

Research Articles

MICELLES CATALYSED OXIDATION OF CYCLOPENTANOL BY N-BROMOISONICOTINAMIDE

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Received : 01-Mar-2020	Revised : 07-Mar-2020	Accepted : 18-Mar-2020
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ABSTRACT

N-bromoisonicotinamide is a valuable oxidant used in oxidation of cyclopentanol catalysed by cationic cetyl trimethyl ammonium bromide in CH₃COOH-water medium at 35⁰C. The reaction rate exhibit first-order to [NBIN], one to zero-order with respect to [cyclopentanol] and inverse effect on [H⁺]. The ionic strength of the medium had no effect on rate. The non-involvement of a free-radical process was observed in oxidation. The reaction is believed to be initiated by formation of cyclic complex with reacting species, HOBr, which undergoes rapid reduction to cyclopentanone.

Keywords: Oxidation, cyclopentanol, cetyl trimethyl ammonium bromide, N-bromoisonicotinamide, free radicals.

INTRODUCTION

Recently considerable attention has been focussed on the newly introduced oxidant N-bromoisonicotinamide being less toxic, economically cheap, having appreciable stability with two electrons¹ system with redox potential = 0.808 volt at 25⁰C. The literature contains the use of NBIN for the oxidation reactions alcohols², and unsaturated acids³. The catalyst CTAB generates more cationic micelles make a process economically feasible to occur. Involving CTAB a variety of organic compounds such

as hydroxy acids⁴, amino acids⁵ have been oxidized. Despite the usefulness of this technique, practically no kinetic information is available for cyclopentanol, although a closely related reaction i.e. oxidation of cyclonols have been studied with different oxidants QDC⁶, NCP⁷, CAT⁸, NBP⁹, etc. The results presented in this paper indicate, the micelles (CTAB) catalysed oxidation of cyclopentanol in aqueous acetic acid medium.

EXPERIMENTAL

Materials

All the chemicals employed in the experiments were of analytical grade. The solvent acetic acid used was purified by fractional distillation method. The solution of oxidizing agent, N-bromoisonicotinamide was prepared in 70% CH₃COOH and standardized iodometrically. Because of its instability, it was stored in the dark at low temperature. The solution of cyclopentanol of desired concentrations was prepared in acetic acid (BDH). Micelles cationic cetyl trimethyl ammonium bromide (CTAB), 99% pure (Adrich) was used as such received without any further purification.

KINETIC METHOD

The kinetic experiments were all carried out in the presence of excess of cyclopentanol over oxidant. In a typical experiment, a 50 ml volumetric flask containing a solution of cyclopentanol in acetic acid, was held for about 30 minutes in a thermostated bath at 35⁰C. NBIN was then added (pre- equilibrated) and the solution vigorously stirred until; homogeneous. The concentration of the NBIN left unconsumed in the mixture was determined by means of an iodometric technique i.e. a 2.0 ml aliquot was withdrawn from the solution and transferred to a 50 ml volumetric flask and liberated iodine was titrated with sodium thiosulphate solution using starch as an indicator. The rate constant (k) was determined by the integration and graphical methods.

RESULTS AND DISCUSSION

(a) The measurement of the initial rates of oxidation of cyclopentanol was found as proportional to the initial NBIN concentrations (Plot of $\ln(a-x)$ vs. time, are linear with unit slope)

(b) The effect of [cyclopentanol] on the rate of oxidation reaction shows fractional-order. It can be seen from the data in Table 1. limiting value of k_{obs} is obtained at higher [cyclopentanol] clearly indicates that the transition state is electron rich as compared with ground state. The convincing evidence that this reaction is initiated by forming a cyclic complex between active species HOBr and substrate, which is known to an important intermediate in the reaction. This is confirmed by plotting the double reciprocal graph between k^{-1} and $[\text{cyclopentanol}]^{-1}$ with positive intercept on Y-axis (Fig.1).

Table 1 : Dependence of rate constants for catalytic reaction on the concentration of cyclopentanol

$[\text{NBIN}] = 2.0 \times 10^{-3} \text{ (mol dm}^{-3}\text{)} ; [\text{H}^+] = 1.0 \times 10^{-3} \text{ (mol dm}^{-3}\text{)} ;$

$[\text{CTAB}] = 1.0 \times 10^{-3} \text{ (mol dm}^{-3}\text{)} ; \text{HOAc-H}_2\text{O} = 30 \% \text{ (v/v)} ;$

Temp. = 308 K

S. No.	$10^2 \times [\text{cyclopentanol}]$ (mol dm ⁻³)	$10^4 \times k \text{ (s}^{-1}\text{)}$
1.	1.25	2.54
2.	2.00	3.75
3.	2.50	3.89
4.	3.33	4.53
5.	4.00	4.71
6.	5.00	4.92

Table 2 : Dependence of rate constants for CTAB catalytic reaction on the concentration of cyclopentanol's oxidation by NBIN

[Cyclopentanol] = 2.0×10^{-2} (mol dm⁻³) ; [NBIN] = 2.0×10^{-3} (mol dm⁻³) ;

[H⁺] = 1.0×10^{-3} (mol dm⁻³) ; HOAc-H₂O = 30 % (v/v) ;

Temp. = 308 K

S. No.	$10^3 \times [\text{CTAB}]$ (mol dm ⁻³)	$10^4 \times k$ (s ⁻¹)
		Cyclopentanol
1.	0.50	2.31
2.	0.80	2.89
3.	1.00	3.75
4.	2.00	5.62
5.	2.50	6.17
6.	3.33	6.83

(c) The rate of reaction has shown inverse effect by the successive addition of H₂SO₄ and isonicotinamide. It was also found that enhancement in the concentration of sodium chloride did not alter the rate constant significantly. The binary solvent mixture of acetic acid (20 to 50%, v/v) had indicated positive effect on rate of reaction.

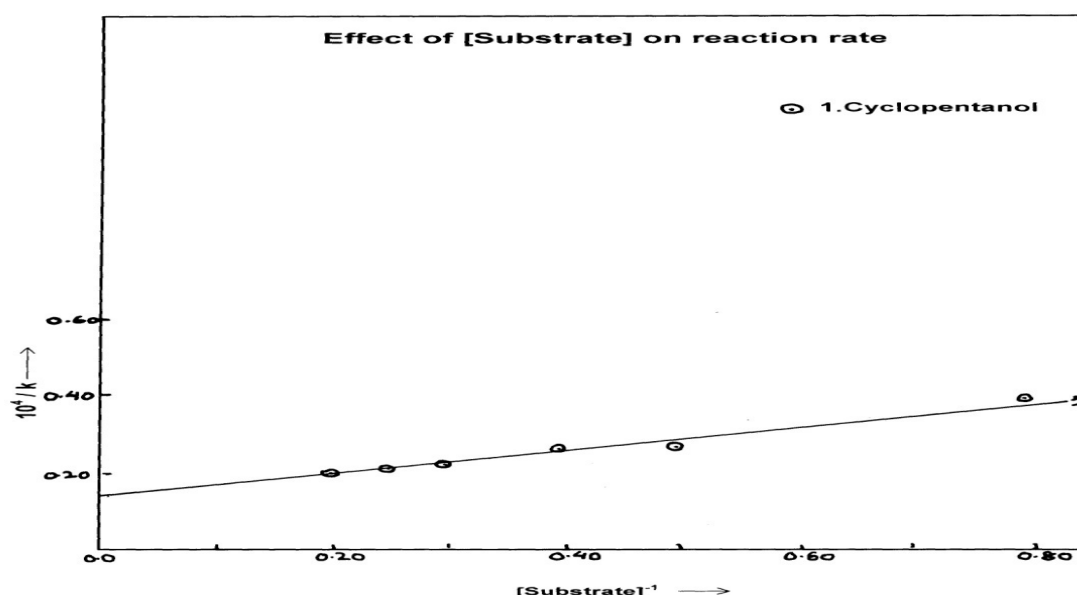


Fig. 1 [NBIN] = 2.0×10^{-3} (mol dm⁻³) ; [CTAB] = 1.0×10^{-3} (mol dm⁻³) ;
CH₃COOH-H₂O = 30 %, (v/v) ; Temp. = 303 K

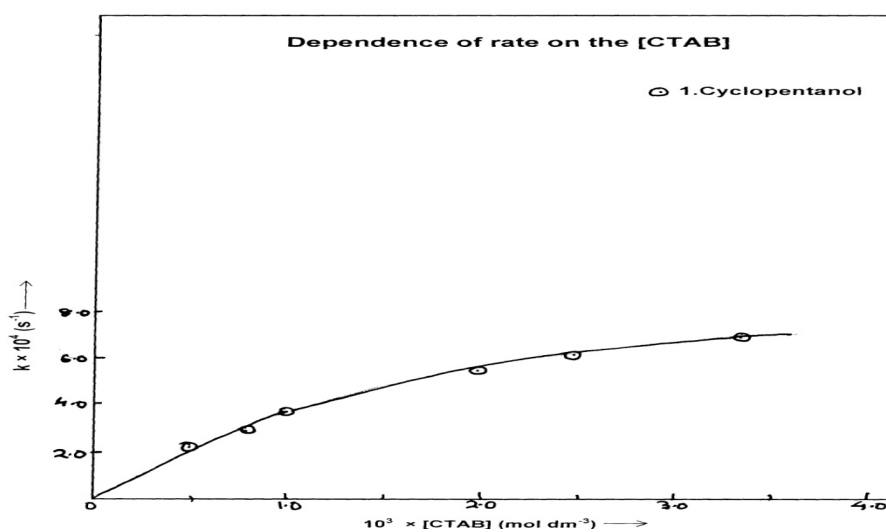
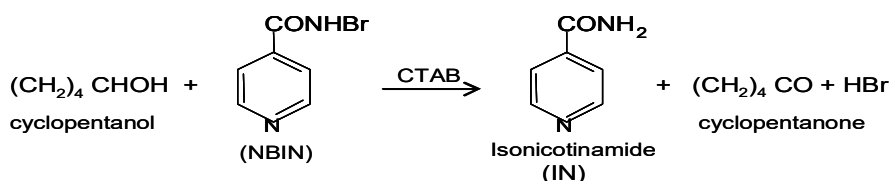


Fig. 2 Plot of k vs. [CTAB]

[NBIN] = 2.0×10^{-5} (mol dm⁻³); [Substrate] = 2.0×10^{-2} (mol dm⁻³);

[H⁺] = 1.0×10^{-5} (mol dm⁻³); HOAc-H₂O = 30% (v/v);

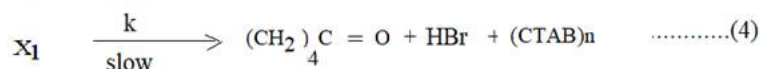
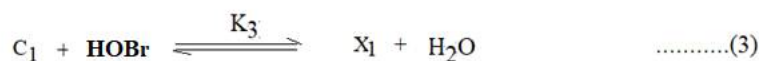
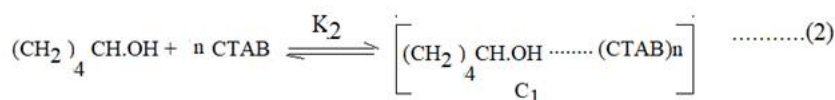
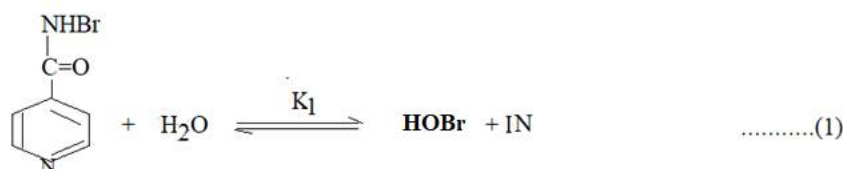
(d) A many fold increase in catalyst [CTAB] micelles in the beginning accelerate the rate of oxidation to a maximum extent (Table 2) later on becomes stagnant showing complex kinetics with fractional-order. Plotting k against [CTAB] expressing in mol dm⁻³ molecule a curve produced shown in Fig.2. Although no direct associative intercationic were involved between CTAB micelles, and solvents. The micellization behaviour of catalyst depends upon he degree of dissociation of CTAB micelles, and negative value of free energy change might be the reason of showing its forming capability of complex.¹⁰(e) The oxidation reaction yielded only cyclopentanone as per to the reaction proceeded stoichiometrically i.e. with a ratio of cyclopentanol to NBIN of 1:1.



The study shows inertness towards the free radical based mechanism. The product cyclopentanone was spectroscopically examined and also identified by forming 2,4-DNP derivative characterized by its M.P. determination.

MECHANISM

A redox type mechanism operating may be summarized based on kinetic data as follows:



The rate expression may be represented as the utilisation of [NBIN] as:

$$k_{\text{obs.}} = \frac{k K_1 K_2 K_3 [\text{cyclopentane}][\text{CTAB}]}{\{[\text{IN}] + K_1\} (K_3[\text{CTAB}])} \quad \text{.....(5)}$$

At higher [substrate] when $K_3 \gg K_1$ and neglecting the terms involved in the denominator equation (6) becomes:

$$k_{\text{obs}} = k \quad \text{..... (6)}$$

The equations (5) and (6) explain all the kinetics findings along with nature of complex formation. The thermodynamic parameters were also experimentally determined for the cyclopentanol- NBIN reaction.

CONCLUSION

The micelles catalyst CTAB shows the limiting value of rate on higher concentration of cyclopentanol. HOBr was the reacting species of oxidant forming cyclic type of complex with substrate was postulated. The acid has shown inverse effect on rate.

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