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Study of oxidation of dyes by N-chlorosuccinimide in aqueous acetic acid medium: A kinetic and mechanistic

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Abstract

Kinetics of oxidation of Dyes by N-Chlorosuccinamide(NCS) in acetic acid medium has been done in the presence of hydrochloric acid. The reaction follows first order kinetics with respect to both [NCS], [Substrate] and [HCl]. Increases in ionic strength increases the rate and addition of the reaction product succinamide has a slight retarding effect on the reaction rate. Increase in the dielectric constant of the medium decreases the rate. Activation parameters have been evaluated from Arrhenius plot by studying the reaction at different temperature [40-55 ^{o}C] and oxidation products are identified. A most probable reaction mechanism is proposed and an appropriate rate law is deduced to account for the observed kinetic data.

Keywords: Kinetics, dyes, N-Chlorosuccinimide, mechanism and oxidation

Introduction

A dye is a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. Both dyes and pigments are colored because they absorb only some wavelengths of visible light. Dyes are usually soluble in water whereas pigments are insoluble. Some dyes can be rendered insoluble with the addition of salt to produce a lake pigment.

Many dyes are organic compounds. These may be natural (from plant sources) or synthetic. Dyes are basic raw materials of various industries and generate a considerable amount of polluted waste water. Without any treatment direct discharge of this polluted contaminants can causes serious environmental pollution by imparting intensive color and their toxicity to the aquatic environment. Due to their synthetic origin and complex aromatic structure dyes become more difficult to degrade by standard biological methods.

In the present work, the kinetic study for the oxidation of dyes with NCS in an aqueous medium was performed. The effects of the concentration of dyes, NCS, temperature and salt effect were also observed.

Materials and Methods

Commercial Sample of Materials

Glacial acetic acid, N-chlorosuccinimide, sodium sulphate,sodium chloride, hydrochloric acid, succinimide were used as such without purification.

Kinetic Methods

All the standard flasks and the reaction bottle were of Pyrex glass with ground joint stoppers. The volumetric apparatus, the pipettes, a burette and standard flasks were standardized by usual methods

An electrically operated thermostat which maintained temperature accurately was used. The bath liquid was water and it was covered with a layer of thermocole bite to minimize heat and water loss due to radiation.

Preparation of Standard Solution

The standard stock solution of NCS was prepared by dissolving the required quantity of it in water and standardized by titrating against standard sodium thiosulphate solution iodometrically. This NCS solution was found to be invariant in its strength over a period of three months. The dyes were prepared by dissolving required quantity of them in acetic acid- H_2O mixture.

Rate Measurements

In a typical experiment, the required quantities of the substrate, sodium chloride, hydrochloric acid, sodium sulphate and acetic acid-water mixture were pipetted out in a double walled beaker provided with an inlet and outlet for circulating water from the thermostat set at the desired temperature and solution were kept in the beaker for nearly an hour to attain the desired temperature. The reaction was started by pipetting out the required quantity of NCS solution. Which had also been thermostated for nearly half an hour. The total volume reaction mixture was always 25ml.

A stop watch was started when half the amount of oxidant was added. The reaction was followed by setting up a cell [Pt$^+$ / SH – NCS // $^-$SCE] made up of the reaction mixture into which the platinum electrode and reference electrode (SCE) were dipped. The emf of the cell was measured periodically using Equip-Tronics, digital potentiometer while the reaction was continuously stirred using a magnetic stirrer.

When the reaction was followed potentiometrically and iodimetrically both the methods gave the same values. All first-order rate constants were expressed in s-1.

Investigation of Stoichiometry

The stoichiometry of the reaction [NCS]: [dye] was determined by taking excess of NCS over the substrate and allowing the reaction for completion.Since the concentration of the substrate taken was less compared to that of NCS, all the substrate taken would have been completely reacted leaving behind the unreacted NCS, the concentration of which was estimated by iodometry. Estimation of unreacted NCS showed that one mole of substrate consumed one mole of NCS.

Results and Discussion

In the present study, crystal violet, methyl violet, methyl orange, methylene blue and acid red have been chosen to study the kinetics and mechanism of oxidation by NCS. The rate of the reaction was measured by following the disappearance of NCS potentiometrically in acetic acid medium. The kinetic study of oxidation had been carried out in the presence of HCl and Na_2SO_4.

Oxidation of Substrate 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.

Table 1: Variation of kobs with [NCS]

[NCS]× 10^3 M	kobs × 10^4 s^{-1}				
	Methyl violet	Methyl orange	Methylene blue	Acid red	Crystal violet
1.0	2.58	2.55	3.14	4.06	3.20
2.0	2.60	2.62	3.20	4.10	3.26
3.0	2.69	2.71	3.25	4.17	3.32
4.0	2.72	2.79	3.31	4.28	3.39

[Crystal violet] = 2.0×10^{-2} M [HCl] = 1.0×10^{-1} M
Temperature = 303K [NaCl] = 1.0×10^{-1} M
Solvent =70% CH3COOH-30% H2O(v/v) [Na2SO4] = 1.0×10^{-1} M

It is seen that the first-order rate constant remain constant with the increase in the initial concentration of the oxidant. But in each kinetic run, the reaction shows no deviation from the first plot. Hence it must be stressed that the reaction is first –order with respect to oxidant at every one of these concentration.

Effect of Variation of Substrate Concentration

The oxidation was carried out with different initial concentration of substrate. The pseudo first order rate constants increases with change in substrate concentration. It is found that the reaction follows first order kinetics with respect to substrate.

Table 2: Variation of kobs with [substrate]

[S] × 10^3 M	kobs × 10^4 s^{-1}				
	Methyl violet	Methyl orange	Methylene blue	Acid red	Crystal violet
1.0	4.29	3.45	3.14	4.04	2.26
2.0	4.90	4.15	4.16	5.48	4.03
3.0	5.25	5.67	5.36	6.22	6.48
4.0	6.34	6.21	6.12	7.33	7.98

[NCS] = 3.0×10^{-3} M [HCl] = 1.0×10^{-1} M
Temperature = 303K [NaCl] = 1.0×10^{-1} M
Solvent = 70% CH3COOH-30% H2O (v/v) [Na2SO4]= 1.0×10^{-1} M

Effect of variation of HCL concentration

The oxidation was carried out with different initial concentration of HCl at constant [substrate
] and [NCS] and the results are given in Table-3. The reaction rate increases with the increase in [HCl].

Table 3: Variation of kobs with [HCl]

[HCl] M	kobs × 10^4 s^{-1}				
	Methyl violet	Methyl orange	Methylene blue	Acid red	Crystal violet
0.5	2.81	2.04	3.23	3.23	2.04
1.0	4.56	3.28	4.48	5.47	3.26
1.5	5.33	4.29	5.26	6.85	5.32
2.0	6.22	5.46	5.98	8.23	6.11

[Substrate] = 2.0×10^{-2} M Solvent =70% CH3COOH-30% H2O (v/v)
Temperature = 303K [NCS] = 3.0×10^{-3} M
[NaCl] = 1.0×10^{-1} M [Na_2SO_4] = 1.0×10^{-1} M

Effect of variation of na$_2$so$_4$ concentration

The oxidation was carried out with different initial concentration of Na_2SO_4 and the results are given in Table-4

Table 4: Variation of kobs with [Na2SO4]

[Na2SO4] M	kobs × 10^4 s^{-1}				
	Methyl violet	Methyl orange	Methylene blue	Acid red	Crystal violet
1.0	3.89	4.55	3.12	3.78	3.12
2.0	3.91	4.58	3.19	3.82	3.42
3.0	3.95	4.62	3.22	3.85	3.61
4.0	4.02	4.67	3.25	3.88	3.98

[Crystal violet] = 2.0×10^{-2} M Solvent = 70% CH3COOH-30% H2O (v/v)
Temperature = 303K [NCS] = 3.0×10^{-3} M
[HCl] = 1.0×10^{-1} M [NaCl] = 1.0×10^{-1} M

Effect of solvent polarity on reaction rate

The influence of solvent dielectric constant on the reaction rate of oxidation of substrate with NCS has been studied in various solvent mixtures of acetic acid and water. The rate of oxidation increases with decreasing dielectic constant at the medium (Table-6).

Table 6: Variation of kobs with solvent polarity

CH3COOH-H2O %	D*	kobs × 10^4 s^{-1}				
		Methyl violet	Methyl orange	Methylene blue	Acid red	Crystal violet
50-50	37.5	2.99	2.53	3.29	3.17	2.39
60-40	31.5	3.63	2.89	3.73	3.81	3.27
70-30	27	4.47	3.28	4.48	5.47	4.18
80-20	20	5.53	4.26	5.61	7.99	5.87

[Crystal violet] = 2.0×10^{-2} M [HCl] = 1.0×10^{-1} M
Temperature = 303 K [NCS] = 3.0×10^{-3} M
[NaCl] = 1.0×10^{-1} M [Na_2SO_4] = 1.0×10^{-1} M

D*= Dielectic constant

The plot of kobs Vs 1/D is linear with positive slope. This may be an indication of the possible reaction between an ion and a dipole.

Effect of temperature on reaction rate

The oxidation of crystal violet was carried out in the temperature range of 313K-328K. The results are shown in Table-7. The Arrhenius plot of log kobs Vs 1/T. The energy of activation (Ea =62.322 kJ/mol), enthalpy of activation (ΔH# = 60.943kJ/mol), entropy of activation (ΔS# = -53.766kJ/mol), free energy of activation (ΔG# =78.344 kJ/mol) and log A = 6.1 have been calculated.

Table 7: Variation of kobs with temperature

Temperature K	kobs × 10^4 s^{-1}				
	Methyl violet	Methyl orange	Methylene blue	Acid red	Crystal violet
313	3.69	2.44	3.25	3.71	2.25
318	4.58	3.28	4.48	5.47	3.43
323	5.97	4.50	6.24	8.39	5.63
328	7.84	5.78	8.05	9.05	7.57

[Crystal violet] = 2.0×10^{-2} M [HCl] = 1.0×10^{-1} M
Solvent =70% CH3COOH-30% H2O (v/v) [NCS] = 3.0×10^{-3} M
[NaCl] = 1.0×10^{-1} M [Na2SO4] = 1.0×10^{-1} M

Mechanism

The active oxidizing species has to be identified before any mechanistic interpretation should be advanced. Under the experimental conditions, the observed first order dependence on the reaction rate NCS ruled out molecular chlorine as the reactive oxidizing species. If NCS is considered to be active species, it cannot rationalize the inverse dependence on the reaction rate succinimide. However negligible effect of ionic strength on the reaction rate rules out Cl_2 as active species. Taking into account all the experimental observations and the above facts in view, it is assumed that Cl2 is the effective oxidizing species in the present investigation. This retardation effect suggests the involvement of pre-equilibrium step in which succinimide is formed. The following mechanism is proposed for the oxidation of dyes by NCS.

$$\mathrm{NCS} + \mathrm{H}^+ + \mathrm{Cl}^- \xrightleftharpoons[K_{-1}]{K_1} \mathrm{SH} + \mathrm{Cl}_2$$

$$\mathrm{Cl}_2 + \mathrm{S} \xrightarrow{K_2} \mathrm{Complex}$$

$$K=\frac{K_1[\mathrm{NCS}][\mathrm{H}^+][\mathrm{Cl}^-]}{K_{-1}[\mathrm{SH}][\mathrm{Cl}_2]}$$

$$[\mathrm{Cl}_2]=\frac{K_1[\mathrm{NCS}][\mathrm{H}^+][\mathrm{Cl}^-]}{K_{-1}[\mathrm{SH}]}$$

$$\mathrm{Rate}=\frac{K_2[\mathrm{S}]K_1[\mathrm{NCS}][\mathrm{H}^+][\mathrm{Cl}^-]}{K_{-1}[\mathrm{SH}]}$$

Rate = K_2 [Cl_2] [S]

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

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