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A Mechanistic Investigation of the Oxidation of Acetals by N-Chloroisonicotin Amide in Aqueous Acetonitrile Medium

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Abstract: N-halo compound, N-chloroisonicotinamide (NCIN), in aqueous acetonitrile medium has 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, isonicotinamide 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. Chloride ions positively influence the rate of oxidation. 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, acetals and N – chloroisonicotinamide.

I. INTRODUCTION

The role of N-halo compounds in this field is very wide. Halogens, N-haloamides and imides are the versatile agents used for the oxidation of a wide variety of organic compounds. Acetals are etherification products of alcohols and aldehydes.[1-3]Generallyacetals result from elimination of one molecule of water from one molecule of carbonyl compound and two molecules of an alcohol.

$$RCHO + 2R'OHRCH (OR')_2 + H_2O \rightleftharpoons$$
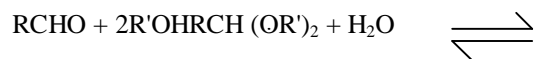
Aldehydes and alcohols are very sensitive to oxidizing agents in alkaline media. By conversion into an acetal, aldehydes, ketones and alcohols are deprived of their sensitivity to two-electron oxidation.[4-6]Acetals play a vital role in bio-organic research in exploring biological activities. The present work reports the kinetics of oxidation of acetalsby NCIN and evaluates the reaction constants.[7-9]

II. EXPERIMENTAL SECTION

NCIN was prepared and the purity was checked iodometrically . All other chemicals were of AnalaR grade. The acetals namelyp-nitrobenzaldehyde di-n-butyl acetal, p-chlorobenzaldehyde di-n-butyl acetal, m-nitrobenzaldehyde di-n-butyl acetal, m-chlorobenzaldehyde di-n-butyl acetal were prepared by the standard methods .[9-12] Kinetic runs were carried out under pseudo-first order conditions ([X☐C6H4 CH(OC4H9)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.[13-17] 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.

A. The Proposed Work Involve The Following Steps
1) Determination of Conditions under which the reaction proceeds with a measurable rate.
2) Effect of acetals Concentration To study the effect of acetals concentration on the specific rate it is proposed to study the reaction at different initial concentrations of acetals.
3) Effect of Substrate Concentration To study the effect of substrate concentration on the specific rate it is proposed to study the reaction at different concentrations of the substrate keeping the concentration of the oxidant constant.
4) Effect of Ionic Strength To study the effect of ionic strength the reaction is proposed to study at various concentrations of sodium per chlorate.

5) *Effect of Dielectric Constant of the Medium on the Reaction Rate* The influence of solvent dielectric constant on the rate of oxidation will be studied by varying the proportion of acetic acid and water keeping the concentration of substrate and oxidant constant at constant temperature.

6) *Effect of Temperature* To determine the thermodynamic parameters the reaction is proposed to carry out at different temperatures.

7) A Suitable Mechanism will be proposed and attempts will be made to find out the structure reactivity correlation.

III.   RESULTS

The reactions are of first order with respect to NCIN. Further, the values of k_{obs} are independent of the initial concentration of NCIN. The reaction is first order with respect to benzaldehyde di-n-butyl acetal also (tables 1-5)

A. *Effect of varying [NCIN] on the rate of oxidation of acetal by NCIN*

[Acetal] = 8.0 $\times 10^{-2}$ M   [NCIN] = 6.0 $\times 10^{-3}$ M

Solvent (v/v) = 90% CH3CN $\times$ 10% H_2O [NaClO4.H2O] = 1.0 $\times 10^{-1}$ M

TABLE-1

[NCIN] $\times 10^3$ (M)	$k_1 \times 10^4$ (s^{-1})			
	p-chlorobenzaldehyde di-n-butyl acetal	*p*-nitrobenzaldehydedi-n-butyl acetal	*m*-chlorobenzaldehyde di-n-butyl acetal	*m*-nitrobenzaldehyde di-n-butyl acetal
1.0	3.00	4.91	2.04	1.04
2.0	3.22	4.80	2.06	1.32
3.0	3.21	4.65	2.14	1.55
4.0	3.38	4.47	2.15	1.61

The rate studies are carried out at different initial concentrations of NCIN. The k1 values at different initial concentrations of NCIN are given in Table-1. It is seen that the pseudo-first order rate constant increases with the increase in initial concentration of the oxidant. But in each kinetic run, thereaction shows no deviation from the first order plot.

B. *Effect of [substrate] On the Rate Of Oxidation Of Acetal By NCIN*

 [NCIN] = 6.0 $\times 10^{-3}$ M   [NaClO4.H2O] = 1.0 $\times 10^{-1}$ M

Solvent (v/v) = 90% CH$_3$CN $\times$ 10% H_2O

TABLE-2

[X$\square$C6H4 CH(OC4H9)2] $\times 10^4$ (s^{-1})	$k_1 \times 10^4$ (s^{-1})			
	p-chlorobenzaldehyde di-n-butyl acetal	p-nitrobenzaldehyde di-n-butyl acetal	m-chlorobenzaldehyde di-n-butyl acetal	m-nitrobenzaldehyde di-n-butyl acetal
1.0	2.59	1.23	1.64	1.21
2.0	3.62	1.66	2.20	1.63
3.0	5.01	2.08	2.88	2.06
4.0	5.92	2.48	3.31	2.72

The dependence of rate on acetal concentration has been determined by measuring the first order rate constants for NCIN disappearance for a wide range of acetal concentrations at 50 $\square$C. The pseudo-first order rate constants are found to increase (Table -2) linearly with the increase in [acetal].

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C. *Effect of Varying Solvent Composition On The Rate of Oxidation Of Acetal By NCIN*

$[X \square C_6H_4CH(OC_4H_9)_2] = 8.0 \square 10^{\square 2}$ M $[NCIN] = 6.0 \square\square 10^{\square 3}$ M

$[NaClO_4. H_2O] = 1.0 \square\square 10^{\square 1}$ M

TABLE-3

CH3CN – H2O% (v/v)	D^*	$k_1 \square\square 10^4 (s^{\square 1})$			
		p-chlorobenzaldehyde di-n-butyl acetal	*p*-nitrobenzaldehyde di-n-butyl acetal	*m*-chlorobenzaldehyde di-n-butyl acetal	*m*-nitrobenzaldehyde di-n-butyl acetal
50-50	36.74	1.72	1.23	1.32	1.63
60-40	36.36	2.62	1.85	2.20	2.27
70-30	35.98	3.62	3.28	3.59	3.05
80-20	35.60	5.06	5.01	4.87	3.98

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).

D. *Effect of Variation Of Ionic Strength For The Oxidation Of Acetal By NCIN*

$[X \square C_6H_4CH(OC_4H_9)_2] = 8.0 \square 10^{\square 2}$ M $[NCIN] = 6.0 \square\square 10^{\square 3}$ M

Solvent (v/v) = 90% $CH_3CN \square\square 10\%$ H_2O

TABLE-4

[NaClO4. H2O] $\square\square 10$ (M)	$k_1 \square\square 10^4 (s^{\square 1})$			
	p-chlorobenzaldehyde di-n-butyl acetal	*p*-nitrobenzaldehyde di-n-butyl acetal	*m*-chlorobenzaldehyde di-n-butyl acetal	*m*-nitrobenzaldehyde di-n-butyl acetal
1.0	3.62	1.23	2.20	1.63
2.0	4.04	3.89	3.60	2.68
3.0	7.67	5.14	4.21	4.74
4.0	9.97	7.06	5.95	5.87

The influence of variation of ionic strength on the rate of oxidation has been studied by varying the concentrations of [NaClO4.H2O]. The reaction rate increases with the increase in ionic strength of the medium (Table-4).

E. *Effect Of Temperature On The Rate Of Oxidation Of Acetal By Ncin*

$[X \square C6H4 CH(OC_4H_9)_2 = 8.0 \square 10^{\square 2}$ M $[NaClO4.H2O] = 1.0 \square\square 10^{\square 1}$ M

$[NCIN] = 6.0 \square\square 10^{\square 3}$ M   Solvent (v/v) = 90% $CH_3CN \square\square 10\%$ H_2O

TABLE-5

TEMPERATURE(K)	$k_1 \square\square 10^4 (s^{\square 1})$			
	p-chlorobenzaldehyde di-n-butyl acetal	*p*-nitrobenzaldehyde di-n-butyl acetal	*m*-chlorobenzaldehyde di-n-butyl acetal	*m*-nitrobenzaldehyde di-n-butyl acetal
318	2.54	0.76	1.51	0.87
323	4.53	1.54	2.75	2.04
328	8.32	3.89	5.01	4.37
333	14.13	7.76	4.37	8.73

The oxidation of aromatic diethers has been studied at four different temperatures □318 K □□333 K□. The temperature dependence on the rates of oxidation is determined by plotting log k2 against reciprocal of temperature. The second order rate constants at different temperatures at constant ionic strength for the NCIN oxidation of acetals under investigation are recorded in Table -5.

IV.   MECHANISM AND RATE LAW

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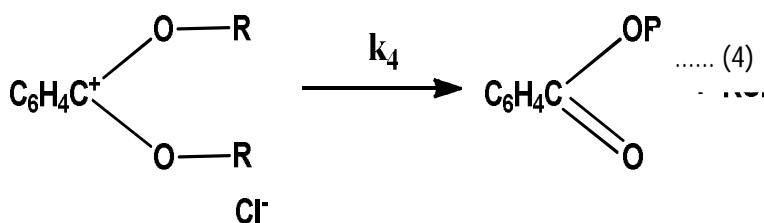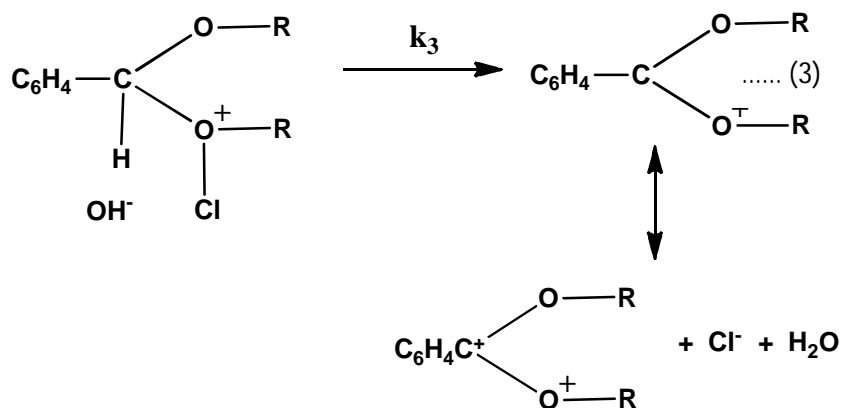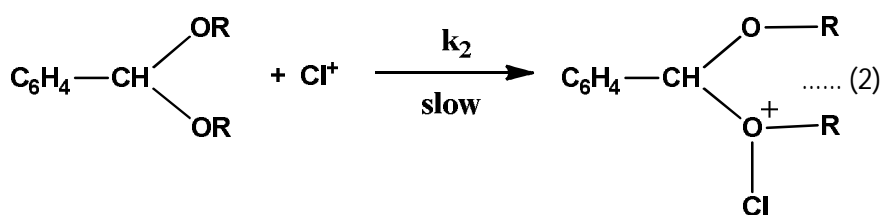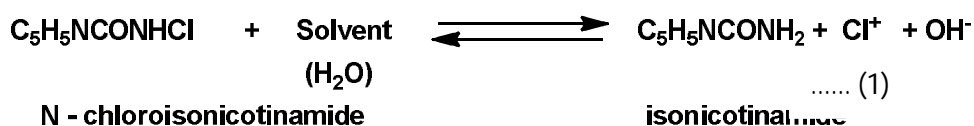
Assuming Cl^+ as the effective oxidizing species, the **rate law** is given as follows :

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

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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