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A Comparative Study of the Oxidation of Benzaldehyde by N-Bromosaccharin and N-Bromophthalimide in Aqueous Acetic Acid Medium

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The kinetics of oxidation of benzaldehyde by N-bromosaccharin and N-bromophthalimide has been investigated in aqueous acetic acid medium in the presence of mercuric acetate over a temperature range of 308–328 K. The rate is first order with respect to both the substrate and oxidants. The stoichiometry of the process is 1 : 1, substrate : oxidant. The effect of ionic strength on the rate is negligible, but the dielectric constant of the medium has a positive influence. The thermodynamic parameters were calculated. Saccharin and H^+ were found to inhibit the rate, whereas, phthalimide did not inhibit the rate.

Key Words: Kinetic Mechanism, Oxidation, Benzaldehyde, N-Bromosaccharin, N-Bromophthalimide, Acetic acid medium.

INTRODUCTION

N-Halo compounds have been used widely as oxidising and halogenating reagents of organic compounds[1–10]. However, the studies of such compounds are very few and hence the present study deals with the comparative study on the oxidation of benzaldehyde using N-bromosaccharin (NBSac) and N-bromophthalimide (NBP) in aqueous acetic acid medium (30–70% v/v) in the presence of mercuric acetate. A suitable mechanism is also proposed.

EXPERIMENTAL

N-Bromosaccharin (NBSac) and N-bromophthalimide (NBP) were synthesized and their purity was ascertained by standard methods[11–13]. Solutions were made in glacial acetic acid distilled afresh by the standard procedures. Benzaldehyde used was SD's sample, distilled under reduced pressure and preserved in an inert atmosphere. All other chemicals used were of AnalaR grade. The kinetics of the reaction in aqueous acetic acid medium was followed iodometrically. Kinetic measurements were made in a thermostat of Concord Instruments with a sensitivity of ±0.1°C.

RESULTS AND DISCUSSION

The stoichiometry of the reaction was carried out by equilibrating the mixture consisting of oxidant, substrate, mercuric acetate (MA) and acid for sufficient length of time and estimating the unreacted NBSac and NBP, showed equivalence of one mole of benzaldehyde (C_6H_5CHO) to one mole of NBSac and NBP. Under the experimental condition, the final product of oxidation was identified as benzoic acid.

Kinetic studies were conducted under the condition where concentration of C_6H_5CHO and MA $\gg$ the oxidants. All the investigations were made in the presence of MA to avoid any possible *in situ* formation of molecular bromine[14]. The plots of ln $(a - x)$ *vs.* time in either case is found to be a straight line indicating that the order with respect to the oxidant is one. The rate of oxidation increased with increase in substrate concentration. The plot of ln k_{obs} *vs.* ln [S] is linear with unit slope indicating first order dependence on the substrate. The Lineweaver-Burk plot of $\frac{1}{k_{obs}}$ *vs.* $\frac{1}{C_6H_5CHO}$ is also linear with a positive intercept on the Y-axis indicating the involvement of C_6H_5CHO in complexation. The reaction rate did not vary with variation in ionic strength. The value of specific rates for various concentrations of the oxidants and C_6H_5CHO are given in Table-1.

TABLE-1
EFFECT OF CONCENTRATION OF OXIDANTS ON BENZALDEHYDE IN THE OXIDATION OF BENZALDEHYDE BY NBSac AND NBP

$[H^+] = 4.0 \times 10^{-3}$ mol dm^{-3} [MA] = 5.0×10^{-3} mol dm^{-3}

[Solvent] = 50% aq. HOAc (v/v) T = 308 K

$[C_6H_5CHO \times 10^{-1}$ mol dm^{-3}	$[x] \times 10^{-3}$ mol dm^{-3}	$k_{obs} \times 10^4$ s^{-1}	
		NBSac	NBP
1.0	1.0	3.10	2.47
1.5	1.0	4.37	3.59
2.0	1.0	6.05	4.85
2.5	1.0	7.16	6.03
3.0	1.0	8.25	7.10
1.0	1.0	2.07*	2.47
1.0	1.5	2.09	2.45
1.0	2.0	2.28	2.54
1.0	2.5	2.38	2.55

*With added saccharin. MA—Mercuric acetate.

The rate of reaction has been studied at various $[H^+]$ and a plot of ln k_{obs} *vs.* ln $[H_2SO_4]$ is linear with a negative slope indicating that the rate is inverse first order with respect to the acid. The rate coefficients were found to decrease as the dielectric constant decreases. A plot of ln k_{obs} *vs.* $\frac{(D-1)}{(2D+1)}$ is linear with a positive slope showing dipole-dipole type of interaction in the slow step of the mechanism. The reaction system did not induce polymerization of added acrylonitrile, confirming the absence of free radicals in the system. Addition of one of the products of the reaction, *viz.*, saccharin showed a retarding effect whereas phthalimide has only negligibly small influence on the reaction.

The activation parameters were calculated from Arrhenius plots and the values are given in Table-2.

TABLE-2
ACTIVATION PARAMETERS FOR THE OXIDATION OF BENZALDEHYDE BY NBSac AND NBP IN 50% Aq-ACETIC ACID MEDIUM

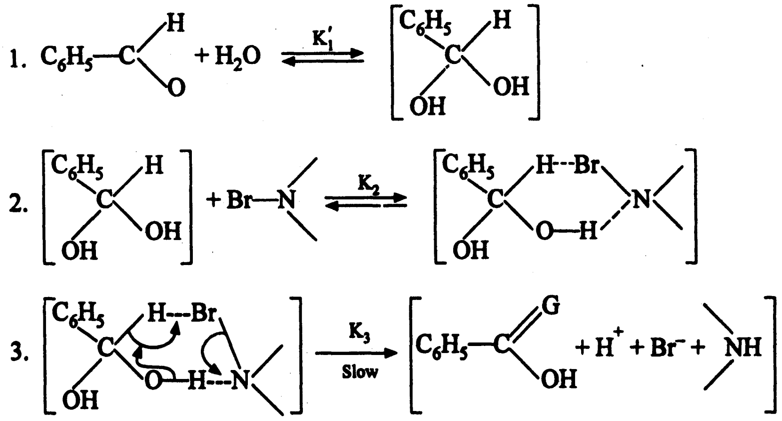
$[Ox] = 1.0 \times 10^{-3}$ mol dm^{-3} $[H^+] = 4.0 \times 10^{-3}$ mol dm^{-3}
$[C_6H_5CHO] = 1.0 \times 10^{-1}$ mol dm^{-3} $[MA] = 5.0 \times 10^{-3}$ mol dm^{-3}
[Solvent] = 50% aq. HOAc (v/v) T = 308–323 K

Oxidants	Ea kj mol^{-1}	$\Delta H^{\#}$ kj mol^{-1}	$-\Delta S^{\#}$ J kj mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}
NBSac	39.8	37.1	167.1	90.2
NBP	57.8	47.8	169.4	101.7

The reactive oxidative species could be either >NBr itself or HOBr. The rate of oxidation is not unaffected by ionic strength; however, it decreases with decrease in the dielectric constant of the medium and the plot of ln k_{obs} *vs.* $\frac{(D-1)}{(2D+1)}$ is linear. These results show that the rate-determining step should involve dipole-dipole type of interaction which also means no ions are involved in that step.

Benzaldehyde is also known to exist in diol form in acid medium[15]. The ***gem***-diol thus formed would more effectively be interacted by the oxidative species than C_6H_5CHO itself. The formation of complex involving the substrate indicates that the diol would be expected to interact with the oxidative species to form the complex which would decompose slowly to give the products. The products might be formed as a result of interaction between the diol and the oxidative species in a concerted step. Since entropy is only about –40 eu in both the oxidations, the slow step is not concerted but only the decomposition of fairly stable intermediate complex.

The interaction of HOBr with either the aldehyde or its diol is less feasible since the O—Br bond of HOBr should be first broken to give Br^+ and OH^-. But, the Br^+ ion formation is much more facile in the case of >NBr as N is highly electronegative owing to the influence of its neighbouring groups in the ring. Further, the breaking of the O—H bond of the substrate to discard the proton which again attaches to the negative oxygen to form —OH bond is not convincing. Based on these facts, a plausible mechanism would be proposed as:



Scheme 1

$$\frac{dx}{dt} = k_3[X] \text{ where } [X] = \frac{K_1K_2[S][Ox]_T}{1 + K_1K_2[S]}$$

The mechanism explains the experimental observations excellently, namely, stoichiometry (1 : 1, C_6H_5CHO : oxidant), ionic strength effect, influence of dielectric constant of the medium, decrease of the pH of the system during the course of the reaction, activation parameters, in particular ΔS, and the absence of free radicals.

Conclusion

From the structural point of view, NBSac is considered to be a better oxidant than NBP, since NBSac contains a sulphuryl group in place of a carbonyl group. This was experimentally verified. The kinetics of the benzaldehyde oxidation by NBSac as well as NBP were carried out in 50% aqueous HOAc medium at 45°C. The k_{obs} values are 3.10×10^{-4} and 2.47×10^{-4} s^{-1} for NBSac and NBP respectively. However, the NBSac oxidation was carried out in presence of added saccharin to make the inhibitory effect of the latter uniform throughout. Under the conditions, the k_{obs} value is only 2.95×10^{-4} s^{-1}; still, it is greater than the k_{obs} value of NBP. Hence, the theoretical prediction is valid.

In both the oxidations, almost all kinetic observations are similar except the following. Neither the mechanism nor the rate law explain the observed inhibitory effects of saccharin and the mineral acid in the NBSac oxidation. Both H^+ and saccharin are responsible for the inactivation of C_6H_5CHO to some extent whereby both of them inhibit the oxidation. Since this step occurs after the slow step, as the products are involved here, it does not appear in the rate law. This inactivated complex is probably very unstable with phthalimide because of relatively less electron-withdrawal ability of the carbonyl group compared to sulphenyl group. The existence of an inactive complex is supported by spectral evidence.

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