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A Kinetic approach to oxidation of p methoxy-benzaldehyde di-nbutyl acetal by n-chloroisonicotinamide in aqueous acetonitrile acid medium: A comprehensive and mechanistic study

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Abstract

N-halo compound, N-chloroisonicotinamide (NCIN), in aqueous acetonitrile medium have been investigated. The new oxidant, N-chloroisonicotinamide is characterized by formal redox potential (1.05 V).The observed rate of oxidation is first order in [oxidant] and [substrate]. An increase in the dielectric constant of the medium decreases the rate. Variation in ionic strength of the medium has no significant effect on the rate and the addition of the reaction product, nicotinamide has a slight retarding effect on the rate. The reaction follows first order dependence of rate on [substrate] and [oxidant]. The rate increases with the decrease in dielectric constant of the medium. Variation of ionic strength and the addition of isonicotinamide has significant effect on the reaction rate. A suitable mechanism has been proposed and a rate law explaining the experimental results is obtained.

Keywords: Kinetics, oxidation, mechanism, N – chloroisonicotinamide

1. Introduction

Chemical kinetics is a branch of chemistry which deals with rate of reaction. The kinetic study of oxidation of organic compound is a useful and powerful method in physical organic chemistry. The role of Nhalo compounds in this field is very wide. They are being used in kinetics, analytical 1 and organic structural investigation. N-Halo compounds are particularly useful in synthesizing organic substrates. The electro negativities of halogens, except fluorine, are less than that of nitrogen. Hence they acquire a positive charge when linked with nitrogen. The electro-negativity of nitrogen is further enhanced by linking it with certain electron withdrawing groups such as acyl group. Thus N-halo compounds are referred as positive halogen compounds.

Recently, considerable attention has been focused on the chemistry of N-halo compounds. N-Chloroisonicotinamide (m.p. 214 ºC) was prepared bypassing a slow stream of chlorine into a solution of isonicotinamide (15 g in 30 mL 3 N HCl) at 32 ºC for 1 h. The NCIN formed as white crystals was filtered and the process of passing chlorine into the filtrate and filtering off the precipitate was repeated till no more precipitate was obtained. N-Chloroisonicotinamide was found to be soluble in water, dimethylsulphoxide, acetic acid, but insoluble in chloroform and carbon tetrachloride.

The kinetic study of oxidation of aromatic diethers by NCIN in acetonitrile is not reported so far and hence need for the title investigation.

Material and Methods

Experimental Section

NCIN was prepared [17] and the purity was checked iodometrically [18]. All other chemicals were of AnalaRgrade. The seven acetals namely benzaldehyde di-n-butyl acetal, p-methoxybenzaldehyde di-nbutyl acetal, p-methylbenzaldehyde di-n-butylacetal, p-chlorobenzaldehyde di-n-butyl acetal, mchlorobenzaldehyde di-n-butylacetal, m-nitrobenzaldehyde di-n-butyl acetal and p-nitrobenzaldehyde din-butyl acetal were prepared by the standard methods [19-21]. Kinetic runs were carried out under pseudo-first order conditions ($[XC_6H_4CH(OR)_2] >> [NCIN]$). 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 NCIN solution and its progress was followed iodometrically by estimating the amount of unconsumed NCIN at regular intervals of time.

Results and Discussion

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

Table 1: Effect of Variation of [NCIN] for the Oxidation of Acetals at 323 $[X\text{-}C_6H_4\ CH\ (OC_4H_9)_2] = 8.0 \times 10^{-2}M$ $[NaClO_4.H_2O] = 1.0 \times 10^{-2}M$ Solvent (v/v) = 90% CH_3CN 10% H_2O

[NCIN] X 10^3(M)	**k_1 X10^4(s^{-1})**
4.0	5.59
5.0	7.83
6.0	9.09
7.0	10.48
8.0	12.2

Table 2: Effect of Variation of [Acetal] for the Oxidation by NCIN at 323 K $[NCIN] = 6.0 \times 10^{-2}M$ $[NaClO_4.H_2O] = 1.0 \times 10^{-2}M$ Solvent (v/v) = 90% CH_3CN-10% H_2O

$[X\text{-}C_6H_4\ CH(OC_4H9)_2])$ X10^2(M)	**k_{1X} 10^4(s^{-1})**
2.0	2.02
4.0	4.36
6.0	7.08
8.0	9.09
10.0	13.28

The influence of solvent dielectric constant on the rate of NCIN oxidation of acetals has been studied in various solvent mixtures of acetonitrile and water. The rate of oxidation increases with the increase in acetonitrile content of the solvent mixture (Table 3).

Table 3: Effect of Variation of Dielectric Constant for the Oxidation of Acetals by NCIN at 323 K [X-C_6H_4 CH(OC_4H_9)$_2$] = 8.0 X10^{-2}M [NCIN] = 6.0X 10^{-2}M [$NaClO_4.H_2O$]] = 1.0 X 10^{-2}M M [$NaClO_4.H_2O$]] =1.0 X10^{-2}M

CH_3CN – H_2O% (V/V)	D	K1X 10^4(S^{-1})
88	36.74	5.99
89	36.36	7.81
90	35.98	9.09
91	35.60	11.01
92	35.22	12.50

The effect of one of the products of the reaction on the rate of oxidation has been studied by adding various concentrations of isonicotinamide, keeping the concentrations of acetal and NCIN constant. There is a decrease in the reactivity with the increase in the initially added concentration of isonicotinamide (Table 4).

Table 4: Effect of Variation of [Isonicotinamide] for the Oxidation of Acetals by NCIN at 323 K [X-C_6H_4 CH(OC_4H_9)$_2$] = 8.0 X 10^{-2}M [NCIN] = 6.0 X 10^{-2}M Solvent (v/v) = 90% CH3CN10% H_2O [$NaClO_4.H_2O$ = 1.0 X 10^{-2}M

[Isonicotinamide] X10^3(M)	k1X 10^4(s^{-1})
0.0	9.09
2.0	7.50
4.0	5.13
6.0	4.22
8.0	3.71

The influence of variation of ionic strength on the rate of oxidation has been studied by varying the concentrations of [$NaClO_4.H_2O$]. The reaction rate increases with the increase in ionic strength of the medium (Table 5).

Table 5: Effect of Variation of Ionic Strength for the Oxidation of Acetals by NCIN at 323 K [X-C_6H_4 CH(OC_4H_9)$_2$] = 8.0 x10^{-2}M [NCIN] = 6.0 X10^{-3}M Solvent (v/v) = 90% CH_3CN 10% H2O

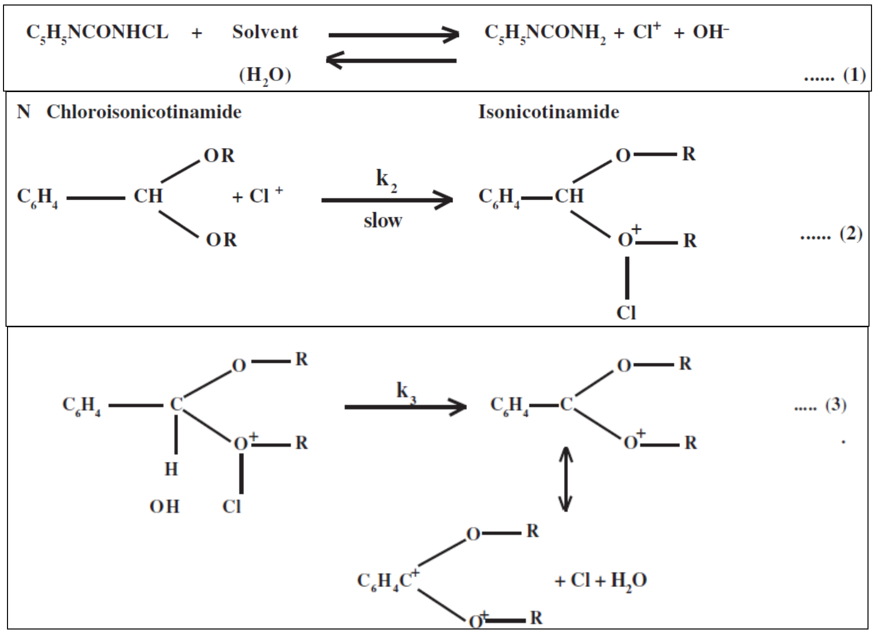
[$NaClO_4.H_2O$] X10 (M)	k10^4(s^{-1})1 X
1.0	9.09
2.0	11.80
3.0	13.41
4.0	14.74

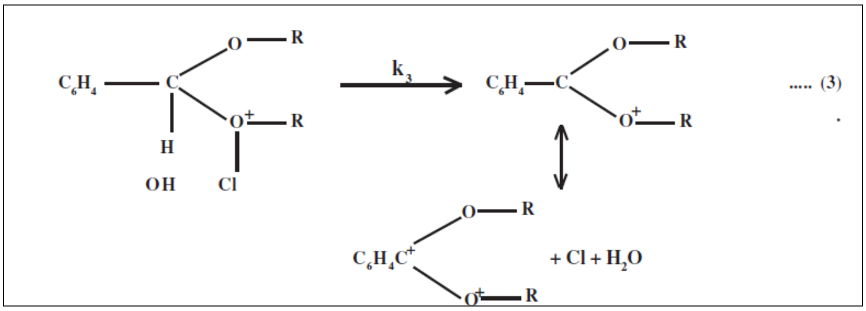
The effect of added isonicotinamide (INA) is studied at different initial concentrations of isonicotinamide. It has as light retarding effect on the reaction rate. The ionic strength of the reaction is varied by the addition of $NaClO_4$ and its influence on the reaction rate is studied. It is found that increase in ionic strength of the reaction medium has no observable change on the rate of the reaction.

Mechanism

The results of NCIN oxidation of acetal in the present investigation can be accounted for, by identifying the rate-determining step.

A probable mechanism may involve electrophilic attack of the positive part of oxidising species on the electron – rich oxygen atom of acetal rather than on the electron – deficient aldehydic hydrogen. The mechanism has been proposed assuming Cl+as the oxidizing species. Solvent consists of a mixture of acetonitrile and water. The reactive oxidizing species may be Cl^+ or solvated Cl $^+$. The reactive species formed in the above equilibrium step attacks the acetal molecule in the rate-determining step.





Assuming Cl+ as the effective oxidizing species, the rate law is given as follows:

$$\frac{-d[NCIN]}{dt} = \frac{k_1 k_2 [C_6H_4CH(OR)_2][NCIN]}{K_{-1}[INA]}$$

The above rate law accounts for the first order dependence on [NCIN] and [acetal]. This also explains the retardation in the rate by the addition of isonicotinamide. The pseudo-first order rate constant increases with the increase in [NCIN].

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