Kinetics and Mechanism of Oxidative Decolourization of Food dyes Tartrazine and Ponceou4R by Trichloroisocyanuric acid in Aqueous Acetic acid Medium

S.Manivannan[1]* R.Karthikeyan[1] and M.Muthubharathi[1]

[1]Dr.Ambedkar Government Arts College, Vyasarpadi, Chennai-600039, India.

Abstract: The kinetics of oxidative decolonization of Tartrazine and Ponceou4R byTrichloroisocyanuricAcid [TCICA] in aqueous acetic acid medium has been investigated at 303K. Kinetic runs were executed under pseudo first-order condition in which large excess of [TCICA] compared with [Dye]. Under identical experimental conditions reactions with both the dyes follow identical kinetics with a first-order dependence on each [Dye], [TCICA] and an inverse fractional order on [H$^+$]. The effect of chloride ion and dielectric constant of the medium have been investigated. The rate of oxidation of Tartrazine is about two-fold faster with TCICA as compared to Ponceou4R. Hypochlorous acid has been postulated as the reactive oxidizing species. A suitable mechanism consistent with the experimental results has been proposed.

Keywords: Food dye, azo dye, trichloroisocyanuric acid, oxidative decolourization, kinetics.

Introduction

Synthetic food dyes are widely used as colorants in common foods and medicines[1]. They are azo dyes. Azo dyes have azo group (N=N) and alkyl or aryl group (R-R'); hence the functional group is R-N=N-R'[2]. Tartrazine and Ponceou4R are the synthetic monoazo dyes, which are widely in drugs and food products. Wastewater released from these industries, in which Tartrazine and Ponceou4R are used is highly colored and toxic in nature. Hence, it leads to environmental and health problems. In this context, physio-chemical methods such as adsorption, photo degradation and coagulation and also biological methods have been developed for removal of dyes from effluents. All of these processes are very expensive and not so simple. Therefore, there is a need for inexpensive and simple methods. The oxidative decolourization ofazo dyes has attracted much attention in recent years[3-8].

N-halogeno compounds have been extensively employed as halogenating and oxidizing agents for substrate. The widespread use of a variety of N-halo compounds arises from the fact that they are good source of positive halogen, hypochlorite and N-anion[9-12]. 1,3,5-trichloro-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione commonly known as Trichloroisocyanuric Acid(TCICA) is a member of N-halogeno compounds, which is a well known synthetic reagent and the kinetic and mechanistic aspects of many of its reactions have been well documented[13-20]. It is to be noted that no systematic kinetic investigation on the oxidative decolorization of azo dyes by Trichloroisocyanuric Acid has been reported in the literature. Here, the results of the kinetics of

oxidative decolorization of Tartrazine (TAZ) and Ponceou4R (P4R) with TrichloroisocyanuricAcid (TCICA) in aqueous acetic acid medium have been reported.

Experimental

Materials and Methods

Tartrazine (Analar), Ponceou4R (Analar) and Trichloroisocyanuric Acid (Aldrich, USA) were used as supplied. Doubly distilled water and purified acetic acid were used. Sodium chloride (Analar) was used as source of chloride ions. Sulphuric acid (BDH/AR) was standardized using sodium hydroxide solution with phenolphthalein as an indicator.

Kinetic Measurements

All of the reactions were carried out under pseudo-first order condition [TCICA]>>[Dye]. The course of the reaction was followed by pipetting out 5mL aliquot of the reaction mixture at various time intervals`(as read by an accurate stop-watch) and analyzing the TCICA concentration iodometrically[21]. The initial rate were evaluated from the plots of log [oxidant] versus time and were reproducible within ±3 %(fig.1)
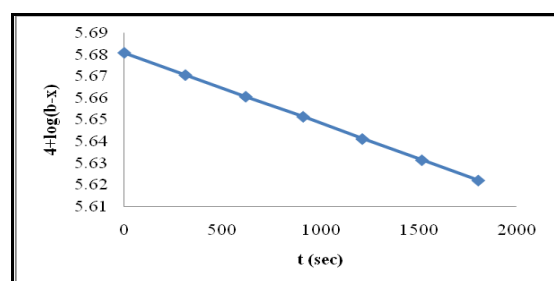

Fig.1 First Order Plot: Log [TCICA] Vs time

Results and Discussion

Reaction Order

The reaction orders were determined from the slope of double logarithmic plots by varying the concentration of dye in turn, while keeping others constant. The plot of log K_{obs} against log [Dye] is linear(r= 0.9662) (Fig.2). The linearity of the plots of log[TCICA] versus time indicates that the order with respect to [TCICA] is unity.(Table 1).
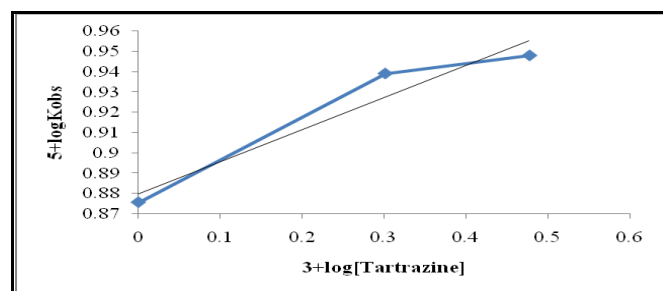

Fig.2 Dependence of Substrate: Log K_{obs}Vs Log [Tartrazine]

Table 1. Rate constant for the oxidative decolourization of Tartrazine and Ponceou4R by TCICA in aqueous acetic acid medium at 30°C

10^3[TAZ] Mol dm^{-3}	10^2[TCICA] Mol dm^{-3}	10^2[NaCl] Mol dm^{-3}	10^3[H$_2$SO$_4$] Mol dm^{-3}	CH$_3$COOH-H$_2$O%(v/v)	10^3[P4R] Mol dm^{-3}	10^5K$_{obs}$s^{-1}
1.0	1.0	-	-	50-50		7.51
1.0	2.0	-	-	50-50		8.69
1.0	3.0	-	-	50-50		8.87
1.0	1.0	-	-	50-50		7.51

2.0	1.0	--	-	50-50		10.24
3.0	1.0	-	-	50-50		11.25
1.0	1.0	1.0	-	50-50		2.16
1.0	1.0	2.0	-	50-50		2.22
1.0	1.0	-	1.0	50-50		2.28
1.0	1.0	-	2.0	50-50		1.97
1.0	1.0	-	3.0	50-50		1.93
1.0	1.0	-	-	75-25		6.06
1.0	1.0	-	-	50-50		7.51
1.0	1.0	-	-	25-75		17.16
-	1.0	-	-	50-50	1.0	3.60

Effect of Added NaCl

The effect of addition of NaCl on the rate of oxidative decolorization of Tartrazine by TCICA was studied by varying the concentration of NaCl in the range of 0.01M to 0.02M   (Table 1). In this case, the order can be taken as fractional with positive slope (Fig.3).

Effect of Mineral Acid

The pseudo first order rate constant decrease with increase in $[H^+]$ in the range of 0.001M to 0.003M (Table 1). The plot of log K_{obs} Versus log $[H^+]$ is linear with negative slope indicating inverse fractional order dependence on $[H^+]$ (Fig.4)
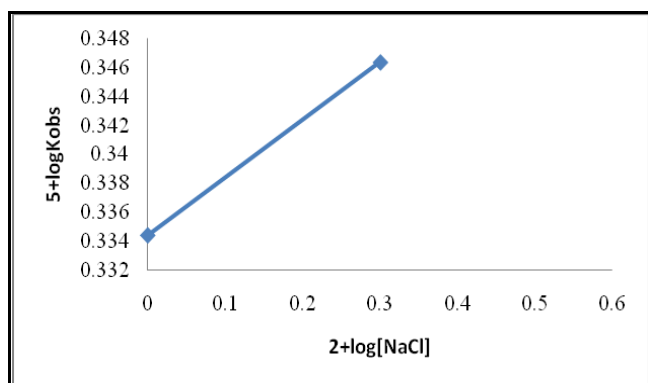

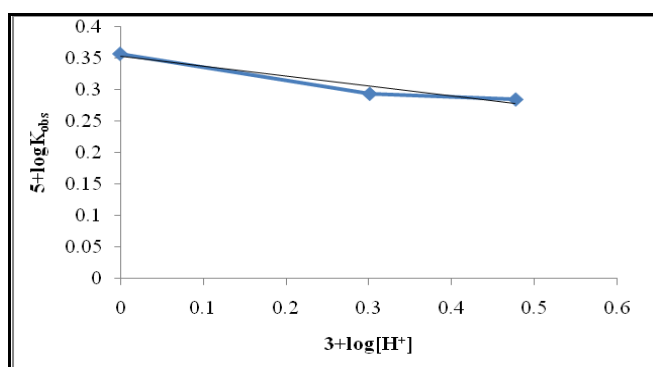
Fig.3 Effect of Added NaCl: Log K_{obs} Vs Log [NaCl]

Fig.4 Effect of Added Mineral acid: Log K_{obs} Vs Log $[H^+]$

Effect of Solvent Composition

The effect of changing solvent composition on the reaction rate was studied by varying the concentration of acetic acid from 25 – 75%. The enhancement of the reaction rate with decrease in the amount of acetic acid may generally be attributed to two factors viz(i) decrease in acidity at constant $[H^+]$ and (ii) increase in dielectric constant with increase in water content. A plot of logK_{obs} against composition of H_2O is linear with positive slope (Fig.5). This support the postulation of HOCl as the reactive species.
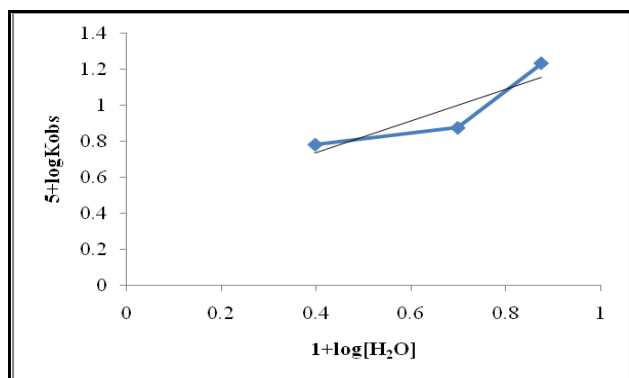
**Fig.5 Effect of Solvent Composition: Log K_{obs} Vs Log [H_2O]**

Effect of Substituent

The oxidative decolorization of Tartrazine and Ponceou4R were carried out in the identical conditions. The values of reaction constants are shown in Table 1. It is interesting to note that the reactivity for substituent is in the order   Tartrazine> Ponceou4R.

It is clear from the data that steric effect and resonance effect of the substituent are important.

Mechanism of Reaction

It is clear from the literature[13,17] that the probable reactive species of TCICA in acid medium is HOCl. The reaction is first order in [TCICA], on each [Dye] and an inverse fractional order in [H^+]. The positive influence of change in [Cl^-] and the enhanced effect of dielectric constant of the medium on the rate of oxidative decolorization. It is quiet likely that under the condition of solvent medium employed the TCICA exists in the following equilibrium[19]


.... (1)
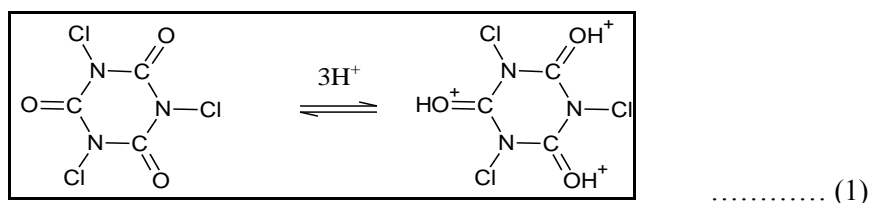
Although TCICA has three such potentially reactive centers, it may be represented as N-Chloro reagent, N-Cl. The protonated form TCIH$^+$ may be represented as

.... (2)
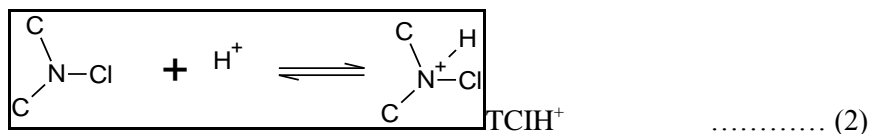
The solvent effect does point out that the reaction with unprotonated dye should be more predominant.Based on the earlier kinetic work on oxidation with N-halo compounds one can reasonably suggest that the most likely oxidizing species is HOCl under acidic condition. If the slow reaction can be traced as interaction of HOCl and dye molecule, in which the azo group –N=N- bond of the moiety is involved and this –N=N- bond break with transfer of electrons. More specifically in the present case, one can suggest a slow step involving a cyclic transition state. The f following mechanism can be proposed for the oxidative decolorization for which the rate law can be derived.

.... (3)

Scheme-1

$$\text{Rate} = K_2 \, [\text{HOCl}] \, [\text{DYE}] \quad\text{------------------------------(6)}$$
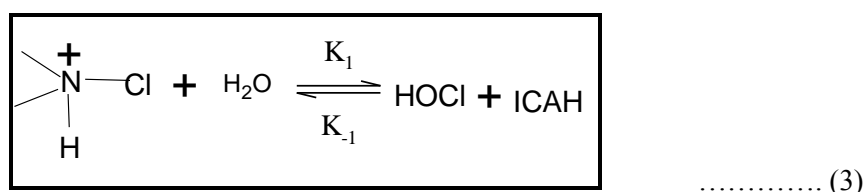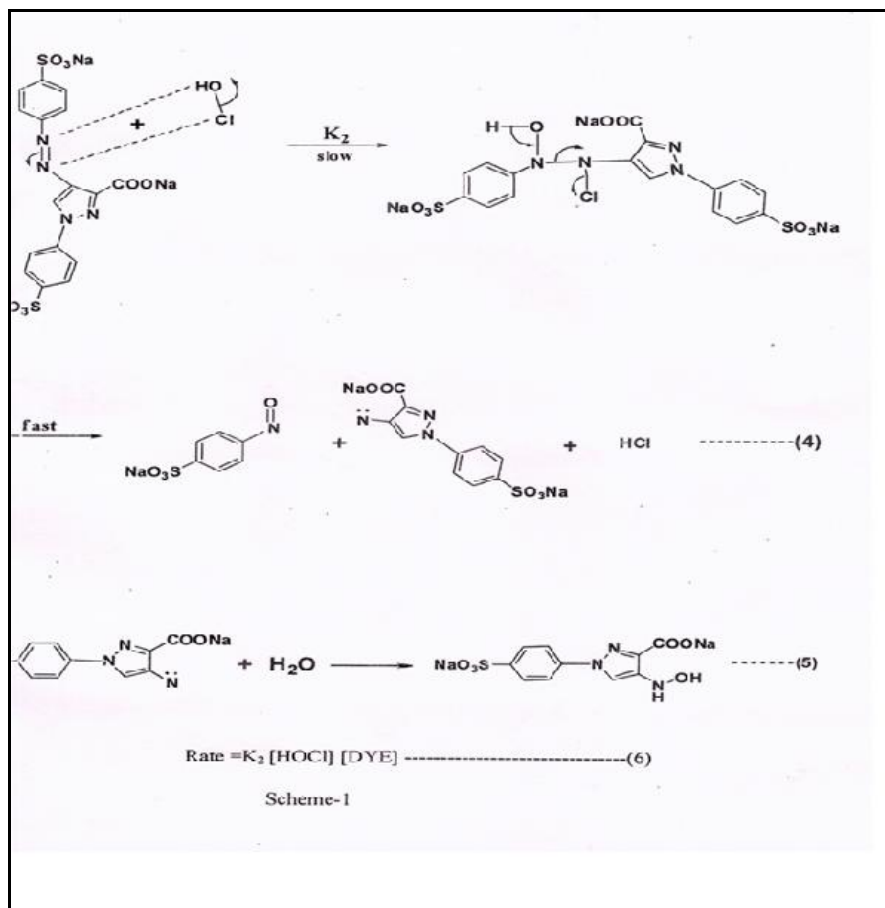
The concentration of the HOCl in the above rate expression may be calculated as follows. On the assumption that all the TCICA is reacting as $TCIH^+$ one can find an expression for [HOCl] as follows.

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

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

$\text{Rate} = K_2 \, [\text{Dye}] \, K_1 \, [TCIH^+] \, [H_2O] \, / \, K_{-1} \, [\text{ICA}] \, [H^+]$ ………………(7)

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

Conclusion

In the present research, optimum conditions for the facile oxidative decolorization of Food Dyes Tartrazine and Ponceou4R with TCICA in aqueous acetic acid medium have been obtained. TCICA decolorize Tartrazine and Ponceou4R Dyes completely within 30 min in aqueous acetic acid conditions. Oxidative decolorization of the Food Dyes with TCICA in aqueous acetic acid medium obeys the experimental rate law: $-d \, [\text{TCICA}]/dt = K \, [\text{Oxidant}] \, [\text{Dye}][H_2O][H^+]$. Hence, this method is a simple and well designed can be implemented for treating Tartrazine and Ponceou4R present in industrial effluents to diminish the toxicity caused by this dyes. In addition to this the kinetic and mechanistic picture of monoazo dye – TCICA reaction system in aqueous acetic acid medium has also been clarified.

References

1. Chivukula M and Ranganathan V, Phenolic Azo Dye Oxidation by Laccase from Puriculariaorvzae. Appl.Environ.Microbiol., 1995,12, 4374-4377.
2. Zollinger H,Color Chemistry – Synthesis, Properties and Applications of Organic Dyes and Pigments.3rd edn, Wiley, Weinheim, 2003.
3. Watanabe T, Claston I.D, The contribution of azo dyes to the mutagenic activity of the Cristais River.Chemosphere., 2005, 60, 55-64.
4. Oakes J, Gratton P. Kinetic investigation of the oxidation of arylazonaphthol dyes in Hypochlorite solutions as a function of pH. J. Chem Soc. Perkin Trans., 1998, 2, 2201-2206.
5. Abrahat E.N. Dyes and their intermediates.EdwardAQrnolds Ltd., London, UK, 1977.

6.   Legrini O, OliverosE. Braun A.M. Photochemical processes for water treatment. Chem. Rev., 1993, 93(2):671-698.

7.   Roxon JJ, Ryan AJ, Wright SE. Reduction of water-soluble azo dyes by intestinal bacteria. Food Cosmet Toxicol.,1967, 5(3): 367–369.

8.   Shubha J.P, and Puttaswamy, Oxidative decolorization of carmosine with acidic Chloramine-T Spectrophotometric, kinetic and mechanistic chemistry,Euro J Chem ,2012, 3(1): 112-118.

9.   Thenraja D,Subramaniam P and Srinivasan C, Kinetics and mechanism of oxidation of aromatic sulfides and arylmercaptoacetic acids by N-chlorosuccinimide, J.Chem.Soc. Perkin Trans. 2002, 2: 2125.

10. Mukaiyama T , Matsuo J.I, Lida D and Kitagawa H, Catalytic oxidation of various Alcoholsto the corresponding carbonyl compounds with N-chlorosuccinimide using a catalytic amount of Sulfenamide, Chem Lett. 2001, 30: 846-847.

11. Brown I.O. and Soper F.G, Studies of N-halogeno-compounds.Part V. The interaction ofdialkychloramines with phenols, J Chem. Soc., 1953, 3576-3580.

12. Larr M.D, and England B.D., Proc.Chem.Soc., 1958, 350.

13. Anil Kumar J and Sondu S., Kinetics and mechanism of oxidation of chalcones by trichloroisocyanuric acid[TCICA] in HOAc-HClO$_4$ medium. Indian J Chem., 2007, 46: 1792-1795.

14. Palaniappan A.N, Rajalakshmi R and SrinivasanS.Mechanistic studies on the oxidation of Schiff's bases by trichloroisocyanuric acid[TCICA] in non-aqueous medium. J Chem.Pharm.Res.,2013, 5: 290-298.

15. Subas C Pati and Chintamani Sarangi, Oxidation of Hydrocarbons: Kinetics andMechanism of Ru(III) catalysed oxidation of Toluene and substituted Toluenes by Trichloroisocyanuric acid[TCICA]. Proc.Indian Natn.Sci.Acad.,1986, 52A:666-675.

16. Vasudevan K.S and Venkatasubramanian N, Chlorination of Ketones by Trichloroisocyanuric Acid-A Kinetic and Mechanistic Study, Indian J Chem Sect A, 1985, 24: 304-307.

17. Mohan R.V.G.K and Sondu S, Kinetics and Mechanism of Ru(III) catalysed oxidation of aliphatic alcohols by trichloroisocyanuric acid in HClO$_4$ medium, React.Kinet.Catal.Lett., 61: 167-172.

18. ManivannanS.Kinetics of oxidation of Propan-2-ol by Trichloroisocyanuric acid in Aqueous acetic acid medium.Int.J.Chem.Sci.,2004, 2(4): 527-532.

19. Gabrela Fonseca Mendonca, Rehabe Ramos Magathaes, Marcio C.S. de Mattos, and Pierre M Esteves, Trichloroisocyanuric Acid in H$_2$SO$_4$: A efficient superelectrophilic reagent for chlorination of Isatin and Benzene derivatives.J.Braz.Chem.Soc., 2005,16,695-698.

20. Manivannan S and Kaveri K, Kinetics of oxidation of amino acid by Trichloroisocyanuric Acid in aqueous acetic acid medium,Int.J.Adv.Chem.Sci.and Applns.,(IJACSA), 2014, 2(2): 49-52.

21. Mathur N.K and Narango C.K, Determination of organic compounds with N-bromosuccinimide and allied reagents, Academic Press, New York, 1975.

*****