Kinetics and mechanism of oxidation of acetals by N-bromoisonicotinamide in acetonitrile medium

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ABSTRACT

Kinetics of oxidation of acetals ($XC_6H_4CH(OR)_2$ by N-bromoisonicotinamide (NBIN) in acetonitrile medium in the presence of sodium perchlorate has been investigated by iodometric method. The observed rate of oxidation is first order in both [NBIN] and [$XC_6H_4CH(OR)_2$]. An increase in the dielectric constant of the medium increases the rate. The variation of ionic strength has no significant effect on the reaction rate and addition of isonicotinamide has retarding effect. The stoichiometry of the reaction is found to be 1:1. The corresponding ester has been identified as the product of oxidation. The reaction fails to induce polymerization of acrylonitrile under the experimental conditions employed. The Hammett reaction constant (ρ) for the reaction is found to be -0.71 at 313 K and -0.73 at 323 K. The isokinetic temperature evaluated from Exner plot is found to be $\beta = 202$ K (r = 0.9938). The Arrhenius and activation parameters for the reaction have been evaluated from Arrhenius plot by studying the reaction at different temperatures. A suitable mechanism is proposed and an appropriate rate law is deduced to account for the observed kinetic data.

Keywords: N-bromoisonicotinamide, acetals, kinetics, oxidation, mechanism.

INTRODUCTION

The chemistry of reactions N-halo compounds is of great synthetic importance [1]. The versatile nature of N-halo compounds is due to their ability to act as sources of halonium ions, hypo halite species and nitrogen anions. They have been widely used as oxidizing and halogenating reagents in organic compounds [2-5]. Acetals are etherification products of alcohols and aldehydes. Acetals play a vital role in bio-organic research in exploring biological activities [6]. Kinetics of oxidation of alcohols by N-bromoisonicotinamide is reported in literature [7]. The kinetics of oxidation of acetals by lead (IV) [8], ceric ammonium nitrate [9], chromic acid [10-11], peroxomonosulphate [12], dimethyl dioxirane [13], pyridinium chlorochromate [14], N-chlorosaccharin [15], N-chlorobenzamide [16] have been reported earlier. Oxidation of substituted aromatic acetals by NBIN has not been reported so far and hence the need for title investigation.

EXPERIMENTAL SECTION

NBIN was prepared [17] and the purity was checked iodometrically [18]. All other chemicals were of AnalaR grade. The seven acetals namely benzaldehydedi-n-butyl acetal, p-methoxybenzaldehyde di-n-butyl acetal, p-methylbenzaldehyde di-n-butyl acetal, p-chlorobenzaldehyde di-n-butyl acetal, m-chlorobenzaldehyde di-n-butyl acetal, m-nitrobenzaldehyde di-n-butyl acetal and p-nitrobenzaldehyde di-n-butyl acetal were prepared by the standard methods [19-21]. Kinetic runs were carried out under pseudo-first order conditions ([$XC_6H_4CH(OR)_2$] >> [NBIN]). Requisite amounts of acetal, sodium perchlorate, acetonitrile and water were taken in a jena glass reaction vessel and placed in a water thermostat maintained at the desired temperature for 30 min. The reaction was initiated by rapid addition of NBIN solution and its progress was followed iodometrically by estimating the amount of unconsumed NBIN at regular intervals of time.

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RESULTS AND DISCUSSION

The rate of oxidation is found to be first order each in $[XC_6H_4CH(OR)_2]$ and [NBIN]. Linear plot of log k_{obs} versus log $[XC_6H_4CH(OR)_2]$ with a slope unity shows first order dependence on the rate of reaction. The log k_{obs} values at different [acetal] are given in Table-1. The log [NBIN] versus time is found be linear indicating first order dependence on the rate of reaction. The log k_{obs} values obtained at different initial concentrations of NBIN reveal that the rates are almost independent of the initial concentration of NBIN (Table-2).

Table-1: Effect of varying [substrate] on the rate of oxidation of acetals by NBIN

[NBIN] = 6.0 x 10⁻³ M,   [NaClO₄] = 1.0 x 10⁻¹ M,   Solvent = 70% CH₃CN – 30% H₂O (v/v),   Temp = 323 K.

$[XC_6H_4CH(OR)_2]$ x 10^2 (M)	k_{obs} x 10^4 (s^{-1})						
	X = H	X = p-OMe	X = p-Me	X = p-Cl	X = p-NO₂	X = m-NO₂	X = m-Cl
6.0	5.66	8.35	6.58	4.21	1.41	2.31	3.11
8.0	7.17	11.64	8.82	5.76	1.98	3.34	4.23
10.0	9.26	14.58	10.39	6.82	2.36	4.37	5.32
12.0	11.28	16.56	13.68	8.45	2.91	5.63	6.23
14.0	13.14	19.91	15.29	9.68	3.39	6.78	7.57
16.0	15.25	22.52	17.53	11.49	3.86	7.62	8.62

Table-2: Effect of varying [NBIN] on the rate of oxidation of acetals by NBIN

[XC₆H₄CH(OR)₂] = 8.0 x 10⁻² M,   [NaClO₄] = 1.0 x 10⁻¹ M,   Solvent = 70% CH₃CN – 30% H₂O (v/v),   Temp = 323 K.

[NBIN] x 10^3 (M)	k_{obs} x 10^4 (s^{-1})						
	X = H	X = p-OMe	X = p-Me	X = p-Cl	X = p-NO₂	X = m-NO₂	X = m-Cl
6.0	7.17	11.64	8.82	5.76	1.98	3.34	4.23
7.0	7.11	11.89	8.67	5.87	1.97	3.37	4.24
8.0	7.16	11.67	8.72	5.88	2.01	3.31	4.23
9.0	7.14	11.78	8.72	5.83	1.89	3.38	4.21
10.0	7.11	11.69	8.81	5.76	1.94	3.34	4.22

Table-3: Effect of varying solvent composition on the rate of oxidation of acetals by NBIN

[XC₄H₄CH(OR)₂] = 8.0 x 10⁻² M, [NBIN] = 6.0 x 10⁻³ M, [NaClO₄] = 1.0 x 10⁻¹ M, Temp = 323 K.

$XC_6H_4CH(OR)_2$	k_{obs} x 10^4 (s^{-1})				
	% CH₃CN – % H₂O (v/v)				
	70-30	75-25	80-20	85-15	90-10
X = H	7.17	6.29	5.72	4.82	3.89
X = p-OMe	11.64	10.74	9.74	8.85	7.82
X = p-Me	8.82	7.46	6.31	5.13	3.68
X = p-Cl	5.76	4.63	3.51	2.36	1.25
X = p-NO₂	1.98	1.80	1.64	1.15	0.49
X = m-NO₂	3.34	2.60	1.87	1.51	1.23
X = m-Cl	4.23	3.62	3.04	2.48	1.01

Table-4: Effect of varying temperature on the rate of oxidation of acetals by NBIN

[XC₆H₄CH(OR)₂] = 8.0 x 10⁻² M, [NBIN] = 6.0 x 10⁻³ M, [NaClO₄] = 1.0 x 10⁻¹ M,
Solvent = 70% CH₃CN – 30% H₂O (v/v)

$XC_6H_4CH(OR)_2$	k_2 x 10^3 M^{-1} (s^{-1})				
	313 K	318 K	323 K	328 K	333 K
X = H	4.46	7.04	8.96	14.05	17.40
X = p-OMe	7.28	8.84	14.58	17.31	28.73
X = p-Me	5.54	7.58	11.03	14.81	21.08
X = p-Cl	3.58	3.95	7.20	7.86	14.11
X = p-NO₂	1.26	2.20	2.47	4.35	5.18
X = m-NO₂	2.06	2.93	4.18	5.81	8.48
X = m-Cl	2.65	3.93	5.29	7.88	10.68

The effect of added isonicotinamide (INA) is studied at different initial concentrations of isonicotinamide. It has a slight retarding effect on the reaction rate. The ionic strength of the reaction is varied by the addition of NaClO₄ and its influence on the reaction rate is studied. It is found that increase in ionic strength of the reaction medium has no observable change on the rate of the reaction.

In order to determine the rate dependence on solvent composition, the ratio of water to acetonitrile is varied. It is observed that an increase in the dielectric constant of the medium increases the rate constant (Table-3). The plot of log k_{obs} versus 1/D (D is the dielectric constant of the medium) is found to be linear with negative slope.

The oxidation of acetals is studied at different temperatures (313-333 K). The results are shown in Table-4. The Arrhenius plot of log k_2 versus 1/T is linear. From the plot, Arrhenius and activation parameters are evaluated (Table-5).

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The effect of substitutents on the rate of oxidation has been studied. The second order rate constant for the oxidation of *meta-* and *para-*substituted benzaldehyde di-n-butyl acetals by NBIN at two different temperatures is given in (Table-6). The electron withdrawing groups retard the rate of reaction and electron releasing groups accelerated the rate of reaction (Table-6). The plot of log k_2 versus Hammett substituents constants (σ) values for the *meta-* and *para-*substituted benzaldehyde di-n-butyl acetals are found to be linear (r = 0.9979) with reaction constant values ρ of -0.71 and -0.73 at 313 K and 323 K respectively [22-24]. A good correlation of rates with the Hammett substituent constants (σ) indicates that the reaction site is directly conjugated with the aromatic ring, but some group is interposed. The negative slope indicates the formation of positively charged activated complex during course of the reaction.

The order of the reactivity of *meta-* and *para-*substituted benzaldehyde di-n-butyl acetals is as follows p-OMe > p-Me > H > p-Cl > m-Cl > m-NO_2 > p-NO_2.
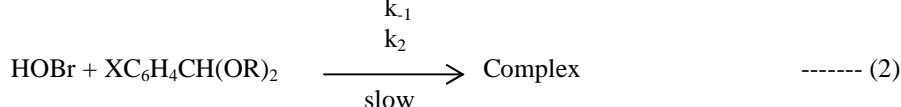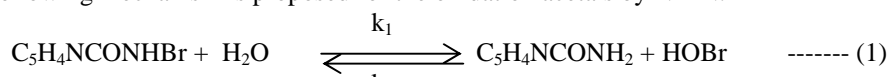
The genuine nature of isokinetic relationships is verified by the Exner plot [25-26] of log k_2 (323 K) versus log k_2 (333 K) with slope 1.05. This linearity of Exner plot is the suggestive of a unified mechanism for the *meta-* and *para-*substituted benzaldehyde di-n-butyl acetals by NBIN. From the slope of the Exner plot, isokinetic temperature (β) is calculated using the following equation [27].

$$\beta = \frac{T_1 T_2 (b-1)}{b T_2 - T_1}$$

The isokintic temperature obtained from slope is 202 K is less than T_1, which indicates an increasing reactivity with increase in temperature. The linear relationship shows that the all the *meta-* and *para-*substituted benzaldehyde di-n-butyl acetals follow a common mechanism.

Mechanism

Under the experimental conditions, the possible oxidizing species are HOBr, H_2OBr^+, Br_2 and NBIN. The observed first order dependence on the reaction rate NBIN rules out molecular bromine as the reactive oxidizing species [28]. If NBIN is considered to be active species, it cannot rationalize the inverse dependence on the reaction rate isonicotinamide. However negligible effect of ionic strength on the reaction rate rules out H_2OBr^+ as active species. Taking into account all the experimental observations and the above facts in view, it is assumed that HOBr is the effective oxidizing species [29] in the present investigation. Addition of isonicotinamide decreases the rate of oxidation. This retardation effect suggests the involvement of pre-equilibrium step in which isonicotinamide is formed. The following mechanism is proposed for the oxidation acetals by NBIN.

$$C_5H_4NCONHBr + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_5H_4NCONH_2 + HOBr \qquad \text{------- (1)}$$

$$HOBr + XC_6H_4CH(OR)_2 \xrightarrow[\text{slow}]{k_2} Complex \qquad \text{------- (2)}$$

$$Complex \xrightarrow[\text{fast}]{k_3} Products \qquad \text{------- (3)}$$

From equation (1)

$$[HOBr] = \frac{k_1 [NBIN] [H_2O]}{k_{-1} [C_5H_4NCONH_2]} \qquad \text{------- (4)}$$

Rate = k_2 [HOBr] [$XC_6H_4CH(OR)_2$]

Applying steady state approximation to HOBr, the following rate law is obtained.

$$Rate = \frac{k_2 k_1 [NBIN] [XC_6H_4CH(OR)_2] [H_2O]}{k_{-1} [C_5H_4NCONH_2]} \qquad \text{------- (5)}$$

Rearranging equation (5)

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$$\text{Rate} = \frac{k_2 k_1 \, [\text{NBIN}] \, [\text{XC}_6\text{H}_4\text{CH(OR)}_2]}{k_{-1} \, [\text{C}_5\text{H}_4\text{NCONH}_2]}$$

The rate law shows that the reaction follows first order kinetics with respect to each [NBIN], [XC$_6$H$_4$CH(OR)$_2$] and retardation effect on [isonicotinamide].

The change in ionic strength does not alter the rate. The reaction rate increases with increase in dielectric constant of the medium. These indicate the reaction is between dipole-dipole in rate determining step [30-31]. The negative entropy of activation ($\Delta S^{\#}$), indicates that the activated complex is cyclic in nature [32].

The structure of the complex and the products formation are given below:
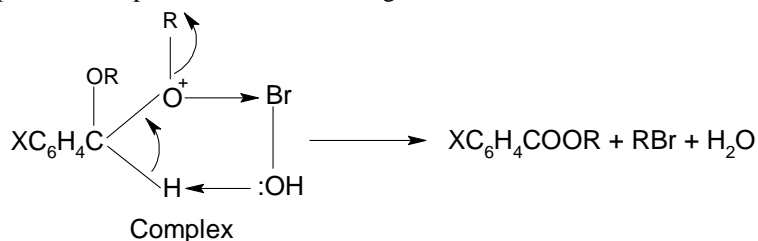
Complex

R = n-butyl

A similar complex is reported [33] in the study of oxidative cleavage of the ethers by bromine.

Table-5: Activation and Arrhenius parameters of oxidation of acetals by NBIN

XC$_6$H$_4$CH(OR)$_2$	k_2 x 10^3 M^{-1} (s^{-1})	Ea (kJ mol^{-1})	log A	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J mol^{-1} K^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
X = H	8.96	59.17	12.53	56.41	-110.22	92.03
X = p-OMe	14.58	60.60	13.24	57.92	-101.55	90.72
X = p-Me	11.03	57.86	12.39	57.59	-104.82	91.39
X = p-Cl	7.20	59.39	12.42	56.73	-111.14	93.49
X = p-NO$_2$	2.47	60.79	12.27	58.10	-115.65	95.46
X = m-NO$_2$	4.18	60.92	12.47	58.23	-110.92	94.06
X = m-Cl	5.29	60.29	12.49	57.61	-110.91	93.43

Table-6: Second order rate constants for the oxidation of acetals by NBIN at 313 K and 323 K.

[XC$_6$H$_4$CH(OR)$_2$] = 8.0 x 10^{-2} M, [NBIN] = 6.0 x 10^{-3} M, [NaClO$_4$] = 1.0 x 10^{-1} M,
Solvent = 70% CH$_3$CN – 30% H$_2$O (v/v)

XC$_6$H$_4$CH(OR)$_2$	Substituent constant (σ)	313 K k_2 x 10^3 M^{-1}(s^{-1})	323 K k_2 x 10^3 M^{-1}(s^{-1})
X = H	0.00	4.48	8.96
X = p-OMe	-0.27	7.28	14.58
X = p-Me	-0.17	5.54	11.03
X = p-Cl	0.23	3.35	7.20
X = p-NO$_2$	0.78	1.26	2.47
X = m-NO$_2$	0.71	2.06	4.18
X = m-Cl	0.37	2.65	5.29

Product analysis and Stoichiometry study

The reaction mixture containing excess of NBIN over acetal in the presence of NaClO$_4$ was kept at room temperature for 36 h. Estimation of unreacted NBIN showed that one mole acetal reacted with one mole of NBIN. The overall stoichiometry of the oxidation reaction may be represented as
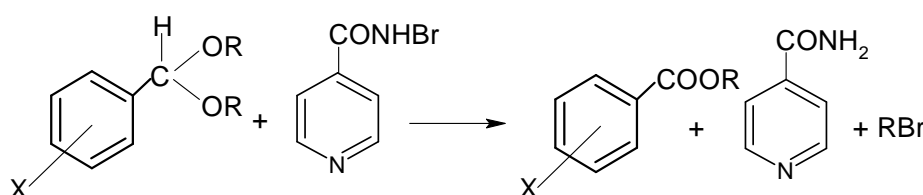
Product analysis was carried out under kinetic conditions, where [acetal] was taken in excess compared to that of [NBIN]. The reaction was allowed to proceed to completion by keeping it in a thermostat at 50 ^{0}C for about 3-4

2320

hours. Then the solution was cooled and shaken with ether. The two layers were separated. The ether layer was washed with water several times and dried with anhydrous sodium sulphate. The corresponding ester has been identified as the major product of oxidation by TLC, IR and NMR spectra.

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