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Research Article

KINETICS AND MECHANISM OF OXIDATION OF BENZALDEHYDE DI-n-BUTYL ACETAL BY N-CHLOROISONICOTINAMIDE IN AQUEOUS ACETONITRILE MEDIUM

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ABSTRACT

N-halo compound, N-chloroisonicotinamide (NCIN), in aqueous acetonitrile medium have been investigated. 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. 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.

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. 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. Acetals play a vital role in bio-organic research in exploring biological activities. The present work reports the kinetics of oxidation of benzaldehyde di-n-butyl acetal by NCIN and evaluates the reaction constants.

Experimental Section

NCIN was prepared and the purity was checked iodometrically. All other chemicals were of AnalaR grade. The acetals name benzaldehyde di-n-butyl acetal prepared by the standard methods. Kinetic runs were carried out under pseudo-first order conditions ([XC6H4CH(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 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)

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

[Acetal] = 8.0×10^{-3}M [NCIN] = 6.0×10^{-3}M
Solvent (v/v) = 90% CH_3CN – 10% H_2O [$NaClO_4.H_2O$] = 1.0×10^{-1} M

Table 1

[NCIN] $\times 10^3$ (M)	$k_1 \times 10^4$ (s^{-1})
1.0	4.91
2.0	4.92
3.0	5.09
4.0	5.24

The rate studies are carried out at different initial concentrations of NCIN. It is seen that the first-order rate constant remain constant with the increase in the initial concentration of the oxidant.

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Effect of [substrate] on the rate of oxidation of acetal by NCIN

[NCIN] = 6.0×10^{-3} M [NaClO4.H2O] = 1.0×10^{-1} M
Solvent (v/v) = 90% CH_3CN – 10% H_2O

Table 2

[X–C6H4 CH(OC4H9)2] $\times 10^4$ (s^{-1})	k1 $\times 10^4$ (s^{-1})
1.0	4.07
2.0	5.23
3.0	6.54
4.0	8.13

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 °C.

Effect of varying solvent composition on the rate of oxidation of acetal by NCIN

[X–C_6H_4 $CH(OC_4H_9)_2$] = 8.0×10^{-2} M [NCIN] = 6.0×10^{-3} M
[$NaClO_4$. H_2O] = 1.0×10^{-1} M

Table 3

CH3CN – H2O% (v/v)	D*	$k_1 \times 10^4$ (s^{-1})
50-50	36.74	2.60
60-40	36.36	3.63
80-20	35.98	5.23
90-10	35.60	7.18

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.

Effect of variation of ionic strength for the oxidation of acetal by NCIN

[X–C_6H_4 $CH(OC_4H_9)_2$] = 8.0×10^{-2} M [NCIN] = 6.0×10^{-3} M
Solvent (v/v) = 90% CH_3CN – 10% H_2O

Table 4

[NCIN] $\times 10^3$ (M)	$k_1 \times 10^4$ (s^{-1})
1.0	4.91
2.0	4.92
3.0	5.09
4.0	5.24

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.

Effect of temperature on the rate of oxidation of acetal by NCIN

[X–C6H4 $CH(OC_4H_9)_2$ = 8.0×10^{-2} M [NaClO4.H2O] = 1.0×10^{-1} M
[NCIN] = 6.0×10^{-3} M Solvent (v/v) = 90% CH_3CN – 10% H_2O

Table 5

Temperature(K)	$k_1 \times 10^4$(s^{-1})
318	4.74
323	6.54
328	10.72
333	16.72

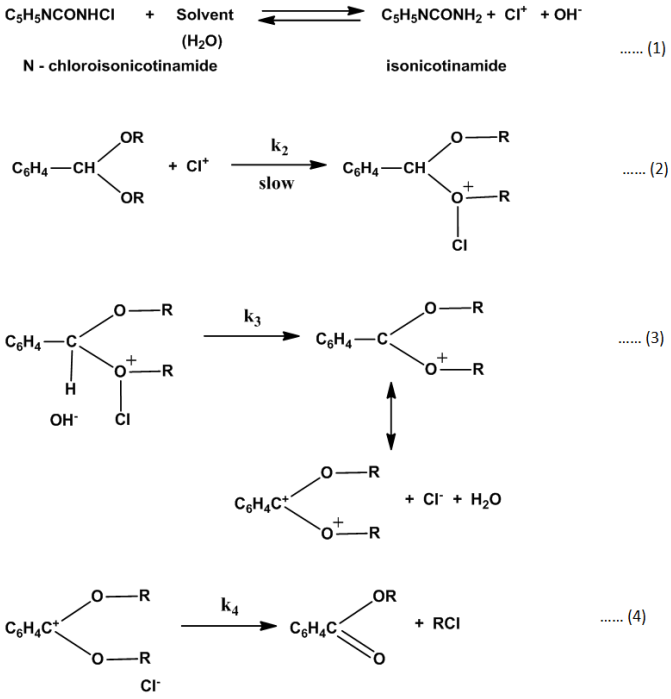
The oxidation of ac has been studied acetal at four different temperatures $k_1 \times 10^4$(s^{-1}). The second order rate constants at different temperatures at constant ionic strength for the NCIN oxidation of acetal under investigation are recorded in Table-5.

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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