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KINETICS AND MECHANISM OF OXIDATIVE DECOLOURIZATION OF FOOD DYE SUNSET YELLOW BY TRICHLOROISOCYANURIC ACID IN AQUEOUS ACETIC ACID MEDIUM – A SPECTROPHOTOMETRIC APPROACH

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ABSTRACT

The kinetics of Oxidative decolourization of Food Dye Sunset yellow by Trichloroisocyanuric acid in aqueous acetic acid medium has been investigated spectrophotometically (λ_{max} = 482nm) at 303K. Kinetic runs were carried out pseudo first order condition in which large excess of [TCICA] compared with [Dye]. The reactions follow a fractional order dependence on [TCICA], first order dependence on [SY] and an inverse fractional order dependence on [H^+]. The effect of dielectric constant of the medium has been studied. HOCl have been proposed as reactive oxidizing species. A suitable mechanism consistent with the experimental results has been proposed.

KEYWORDS: Food Dye, azo dye, trichloroisocyanuric acid, oxidation, decolourization, kinetics.

INTRODUCTION

Variety of dyes used in food industries usually have a synthetic origin and multifaceted aromatic molecular structures which make them more stable and complicated to biodegraded.[1, 2] Predominantly azo dyes which contain one or more nitrogen to nitrogen double bonds (-N=N-) constitutes a significant portion that are widely used in industries to-day. Therefore azo dye effluents generated by food and dye industries is a main issue in decomposition of colours.[3] The release of the high coloured effluents contains azo dyes into the environment leads to health problems. The removal of dyes form effluents is effected by the development of physio-chemical methods such as adsorption, photo degradation and coagulation and biological methods. The above methods are expensive and complicated. In recent years oxidative decolourization of azo dyes has been focused much attention.[4-8] N-halo compounds have been extensively employed as halogenating and oxidizing agent for organic substrates. Also the widespread use of variety of N-halo compounds arises from the fact that they are good sources of positive halogen.[9-11] Among the large variety of N-halo compounds Trichloroisocyanuric Acid[TCICA]- 1, 3, 5- trichloro-1, 3, 5-triazine-2, 4, 6-(1H, 3H, 5H)-trione is found to be more versatile oxidizing and halogenating reagent and its kinetic and mechanistic aspects of many reactions have well documented.[12-15] The most important aim of the work was to promote the decolourization of food dyes by Trichloroisocyanuric acid [TCICA] in aqueous acetic acid medium have been investigated kinetically.[16] Here the results of the kinetics of oxidative decolourization of sunset yellow (SY) with Trichloroisocyanuric acid (TCICA) in aqueous acetic acid medium investigated spectrophotometrically have been reported.

Experimental

MATERIALS AND METHODS

Sunset Yellow (Analar) and Trichloroisocyanuric Acid (Aldrich, USA) were used as supplied. Doubly distilled water and purified acetic acid were used. Sulphuric acid (BDH/AR) was used as purchased.

Preparation of Standard Solutions: The required amount of Trichloroisocyanuric acid (TCICA) transferred into a 100ml standard measuring flask and made up with 50%(v/v) of acetic acid and water. Similarly the required amount of Sunset Yellow was weighed and transferred into a separate 100ml smf and made up with 50% (v/v) acetic acid and water. About 5.5 ml of H_2SO_4 acid pipette out into a 100ml smf and made up with distilled water for 2N concentration.

Instrument used: Systronic model-105- Spectrophotometer with quartz cuvettes.

Kinetic Measurement

Most of the experiments were carried out under the pseudo – first order condition by taking large excess of the TCICA. The Dye concentrations were estimating spectrophotometically.[7]

The course of the reaction was followed y pipetting out the reaction mixture into a clean cuvette, 100% transmission were taken for reaction mixture without dyes. The Optical Density (Absorbance) was measured with various time intervals (by reading accurate stop watch). The rate was evaluate from a plot of log (D_0/D_t) versus inverse of time, the rate constant being calculated from the slope and were reproducible ± 3 %(Fig.1).

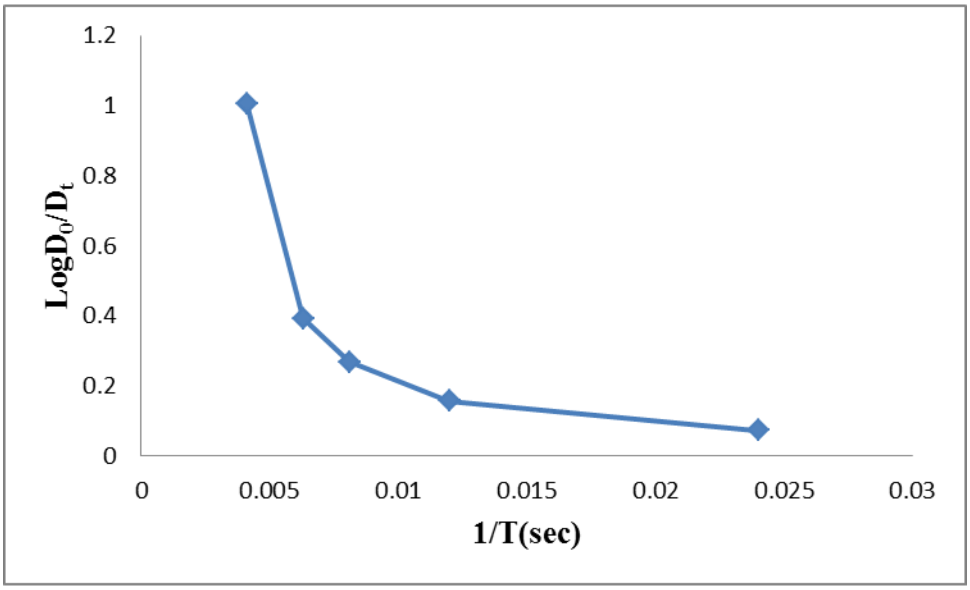


Fig 1: First Order Plot: Log (D_0/D_t) Vs Time^{-1}.

RESULT AND DISCUSSION

Trichloroisocyanuric acid has been successfully employed to bring the oxidative decolourization of food dyes in which HOCl is considered as the active oxidizing species under acidic condition. A study of the oxidative decolourization of food dye sunset yellow was undertaken. The reaction was followed spectrophotometrically by measuring the decrease in absorbance of sunset yellow at 482nm as a function of time.

Reaction Order

The reaction orders were determined for the slope of double logarithmic plots by the changing the concentrations of dye in t urn, while keeping others constant. The plot of log K_{obs} against log [SY] is linear (r = 0.9232) (Fig.2). It is observed that the order of the reaction is fractional with positive slope with respect to the oxidizing agent vide (Table 1).

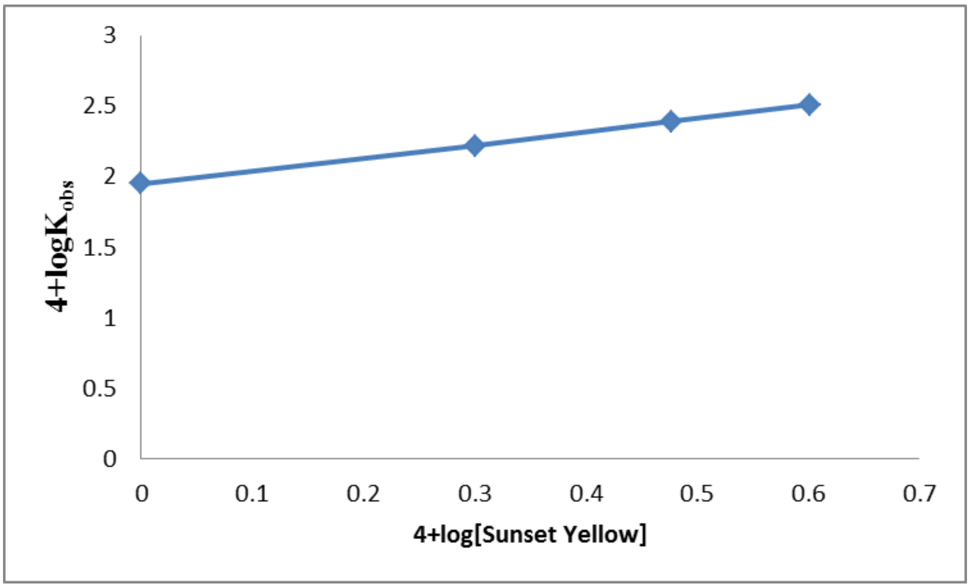


Fig 2: Dependence of Substrate: Log K_{obs} Vs Log [Sunset Yellow].

Table 1: Rate constant for the oxidative decolourization of Sunset Yellow by TCICA in aqueous acetic acid medium at 303K.

10^4[SY] Mol.dm^3	10^3[TCICA] Mol.dm^3	10^2[H_2SO_4] Mol.dm^3	CH_3COOH – H_2O%(v/v)	10^3 K_{obs} S^{-1}
1.0	1.0		50-50	8.83
1.0	2.0		50-50	9.46
1.0	3.0		50-50	10.09
1.0	4.0		50-50	10.72
1.0	1.0		50-50	8.83
2.0	1.0		50-50	16.59
3.0	1.0		50-50	24.35
4.0	1.0		50-50	32.11
1.0	1.0	1.0	50-50	5.29
1.0	1.0	2.0	50-50	4.38
1.0	1.0	3.0	50-50	3.04
1.0	1.0		75-25	5.39
1.0	1.0		50-50	8.83
1.0	1.0		25-75	9.98

Effect of added mineral acid

The effect of acid was studied by changing concentration of H_2SO_4 was added in the range of 0.01M to 0.03M. It was found that the rate was affected by the change shown in Table 1. The plot of $\log K_{obs}$ Vs $\log[H^+]$ is linear with negative slope indicating inverse fractional order dependence on $[H^+]$ (Fig.3).

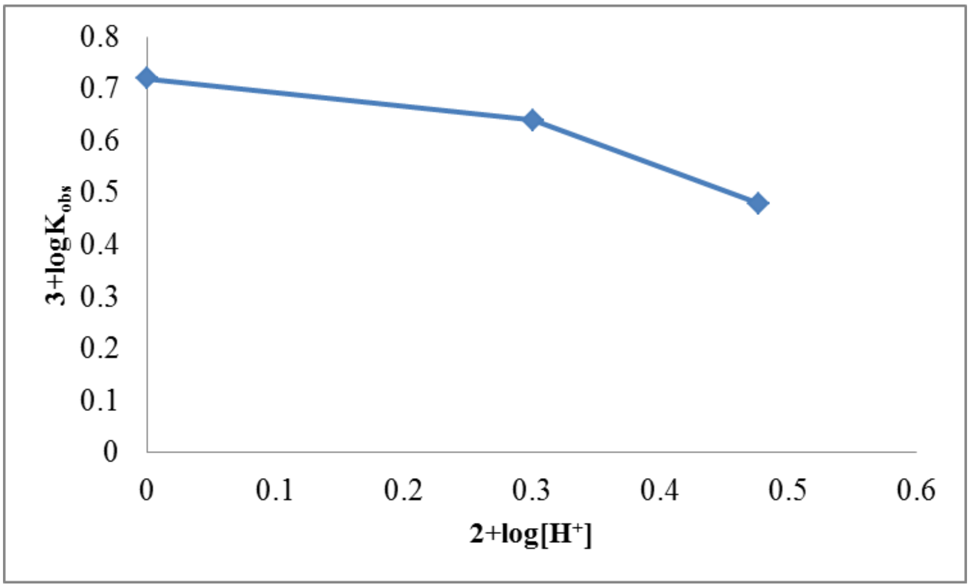


Fig 3: Effect of Added Mineral acid: LogK$_{obs}$ Vs Log[H$^+$].

Effect of solvent composition

The effect of changing solvent composition on reaction was studied by varying the concentration of acetic acid from 25 – 75%. The pseudo first order increases with decrease acetic acid content of the solvent mixture (Table 1). A plot of logK$_{obs}$ against composition of H_2O is linear with positive slope of nearing to unity (Fig.4).

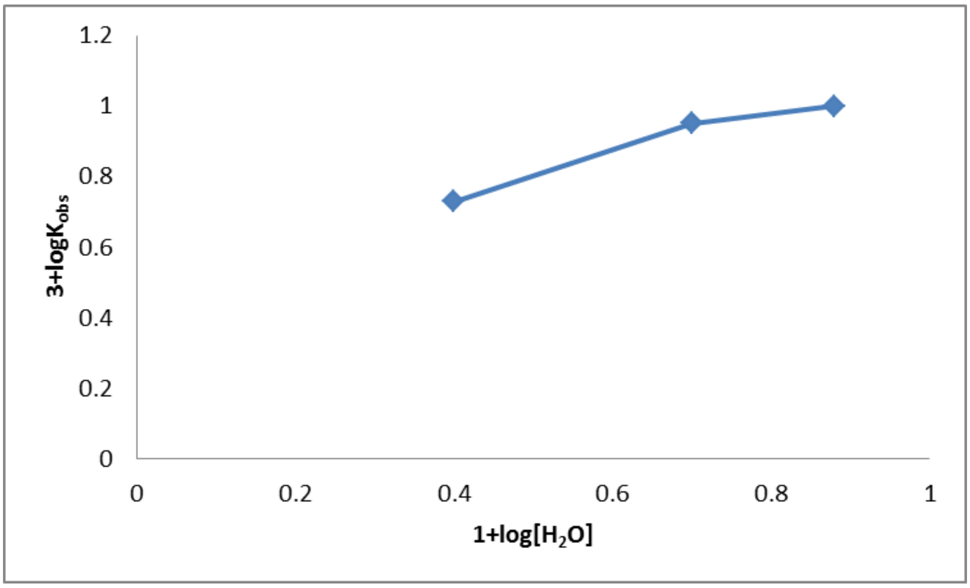
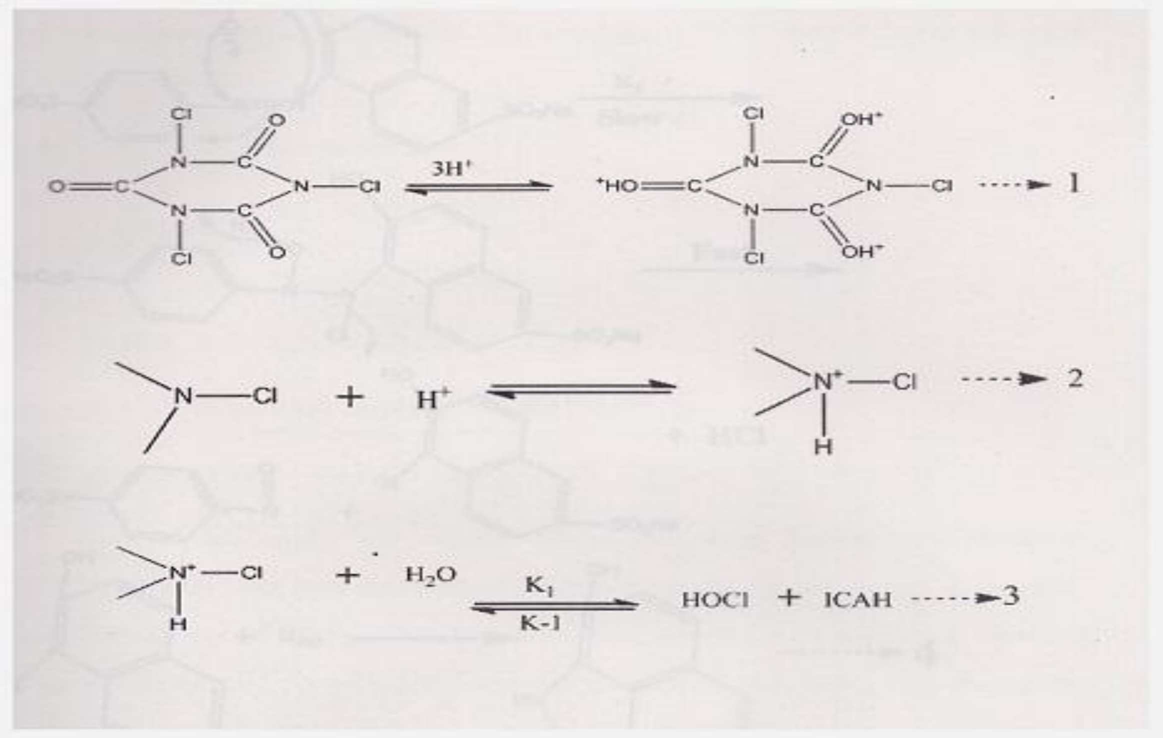


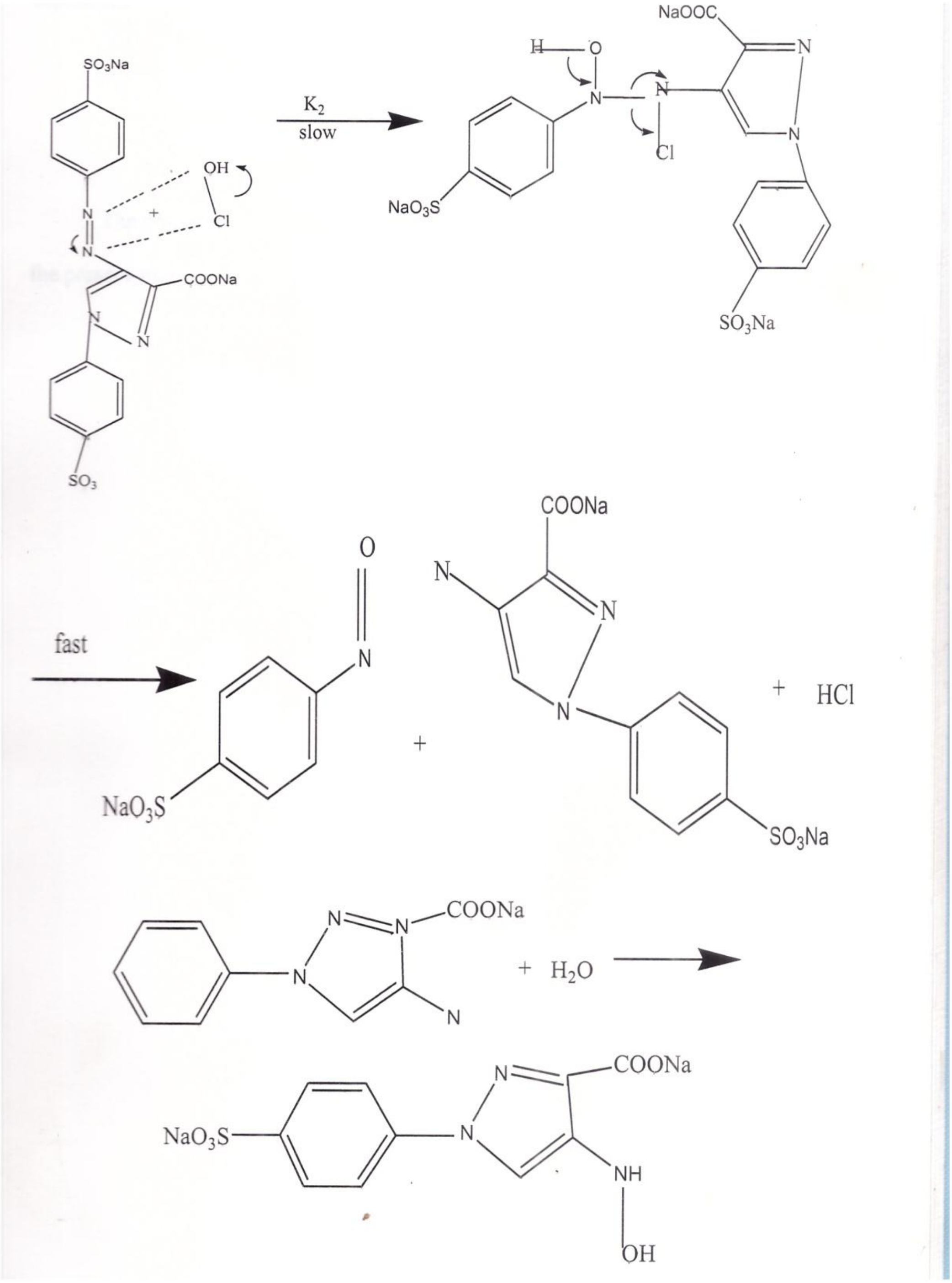
Fig 4: Effect of Solvent Composition: LogK$_{obs}$ Vs Log[H$_2$O].

Mechanism of Reaction

It is clear from the literature[14, 16] that the probable reactive species of TCICA in acid medium is HOCl. The reaction is fractional order in [TCICA], first order in [SY] and an inverse fractional order in [H^+]. The enhanced effect was observed of dielectric constant of the medium on the rate of oxidative decolourization. In solvent medium employed the TCICA exists in the following equilibrium.



The solvent effect does point out that the reaction with unprotonated dye should be more predominant. Based on the earlier kinetic work on oxidation with N-halo compounds one can reasonably suggest that the most likely oxidizing species is HOCl under acidic condition. If the slow reaction can be traced as interaction of HOCl and dye molecule in which the azo group –N=N- is involved and this –N=N- bond break with transfer of electrons. A cyclic transition state is responsible for the slow step in the present case. The following mechanism can be proposed for t he oxidative decolourization of Sunset Yellow for which rate law can be derived.



Rate = K_2[HOCl][SY]……………………………….(4)

Scheme – 1

The concentration of the HOCl in the above rate equation may be calculated as follows. On assumption that all the TCICA is reacting as $TCIH^+$

[HOCl] = $K_1[TCIH^+][H_2O] / K_{-1}[ICAH]$

= $K_1[TCIH^+][H_2O] / K_{-1}[ICA]\,[H^+]$

Rate = $K_2\,[SY]\,K_1[TCIH^+][H_2O] / K_{-1}[ICA]\,[H^+]$ ……………………..(5)

The proposed mechanism is consistent with all the experimental data obtained in the present investigation.

CONCLUSION

In the present Investigation optimum conditions for the easy oxidative decolourization of food dye Sunset Yellow with TCICA in aqueous acetic acid medium have been obtained.

The results of the kinetic investigation of the oxidative decolourization of food dye Sunset Yellow by TCICA by spectrophotometric methods by measuring absorbance at 482nm are presented. The kinetic picture revels that fractional order depends on TCICA. A first order dependence on the food dye and inverse fractional order dependence on $[H^+]$. There is positive dependence on $[H_2O]$ dielectric constant of the medium. Thus, it may be concluded that the reaction between TCICA and food dye proceeds by rapid formation of cyclic transition state formed between HOCl generated by $TCIH^+$, unprotonated food dye which then reacts in slow steps with breaking of azo group –N=N- bond of food dye with transfer of electrons. Therefore, this method is a simple and well designed can be implemented for treating industrial waste water containing sunset yellow to decrease the toxicity caused by this dye.

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