

Kinetics of Oxidation of Furfural by N-bromosaccharin in Aqueous Acetic Acid Medium

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The kinetics of oxidation of furfural by N-bromosaccharin (NBSA) has been studied in 50% (v/v) acetic acid-water mixture. The reaction shows first order dependence each in [NBSA], [Furfural] and $[H^+]$ ions. Increase in acetic acid content of the solvent medium decreases the rate of reaction. Activation parameters have been calculated. A suitable mechanism has been proposed in consistency with the kinetic data.

Key words: Kinetics, oxidation, furfural, n-bromosaccharin, acetic acid medium.

INTRODUCTION

Kinetics of oxidation of aromatic compounds by N-halo compounds has received considerable attention¹⁻⁴. Oxidations of aromatic aldehydes by trichloroisocyanuric acid (TCICA)⁵, N-bromobenzamide (NBB)⁶, N-bromosuccinimide (NBS)⁷ and 1-chlorobenzimidazole (CBI)⁸ have been studied. The literature survey reveals that there is no report about the reaction of furfural with N-bromosaccharin and in the present investigation the reaction kinetics of furfural with NDSA has been studied in presence of perchloric acid and mercury(II) acetate.

EXPERIMENTAL

N-Bromosaccharin (NBSA) was prepared by literature method. Acetic acid was purified by standard method and the fraction distilling at 118°C was collected. Furfural (BDH, AnalaR) was used after distillation. Analytically pure other chemicals such as sodium perchlorate (Germany), mercury(II) acetate and perchloric acid (BDH, AnalaR) were used.

The product analysis shows the presence of furoic acid (furan-2-carboxylic acid) as the product which is confirmed by spectral analysis and by TLC.

Kinetic measurements

The pseudo-first order conditions were attained by keeping a large excess (10-fold or more) of furfural over NBSA. The reactions were followed potentiometrically up to 70% completion, by following the potentials of the reaction mixture containing varying concentrations of [NBSA]/[SA] couple (SA = saccharin) at regular time intervals using a platinum-saturated calomel electrode

assembly. The pseudo-first order rate constant, k_1 , was computed from the linear ($r > 0.98$) plots of $\log(E_1 - E_0)$ vs. time. When the kinetic run was done by iodometry, the same result was obtained with $k \pm 2\%$.

Preliminary experiments showed that the reaction was not sensitive to change in ionic strength; hence no attempt was made to keep it constant.

RESULTS AND DISCUSSION

Under the condition of $[NBSA] \ll [\text{furfural}]$, the disappearance of NBSA followed first order kinetics as evidenced by the linear plots of $\log(E_1 - E_0)$ vs. time. The effect of varying initial $[NBSA]$ at constant $[\text{furfural}]$ also showed the order with respect to NBSA to be one (Table-1). The data in Table-1 also reveal a first order dependence of rate on $[\text{substrate}]$. The effect of $[H^+]$ was investigated in the range of 0.02 to 0.08 M. There was a proportional increase in rate on increasing $[H^+]$. At relatively higher $[H^+]$ the order in $[H^+]$ is decreased.

TABLE-1
EFFECT OF VARYING [SUBSTRATE] AND [OXIDANT]
ON REACTION RATE

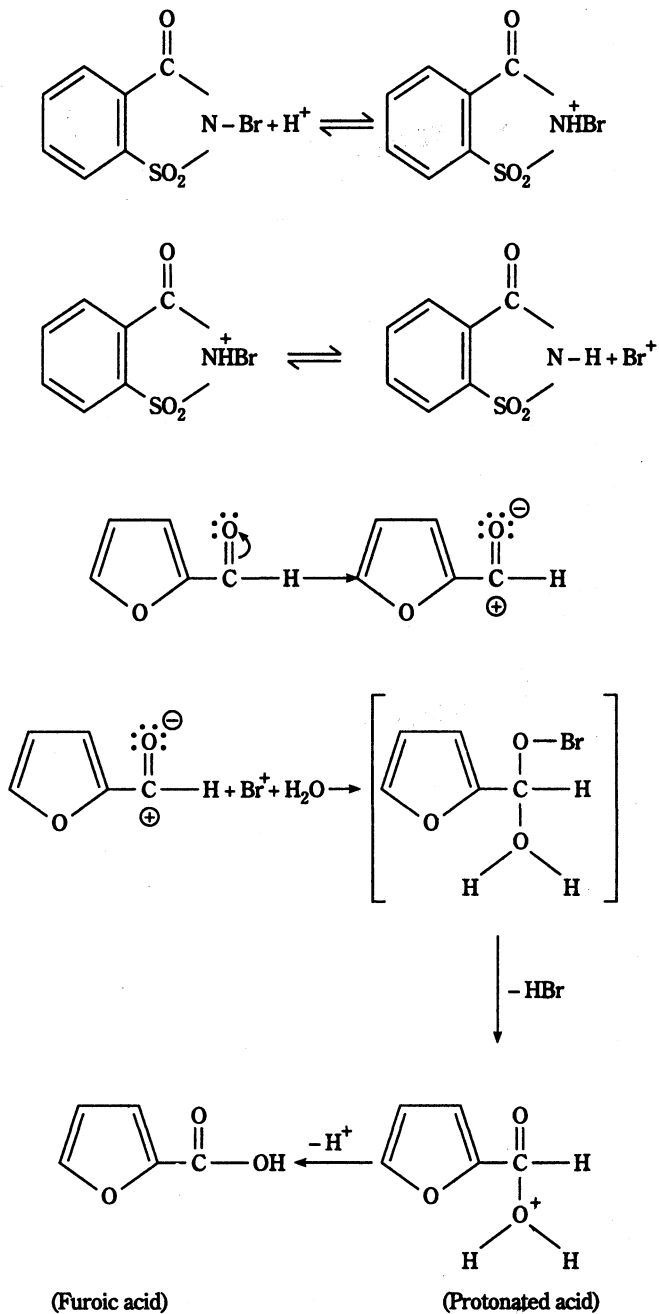
$[HClO_4] = 0.4 \text{ mol dm}^{-3}$, Solvent = HOAc 50% (v/v) Temp. = 303K		
$[NBSA] \times 10^3$ (mol dm^{-3})	$[Furfural] \times 10^2$ (mol dm^{-3})	$k_1 \times 10^4$ (s^{-1})
1.5	2.8	1.31
1.8	2.8	1.38
2.0	2.8	1.30
2.4	2.8	1.34
2.8	2.8	1.35
2.8	4.2	2.03
2.8	5.6	2.70
2.8	7.0	3.35
2.8	8.4	3.92

It was observed that the change in concentration of mercuric acetate over a four-fold range 0.025 M to 0.1 M had negligible effect on the rate. The function of added mercuric acetate is only to fix up Br^- formed in the course of the reaction as $HgBr_2$ or $HgBr_4^{2-}$.

Increase in the percentage of acetic acid in the binary mixture decreased the rate indicating dipole-dipole type of reaction. Addition NBSA does not affect the rate.

In acidified aqueous acetic acid solution of NBB, possible oxidizing species are NBB itself, $HOBr$, $PhCONBr_2$, Br_2 , $AcOBr$ and their protonated forms. The absence of any effect of the parent amide on the reaction rate precludes a hydrolysis of NBSA in the pre-equilibrium and rules out the formation of $HOBr$, $PhCONBr_2$, Br_2 and $AcOBr$ as the reactive oxidizing species. This also rules out the initial formation of a hypobromite ester by nucleophilic attack on the carboxyl

group. The strict first order dependence of the reaction rate on NBSA also rules out PhCONBr_2 and molecular bromine as the reactive oxidizing species. Thus the reactive species in the reaction appears to be the N-bromosaccharin itself or its



protonated form. This is in contrast to the observation in oxidations by NBS and N-bromoacetamide¹⁻⁴.

The following scheme and rate law have been proposed for the reaction:

$$\text{Rate} = k_{\text{obs}} [\text{NBSA}][\text{furfural}][\text{H}^+]$$

The above rate law satisfies all the experimental observations.

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