole) were mixed together with mercuric acetate (0.5 Mole) in 40 % 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 product obtained was corresponding cyclohexanone which is characterized by TLC, 2, 4- DNP derivatives¹⁴ and its physical constant.



RESULT AND DISCUSSION

Order of Reaction: The kinetics of oxidation of cyclohexanol by NBP in 40 % 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 found to be linear (plot not shown) indicating first order dependence of the reaction rate and from the slopes of such plots pseudo first order rate evaluated. The rate constant (k') have been found to increase with increase in the concentration of cyclohexanol and plot of $\log k'$ Vs $\log [\text{cyclohexanol}]$ was linear (figure 1) with slope less than unity for the cyclohexanol indicating a fractional order dependence on rate (Table 1). The dependence of the reaction rate on hydrogen ion concentration has been investigated at different initial concentrations of H_2SO_4 and keeping the concentration of the other reactants constant. There was no significant change in rate constant was observed with variation of H^+ ion.

Table: 1 Effect of variation of reactants on pseudo order rate constant k' at 303K.

$\text{Hg}(\text{OAc})_2 = 2.00 \times 10^3 \text{ (mol dm}^{-3}\text{)}$ 40% AcOH medium

$10^2 \times [\text{cyclohexanol}]$ (mol dm^{-3})	$10^3 \times [\text{NBP}]$ (mol dm^{-3})	$k' \times 10^4 \text{ (s}^{-1}\text{)}$
1.00	1.00	1.98
2.00	1.00	3.26
3.00	1.00	4.12
4.00	1.00	4.83
5.00	1.00	5.41
6.00	1.00	6.17
1.00	1.00	1.98
1.00	2.00	4.54
1.00	3.00	7.49
1.00	4.00	10.02
1.00	5.00	12.00
1.00	6.00	13.59

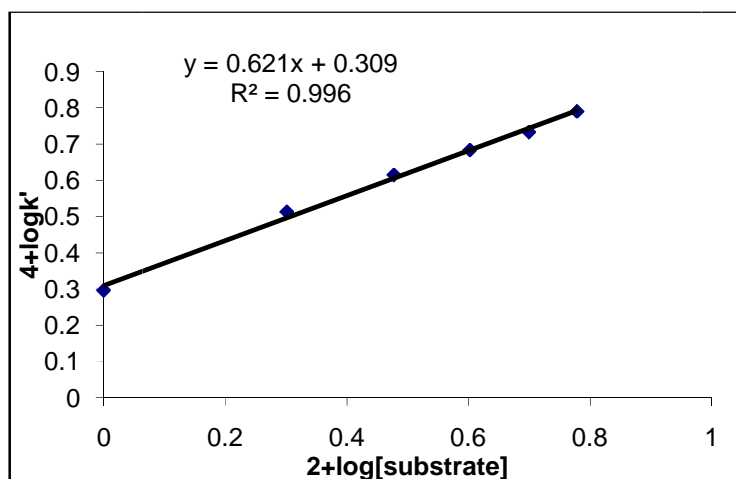


Figure: 1 Plot of order on substrate.

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. 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. Variation of phthalimide, one of the products of oxidation, had negligible effect on the rate of reaction. The reaction neither induces polymerization nor retards the reaction rate by variation of acrylonitrile, 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 40-80 %. The rate constants suggest that the rate of reaction decreases with increasing acetic acid content of the solvent mixture. The plot of $\log k'$ Vs $1/D$ was found to be linear with negative slope (Figure 2) indicating the involvement of two dipoles or a negative ion – dipole reaction. This reveals that there is formation of a charge separated complex in the rate limiting step which is in agreement with Amis¹⁵. A plot of $\log k'$ versus $(D-1/2D+1)$ has been found to be linear (figure not shown) in accordance with Kirkwoods¹⁶ theory of dipole – dipole type reaction.

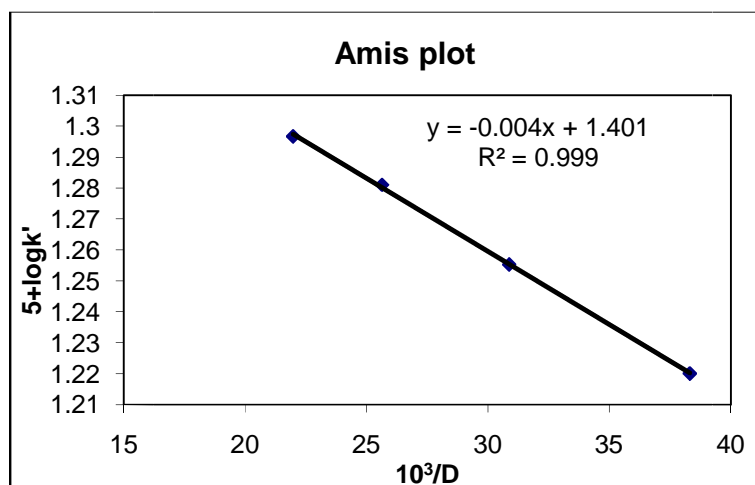
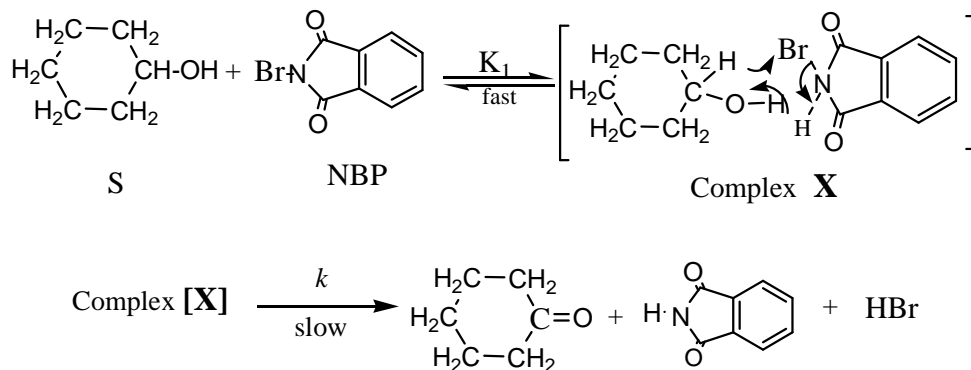


Figure: 2 Amis plot

Reactive Species and Mechanism: Earlier reports reveal that NBS, NBP and NBSA are stable oxidizing and brominating agents and behave in a similar way. NBP like other similar N-halo imides may exist in various forms in acid medium viz. free NBP, protonated NBP, Br^+ , HOBr , $\text{H}_2\text{O}^+\text{Br}$. In absence of mineral acid, the possibility of Br^+ , NBPH^+ , or H_2OBr^+ being the reactive oxidizing species is ruled out. If HOBr is the reactive oxidizing species, then the rate of reaction should be an inverse function of phthalimide (NHP) that is not observed in the present study. Also the possibility of brominating action of bromide is ruled out due to the presence of mercury (II) acetate that eliminates Br^- through complexation. The rate constants suggest that the rate of reaction decreases with increasing acetic acid content of the solvent mixture. This observation coupled with slight enhancement in the reaction rate with ionic strength of the medium also supports the participation of neutral molecule in the rate-determining step. Therefore (free) NBP is the probable oxidizing species under the present experimental condition¹⁷.

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



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

$$k' = \frac{kK_1[\text{S}]}{1+K_1[\text{S}]} \quad (2)$$

Reciprocal of eqⁿ (2) gives,

$$\frac{1}{k'} = \frac{1}{kK_1[\text{S}]} + \frac{1}{k} \quad (3)$$

The kinetics results suggest the possibility of formation of binary complex involving of oxidant and substrate is strongly favored. Such complex formation was also proved kinetically by the non-zero intercept of the double reciprocal plot of $1/k'$ Vs $1/[\text{S}]$. From the intercept and slopes of the plots of $1/k'$ versus $1/[\text{S}]$ decomposition rate constant k and the formation constant K_1 were evaluated (Table 2). Evidence is also provided by the fractional order found in substrate. The results are interpreted in terms of a cyclic mechanism involving a rate determining abstraction of the α -H as a hydride anion.



Table: 2 Decomposition rate constant (k) and formation constant (K_1) at 303K.

Cyclic alcohol	$k \times 10^4 \text{ (s)}^{-1}$				K_1 ($\text{dm}^3 \text{ mol}^{-1}$)
	303 K	308 K	313 K	318 K	
Cyclohexanol	9.39	9.74	11.13	12.83	26.65

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. From these plots, the activation parameters were evaluated (Table 3). The thermodynamic parameter for equilibrium step and rate determining step of the scheme was evaluated. The observed negative values of ΔS^\ddagger could be attributed to the greater rigidity and cyclic structure of the transition state. 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. 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.

Table: 3 Activation parameters of cyclic alcohols at 303K.

Cyclic alcohol	E_a KJmol^{-1}	ΔH^\ddagger KJmol^{-1}	ΔG^\ddagger KJmol^{-1}	ΔS^\ddagger $\text{JK}^{-1}\text{mol}^{-1}$	LogA
Cyclohexanol	17.04	14.52	67.01	-221.14	3.91

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