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SYNTHETIC UTILITY OF N-CHLOROSUCCINIMIDE IN THE OXIDATION OF ISATIN IN AQUEOUS ACETONITRILE MEDIUM – A KINETIC AND MECHANISTIC STUDY

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ABSTRACT

The oxidation kinetics of isatin by N-chlorosuccinimide (NCS) in acetonitrile has been investigated. The reaction follows first order kinetics with respect to [oxidant] and [H^+] and fractional order dependence on [substrate]. A decrease in the dielectric constant of the medium increases the rate. Chloride ions positively influence the rate of the reaction. The variation of ionic strength has no significance effect on the reaction rate and addition of succinamide has retarding effect. Activation parameters of the reactions has been determined by studying the reaction at different temperature (40-55°C). Based on the kinetic results and product analysis, a probable mechanism has been proposed for the oxidation of isatin by NCS.

Keywords: kinetics, oxidation, isatinand N-chlorosuccinimide

INTRODUCTION

The chemistry of reactions N-halo compounds is of great synthetic importance. The versatile nature of N-halo compounds is due to their ability to act as sources of halonium ions, hypohalite species and nitrogen anions **[1-5]**. They have been widely used as oxidizing and halogenating reagents in organic compounds. Isatin, associated with amino heterocycles, have been used as pigments and dyes, since they are well known color reagents for amino acids **[6-7]**. Isatin is used largely in the manufacture of vat dyes and also as an analytical reagent for the estimation of a number of industrially important compounds. The synthetic versatility of isatin has been evolved from the interest in the biological and pharmaceutical properties of its derivatives **[8-11]**.

N-chlorosuccinimide is an adaptable reagent and its magnitude is not limited to chlorination and oxidation. It catalyzes many chemical reactions, including halocylisation, formation of heterocyclic systems, formation of new C-C bonds, rearrangements and functional group transformations.

EXPERIMENTAL METHODS

Conductivity water was used in all experiments. It was obtained by purifying water with shift ion interchange and then distilling with alkaline permanganate from an all glass apparatus.

Potassium iodide, starch, sodium thiosulphate, sodium chloride, perchloric acid and acetonitrile exist in analytically pure state and were used in the absence of further distilation.

KINETIC METHODS

PREPARATION OF STANDARD SOLUTION

The standard stock solution of NCS was prepared by dissolving imperative quantity of it in water. The isatin solution was prepared in acetonitrile.

Kinetic measurements

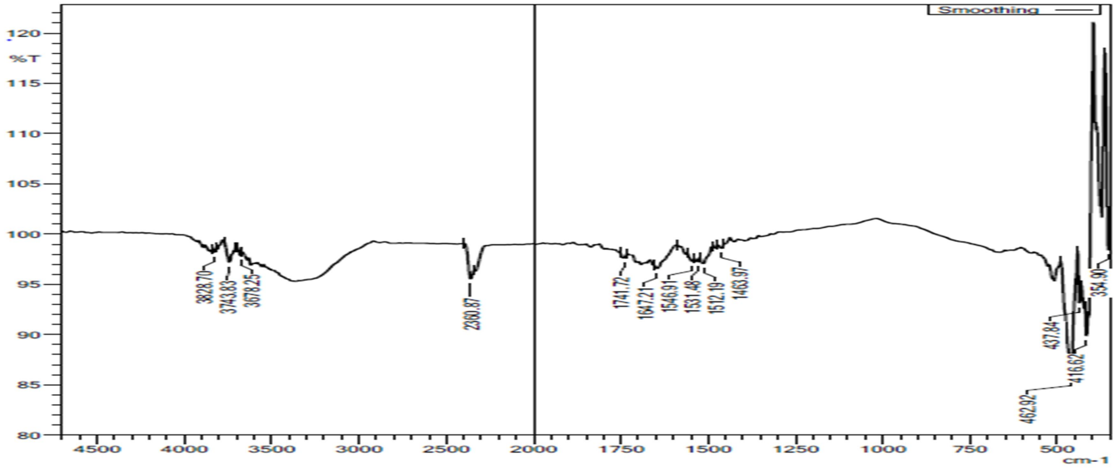
In a habitual experiment, the needed quantities of isatin, acetonitrile, perchloric acid, water mixture were pipetted out in a clean dried reaction bottle, kept in a thermostat, set at the desired temperature at 318K. The reaction was started by pipetting out the essential quantity of NCS solution, which was previously thermostated for about quarter of an hour. The total volume of the reaction mixture was consistently 25 ml. For every five minutes, the reaction passage was travel behind potentiometrically.

Investigation of stoichiometry

For the stoichiometry of the reaction, [NCS] was taken in excess over the [substrate] and the reaction is permitted for execution. Since the strength of isatin taken was less balanced to that of [NCS], all the isatin would have been entirely reacted leaving behind the unreacted NCS. Approximation of passive [NCS] showed that one mole of the isatin consumed one mole of NCS.

Product study

For product study, the substrate was taken in more contrast to strength of oxidant. The reaction mixture was kept aside at 45°C for 5 hours for the execution of the reaction. After that the residual mixture was streamed into a separating funnel. Solvent ether was added and shaken well. The ether layer was separated and the product was analysed. Product analysis shows the presence of anthranilic acid, the major product which is confirmed by IR.



Graph 1: FT-IR Spectrum of the Product

RESULTS AND DISCUSSION

In the present study, isatin has been selected to study the kinetics and mechanism of oxidation by NCS. The rate of the reaction was estimated by following the extinction of NCS potentiometrically in acetonitrile medium. The kinetic study of oxidation had been switched out in the presence of NaCl and $HClO_4$.

OXIDATION OF ISATIN WITH NCS

EFFECT OF VARIATION OF NCS CONCENTRATION:

The oxidation was carried out with different initial concentration of NCS and the results are given in **(Table 1) & (Figure-1)**.

$[C_8H_5NO_2]=2.0\times10^{-2}$ M $[HClO_4] = 1.0\times10^{-1}$ M [NaCl]= 1.0×10^{-1} M

Temperature = 318 K solvent=70% Actonitonitrile-30% water

It is seen that the first order rate constant increase with the increase in initial concentration of the oxidant. In each kinetic run, the reaction shows no deviation from the first order plot of log[NCS] Vs time **(Figure 1)**.

EFFECT OF VARIATION OF SUBSTRATE CONCENTRATION

[NCS]=3.0×10^{-3} M $[HClO_4] =1.0\times10^{-1}$ M [NaCl]= 1.0×10^{-1} M

Temperature=318K

Solvent = 70% Acetonitrile - 30% water

A plot of $\log k_{obs}$ Vs log [substrate] is linear with slope indicating fractional order dependence on isatin concentration **(Table 1 & Figure 2)**.

EFFECT OF VARIATION OF $HClO_4$ CONCENTRATION:

The oxidation was carried out with different initial concentration of $HClO_4$ and the results are given in **(Table 1) & (Figure 3)**.

$[C_8H_5NO_2] = 2.0\times10^{-2}$ M
$[NCS] = 3.0\times10^{-3}$ M $[NaCl] = 1.0\times10^{-1}$ M

Temperature = 318 K
Solvent = 70% Acetonitrile -30% Water

The rate of reaction increase with increase in the initial concentration of $HClO_4$. The plot of log kobs Vs log $[HClO_4]$ with unit slope indicates the first order dependence of rate on $[HClO_4]$.

EFFECT OF VARIATION OF NaCl CONCENTRATION:

The oxidation was carried out with different initial concentrations of NaCl and the results are given in **(Table 1) & (Figure 4)**.

$[C_8H_5NO_2] = 2.0\times10^{-2}$ M

$[NCS] = 3.0\times10^{-3}$ M

Temperature = 318 K

Solvent =70% Acetonitrile -30% Water

The rate of reaction increase with increase in the initial concentration of NaCl. A plot of $\log k_{obs}$ Vs log [NaCl] is linear **(Figure 4)**.

EFFECT OF SOLVENT POLARITY ON REACTION RATE

The influence of solvent dielectric constant on the reaction rate of oxidation of isatin with NCS has been studied in various solvent mixtures of acetonitrile and water. The rate of oxidation increases with decrease in dielectric constant at the medium.

EFFECT OF TEMPERATURE ON REACTION RATE:

The oxidation of isatin was carried out in the temperature range 313-328 K. The results are shown in **Table 2**. The energy of activation (Ea = 74.06 $KJmol^{-1}$), enthalpy of activation ($\Delta H^{\neq}$= 70.65 KJ mol^{-1}) ,entropy of activation ($\Delta S^{\neq}$ = -26.92 KJ mol^{-1}) free energy of activation($\Delta G^{\neq}$ = 83.49 KJ mol^{-1}) and log A (9.13) have been calculated.

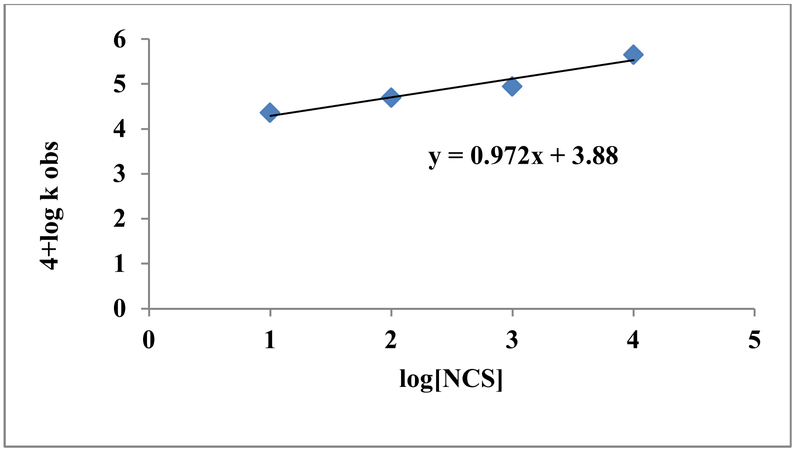


Figure 1: Plot of log [NCS] Vs log k_{obs}

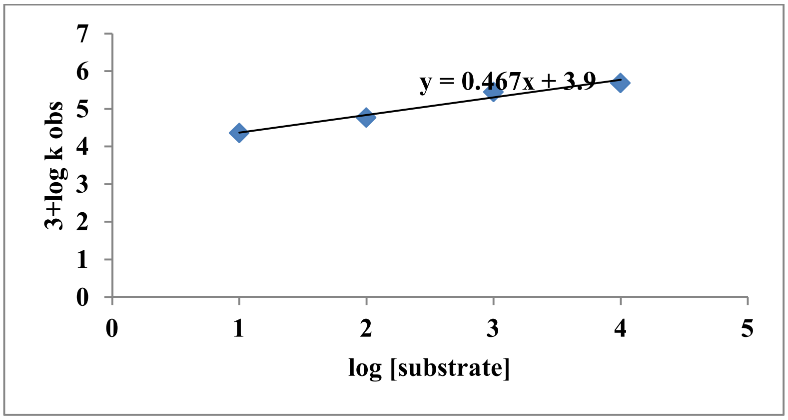


Figure 2: Plot of log[substrate]Vs log k_{obs}

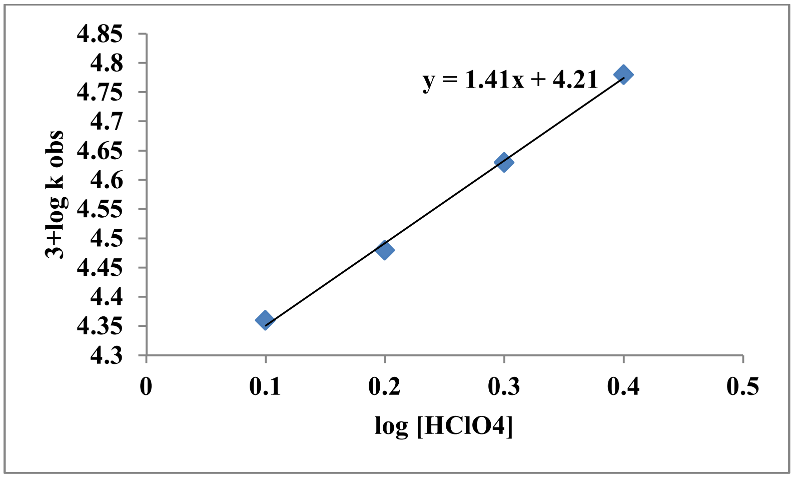


Figure 3: Plot of log[$HClO_4$]Vs log k_{obs}

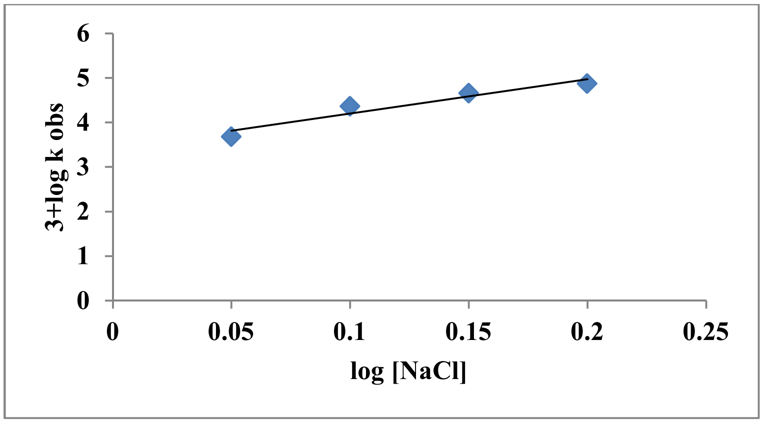


Figure 4: Plot of log [NaCl] Vs log k_{obs}

Table 1: Effect of variation of [NCS], [isatin], [$HClO_4$], [NaCl] and [ACN] on the reaction rate at 318K

[NCS]x 10^3M	[Isatin]x 10^2M	[$HClO_4$]x10^1M	[NaCl]x10^1M	ACN % (v/v)	k 10^4 (S^{-1})
1.0	1.0	0.10	0.10	70-30	2.89
2.0	1.0	0.10	0.10	70-30	3.52
3.0	1.0	0.10	0.10	70-30	4.36
4.0	1.0	0.10	0.10	70-30	5.65
3.0	1.0	0.10	0.10	70-30	4.36
3.0	2.0	0.10	0.10	70-30	4.77
3.0	3.0	0.10	0.10	70-30	5.45
3.0	4.0	0.10	0.10	70-30	5.69
3.0	1.0	0.10	0.10	70-30	4.36
3.0	1.0	0.20	0.10	70-30	4.48
3.0	1.0	0.30	0.10	70-30	4.63
3.0	1.0	0.40	0.10	70-30	4.78
3.0	1.0	0.10	0.05	70-30	3.68
3.0	1.0	0.10	0.10	70-30	4.36
3.0	1.0	0.10	0.15	70-30	4.66
3.0	1.0	0.10	0.20	70-30	6.87
3.0	1.0	0.10	0.10	50-50	2.78
3.0	1.0	0.10	0.10	60-40	3.49
3.0	1.0	0.10	0.10	70-30	4.36
3.0	1.0	0.10	0.10	80-20	5.87

Table 2

[Temperature]	$k_{obs}\times10^4s^{-1}$
313	3.67
318	4.36
323	5.87
328	7.59

MECHANISM

Under the experimental conditions, the possible oxidizing species are Cl_2, HOCl and $NCSH^+$ in aqueous solution. If $NCSH^+$ is the active oxidant, the reaction must show hydrogen ion catalysis only **[15-16]**. Since both hydrogen and chlorine ions are found to catalyze the reaction in the present case, molecular chlorine has been assumed to act as the effective oxidant **[17-18]**.

$$NCS+H^{+}+Cl^{-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH+Cl_2 \qquad \longrightarrow \qquad (1)$$

$$Cl_2+S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Complex \qquad \longrightarrow (2)$$

$$Complex \xrightarrow{k_3} Product \qquad \longrightarrow (3)$$

Rate $=k_3[Complex]$

Applying steady-state approximation to the molecular chlorine and the complex, the following rate law deduced.

$$k_1[NCS]\,[H^{+}]\,[Cl^{-}]-k_{-1}\,[SH][Cl_2]-k_2\,[Cl_2]\,[S]=0 \qquad \longrightarrow (4)$$

$$K_1[NCS]\,[H^{+}]\,[Cl^{-}] \longrightarrow [Cl_2]\,\{k_{-1}[SH]+k_2[S]\} \qquad \longrightarrow (5)$$

$$[Cl_2]=\frac{k1[NCS]\,[H+]\,[Cl\ \ ]}{k-1\,[SH]+k2[S]} \qquad \longrightarrow \qquad (6)$$

$$K_2[Cl_2]\,[S]-k_2[complex]-k_3\,[complex]$$

$$K_2\,[Cl_2]\,[S]=[Complex]\,\{k_{-2}+k_3\}$$

$$[Complex]=\frac{k2\,[Cl2]\,[S]}{k-2+k3}$$

$$Rate=\frac{k3k2[Cl2][S]}{k-2+k3}$$

$$Rate\ =\frac{k3k2k1\,[NCS]\,[H+]\,[Cl-]\,[S]}{k-2\ +\ k3\,\{k-1[SH]\ +\ k2\,[S]\}}$$

The rate law shows that the reaction follows first order kinetics with respect to each [NCS] and [$HClO_4$].

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