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Catalytic Effect of A-Cyclodextrin on the Oxidation of Acetophenones Using N-Bromosaccharin as Oxidant in Aqueous Acetic Acid Medium

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The kinetics of oxidation of acetophenone and substituted acetophenones by N-bromosaccharin has been investigated in aqueous acetic acid medium in the temperature range 308–323 K. The reaction is found to be first order with respect to acetophenone and zero order with respect to the concentration of the oxidant. No salt effect is observed and the reaction does not induce polymerisation of added acrylonitrile. A positive catalytic effect has been noticed on the addition of A-cyclodextrin. Thermodynamic parameters such as $\Delta S^{\#}$, $\Delta H^{\#}$, and $\Delta G^{\#}$ have been evaluated and presented.

Key words: Cyclodextrin, oxidation, acetophenone, n-bromosaccharin, kinetic study.

INTRODUCTION

N-halo compounds have been used as oxidising and halogenating agents in organic synthetic purposes.[1–11] Kinetic studies on such oxidations of ketones using N-bromosaccharin (NBSac) are scanty. This prompted us to undertake the title investigation. Cyclodextrins are known to enhance the rate of oxidation of ketone by hypohalite in alkaline medium[12]. Hence in the present work an attempt was also made to investigate the effect of added cyclodextrin on the NBSac oxidation of acetophenone and some of its *para* substituted derivatives. It has been reported that NBSac is strongly polar and in polar medium it undergoes heterolytic fission to give bromonium ion rather than homolytic cleavage to give free radicals.[13]

EXPERIMENTAL

All the chemicals used were AnalaR grade or equivalent. Acetic acid and acetophenone were purified by distillation before use. Mercuric acetate (Sarabhai Chemicals), sulphuric acid, potassium iodide, cyclodextrin (Aldrich) and thiosulphate were used as such. NBSac was prepared by standard methods given in the literature.

All the experiments were conducted under conditions of tenfold excess of ketone

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concentration over that of NBSac. The reactions were carried out in 20% (v/v) acetic acid-water mixture in the presence of 0.0025 M Hg $(OAc)_2$ and 0.005 M sulphuric acid in the temperature range 308–323 K. The stoichiometry of the reaction was determined by equilibriating excess concentration of oxidant over the substrate and estimating the concentration of the unreacted oxidant. The kinetics were monitored by estimating the unreacted oxidant iodometrically at known time intervals. Mercuric acetate was used to prevent formation of Br_2 due to reaction of Br with the oxidant and Br_2 taking part in parallel oxidation reactions.

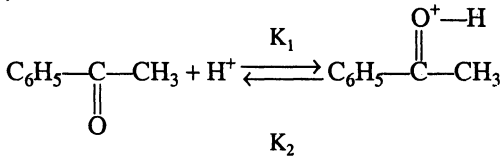
RESULTS AND DISCUSSION

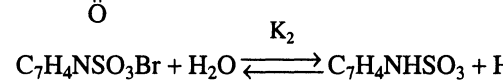
The stoichiometry of the reaction shows that one mole of acetophenone is equivalent to three moles of NBSac. Under the experimental conditions a qualitative analysis indicates the product of oxidation as benzoic acid. The reaction system did not induce polymerisation of added acrylonitrile, confirming the absence of free radicals in the system. The kinetic data obtained at various concentrations of NBSac fit into zero order rate expression with respect to the oxidant concentration.[14, 15] The zero order rate constants were computed from the slopes of the plot of [NBSac] *vs.* time.

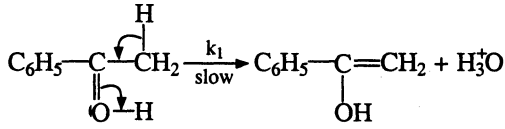
The order of the reaction with respect to the concentration of acetophenone was studied in the concentration range of 0.01 to 0.03 M. The rate constants are evaluated from the plots of concentration *vs.* time graphs.

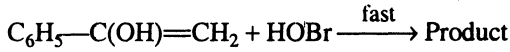
The rate constants evaluated showed their dependence on the concentration of acetophenone. Experiments were also conducted in the range of 0.0025 M to 0.1 M sulphuric acid and a fractional order dependence on $[H]^+$ was found. With different aqueous acetic acid mixtures, increase in rate with decrease in acetic acid content of the solvent was observed. Further, the plot of log k *vs.* $\frac{D-1}{2D+1}$ is linear suggesting dipole-dipole type of interaction in the reaction path. That an ion-ion type reaction has not taken place is shown by the absence of any salt effect. Addition of saccharin has a retarding effect on the rate as it shifts the equilibrium in step 2 to the left of the mechanism.

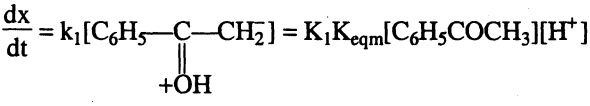
The reactive oxidant species of NBSac oxidation in aqueous acetic acid can be protonated NBSac, Br radical, Br_2, Br^+, HOBr etc. The fact that added acrylonitrile has no effect on rate rules out reaction by Br radical, Br_2 molecule etc. Catalysis by H^+ has been shown by the increase in rate with increase in the concentration of H^+. This favours the protonated NBSac as well as HOBr as the reactive species. Rate retarding effect on addition of saccharin is indicated. This is indicative of either protonated NBSac or HOBr as the reactive species. However, rate retarding effect on addition of saccharin rather rules out oxidation by NBSac itself and it supports reaction by HOBr. When Br^+ or HOBr are the active species the oxidation rate would diminish by added saccharin. HOBr may be considered as the reactive species and it attacks the enol form of acetophenone. The fact that the rate is accelerated by addition of mineral acid points to formation of larger proportion of HOBr from NBSac on addition of acid. The mechanism could be depicted as









so that 

supports reaction by HOBr.

The activation parameters were calculated from Arrhenius plots and the values are given in Table-2. These are comparable with those observed in similar oxidation studies.

TABLE-1
EFFECT OF CONCENTRATION OF NBSac AND ACETOPHENONE ON OBSERVED RATE CONSTANT IN THE OXIDATION OF ACETOPHENONE BY NBSac.

[NABac] = 1.0×10^{-3} mol dm^{-3}	[H^+] = 5.0×10^{-3} mol dm^{-3}
[AcP] = 1.0×10^{-2} mol dm^{-3}	[MA] = 2.5×10^{-3} mol dm^{-3}
[Solvent] = 20% aq. HOAc (v/v)	T = 308 K

[AcP] $\times 10^2$ mol dm^{-3}	[NBSac] $\times 10^3$	$k_{obs} \times 10^8$ mol dm^{-3} s^{-1}
1.0	1.0	3.20
1.5	1.0	4.90
2.0	1.0	6.50
2.5	1.0	7.80
3.0	1.0	9.50
1.0	0.5	3.30
1.0	1.0	3.20
1.0	1.5	3.33
1.0	2.0	3.32

The effects of α and β cyclodextrins on the rate of oxidation showed that the α-form of cyclodextrin exhibited more catalytic effect compared to the β-form. The rate-coefficients for the oxidation of acetophenone and its substituted derivatives have been determined and are given in Table-2.

TABLE-2
SUBSTITUENT EFFECTS AND ACTIVATION PARAMETERS FOR THE OXIDATION OF ACETOPHENONES BY NBSac

[NBSac] = 1.0×10^{-3} mol dm^{-3} $[H^+] = 5.0 \times 10^{-3}$ mol dm^{-3}
[Substrate] = 1.0×10^{-2} mol dm^{-3} [MA] = 2.5×10^{-3} mol dm^{-3}
[Solvent] = 20% aq. HOAc (v/v)

Substrate	$k \times 10^8$ mol dm^{-3} s^{-1} at 308 K		E_a kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	ΔS K^{-1} J mol^{-1}	ΔG kJ mol^{-1}
	Normal	Catalysed AcyD				
MNA	1.10	2.58	58.19	57.55	310.73	122.46
PNA	1.20	2.66	69.28	68.02	175.61	122.11
PBA	1.30	3.60	72.74	75.57	15.591	128.88
AcP	3.30	4.50	56.36 *49.80	55.42	209.88	121.11
PCA	3.80	5.0	55.42	51.96	218.91	199.38
PMA	28.16	–	–	–	–	–

*in the presence of A-cyclodextrin.(ACy-D).

The lower value of E_a indicates the catalytic activity of cyclodextrin on the oxidation.

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