

A Kinetic and Mechanistic Study on the Reduction of Dithizone by Stannous Chloride (acidic medium) in Micellar System

Radjarejesri. S.^{a,b} and Sarada. N.C.^{a*}

^a*Chemistry Division, School of Advanced Sciences,
VIT University, Vellore, Tamilnadu, India*

^{*}*Corresponding Author E-mail: ncsarada@yahoo.com*

^b*Department of Chemistry, Sona College of Technology,
Salem, Tamilnadu, India*

E-mail: uma.seshayer@gmail.com

Abstract

Kinetic studies on the reduction of dithizone by stannous chloride was carried out in acidic medium (HCl) at room temperature. The study was made in the presence of cationic surfactant, Cetyl Trimethyl ammonium Bromide (CTAB) and anionic surfactant, Sodium Dodecyl Sulphate (SDS). The reduction of dithizone in the presence of CTAB is much faster than in the absence of surfactant in acidic medium. As the concentration of acid increases the rate of the reaction also increases. No significant change was observed with SDS. The significant rate enhancement of these reactions in presence of CTAB micelles is due to the hydrophobic and electrostatic interactions between the substrate, reductant and micelles. These effects are discussed on the basis of interactions of the above compounds and micelles of different charge type. Mechanism of the reaction has been proposed consistent with the experimental findings. The binding constant between the substrate and CTAB micelles in HCl medium has been calculated by analyzing the data using pseudo phase model and found to be 757 M^{-1} .

Keywords: Cetyl trimethyl ammonium bromide, Sodium dodecyl sulphate, Dithiazone, Stannous chloride, Binding constant, Micellar media.

Introduction

The interest in catalysis of organic reactions by micelles formed by the aggregation of

surfactant molecules has increased due to the similarity between micelles and cell membrane, which is used as models for enzyme-catalyzed reactions⁽¹⁻³⁾. Azo dyes are well known for the analytical applications^(4, 5) and also have strong pharmacological activities^(6, 7). Many reducing agents such as sodium sulphite, hydrazine, titanous chloride, lithium aluminium hydride^(8, 9), etc. can bring about the reduction of azo compounds. Ogawa et al studied about the reduction of azo compounds and found that sodium sulphite reduces them to hydrazo derivatives and then gradually to amines, whereas SnCl₂ reduces azo compounds directly to amines⁽¹⁰⁾. SnCl₂ is a reducing agent which is used widely in solution where Sn²⁺ ion ($\text{Sn}^{4+} + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}$) is the active species for reduction purpose. When HCl concentration increases, SnCl₂ becomes SnCl₃⁻ ($\text{SnCl}_2 + \text{HCl} \rightleftharpoons \text{HSnCl}_3$) or SnCl₄²⁻ ($\text{SnCl}_2 + 2\text{HCl} \rightleftharpoons \text{H}_2\text{SnCl}_4$) ion⁽¹¹⁾. When HCl concentration is higher, SnCl₂ acts as a stronger reducing agent. The rate of reduction of SnCl₂ in presence of higher concentration of HCl enhances the rate of dithizone in CTAB. The transfer of solutes from water to the micelles is a diffusion process and hence much faster than most chemical reactions. Micelles equilibrate rapidly with monomeric surfactant and hydrophobic solutes, and are partitioned between bulk solvent and the micelles. Hence, in micelles the reactions may occur at higher rates than in bulk solvent⁽¹²⁾. Our first paper was on the kinetics of the reduction of Dithizone by sulphite ions⁽¹³⁾ in micellar media, previous paper being the kinetic studies on reduction of dithizone by stannous chloride⁽¹⁴⁾ in aqueous medium in the presence and absence of surfactants and now we have attempted to explore the use of micellar media for the kinetics of the reduction of azo compounds by stannous chloride in acidic media.

Experimental procedure

Materials required

Dithizone, stannous chloride, hydrochloric acid, acetic acid, CTAB and SDS of AR grade. All the solutions were prepared in double distilled water. Ionic strength was maintained constant with NaCl for the reaction in absence of CTAB and showed an increasing effect in presence of CTAB. The reactions showed no effect or in other words remained constant in presence of SDS.

Kinetic measurements

The reactions were followed spectrophotometrically (Shimadzu160A) by observing decrease in absorbance of dithizone at 603.5nm. All the kinetic runs were recorded at room temperature. The product identified was an amine by IR spectroscopy, and also the literature reveals that SnCl₂ reduces the azo compounds directly to amines⁽¹⁰⁾. The progress of the reaction was monitored by the decrease in absorbance upto two half-lives.

Results and Discussions

The kinetics of reduction of dithizone by stannous chloride in acidic medium was investigated at several initial concentrations.

Kinetic studies in acidic medium in the absence of surfactants

Similar kinetic runs were monitored at varying dithizone concentrations in acidic medium in the range $2.0 \times 10^{-4} - 5.0 \times 10^{-4}$ M (Table I). The rate of reduction on the SnCl_2 concentration was examined by monitoring the kinetic runs at varying $[\text{SnCl}_2]$ in the range of $0.5 \times 10^{-3} - 3.0 \times 10^{-3}$ M (Table I) in acidic medium. As in the case of aqueous medium, the added NaCl influence was also studied by varying the concentration of NaCl (Table I). The effect of added NaCl was negligible in this case also.

Kinetic studies in acidic medium in presence of surfactants

The reduction of dithizone by stannous chloride in acidic medium was also studied in presence of cationic surfactant (CTAB) and anionic surfactant (SDS). The effect of the $[\text{dye}]$, $[\text{SnCl}_2]$ and $[\text{NaCl}]$ on the rate of reduction was studied in presence of 0.1M CTAB and rate constant was higher than that in the aqueous medium. The rate of the reaction when compared to the aqueous medium in presence of CTAB was 57 times greater in acidic medium. Effect of cationic micelles on the rate of reduction of dye by SnCl_2 was studied by varying the CTAB concentration in the range 0.1×10^{-3} to 10×10^{-3} (Fig.1). Similarly effect of anionic surfactant on the rate of reduction of dithizone by SnCl_2 was studied by varying the SDS concentration in the range of 0.1×10^{-3} to 10×10^{-3} (Fig.1). From the figure it is clear that there is no reaction with SDS.

Based on the observed results the following scheme of mechanism is proposed for the reduction of dithizone by SnCl_2 . (Scheme 1)

The observed rate law under experimental conditions may be given as

$$-\frac{d[\text{dithizone}]}{dt} = k_1 [\text{S}] [\text{SnCl}_2] \quad (1)$$

According to the scheme 1, the rate of disappearance of dithizone is given by,

$$\text{Rate} = k_1 [\text{S}] [\text{SnCl}_2] + k_2 [\text{SH}^+] [\text{SnCl}_2] \quad (2)$$

The total concentration of the substrate can be expressed as

$$[\text{S}]_T = [\text{S}] + [\text{SH}^+] \quad (3)$$

The concentration of S and SH^+ in terms of S_T and the protonation constant (K_p) can be given as

$$[\text{S}] = \frac{[\text{S}_T]}{1 + K_p [\text{H}^+]} \quad (4)$$

$$[\text{SH}^+] = \frac{[\text{S}_T] K_p [\text{H}^+]}{1 + K_p [\text{H}^+]} \quad (5)$$

Substituting for $[\text{SH}^+]$ and $[\text{S}]$ in equation (2), the rate of the reaction can be expressed as,

$$\text{Rate} = \frac{k_1 + k_2 K_p [H^+] [S_T] [SnCl_2]}{1 + K_p [H^+]} \quad (6)$$

The observed rate law is consistent with the rate equation. Hence on comparing equation (6) and equation (2), it yields,

$$\frac{k^1}{1 + K_p [H^+]} = \frac{k_1 + k_2 K_p [H^+]}{1 + K_p [H^+]} \quad (7)$$

Equation (7) explains the rate dependence on H^+ . The above mechanism holds good for both type of reactions in aqueous as well as acidic medium.

Influence of CTAB on k_ψ

The fundamental process in micellar catalysis or inhibition is the counter ion binding with the micelle. They provide an unusual medium affecting the rate of reaction. Depending upon the electrical charge on their head groups, the micelles can either attract the reactive ions or repel them. Thus the reactions are catalyzed or inhibited as the micelles bring the solubilised substrate and reactive ions together.

In presence of varying concentrations of CTAB, the effect of CTAB on the reaction rate was investigated in acid medium. The micelles catalyzed the reaction (Table I). The values listed in the Table I shows very high increase in rate of reaction with CTAB in acidic medium. The catalysis observed under these experimental conditions was in good agreement with similar bimolecular reactions and the catalytic effect of CTAB on k_ψ can be explained in terms of pseudo phase model of micelles. The reaction rate has increased considerably with increase in the concentration of CTAB.

A constant value of k_ψ was observed at higher concentrations of CTAB and also the reaction mixture became turbid at $[CTAB] > 2 \times 10^{-2} M$ in acidic medium due to solubility problem of CTAB. Most of the micellar mediated organic reactions are believed to occur inside the Stern layer or at the junction region of the Stern of Gouy-Chapman layers⁽¹⁶⁾. The key factor involved in the kinetic micellar effect is that the electrostatic and hydrophobic interaction between surfactant and substrate increases the concentration of reactants, ionized hydroxyl acid in the Stern layer. The enhancement in k_ψ is due to the increase in the concentration of CTAB where the molarity of reactants in the Stern layer is increased and at higher concentrations, k_ψ was observed a constant.

Quantitative treatment of micellar catalysis

The data of variation of observed rate constant k_ψ with CTAB concentration is analyzed on the basis of following model.

Theoretically by making certain simplifications and assuming that only one substrate is incorporated into the micelle and that the aggregation number N of the micelle is independent of the substrate. On the basis of these assumptions Piszkiwicz⁽¹⁵⁾ proposed a model for micellar catalyzed reaction similar to the Hill model⁽¹⁶⁾ of

enzyme kinetics. This model is applicable especially at low surfactant concentrations. In this model the assumption is that “n” number of surfactant molecules (D) and substrate (S) aggregate to yield the catalysis aggregate D_nS which then reacts to yield the product (P). This is represented by the following Scheme 2.

K_s is the micelle – substrate binding constant expressed in terms of micellised surfactant. Under the experimental conditions, Scheme 2 gives the following expression for the observed rate constant (k_ψ) in the presence of CTAB micelles.

$$k_\psi = \frac{k_w + k_m K_s (C_D - cmc)}{1 + K_s (C_D - cmc)} \quad (8)$$

Here, C_D is the concentration of the detergent. Equation (8) can be rearranged as

$$k_\psi - k_w = \frac{K_s (C_D - cmc)}{k_m - k_\psi} \quad (9)$$

As required by the equation (9), a plot of $k_\psi - k_w / k_m - k_\psi$ Vs C_D is found to be linear for the reduction of dithizone in presence of CTAB in acidic medium (Fig. 2). K_s values obtained from the plots for the reduction of dithizone in acidic medium in presence of CTAB was found to be 757 M^{-1} . This value indicates significant binding between the substrates and CTAB micelles.

Raghavan and Srinivasan justify⁽¹⁷⁾ the model given in Scheme 2 to the bimolecular reaction under investigation considering the arguments put forward. A similar idea was given by Romsted⁽¹⁸⁾ as well as Reeve. The model is represented by Scheme 2 where D, S and N refer to the detergent monomer, substrate and the nucleophile, respectively. The products are assumed to result from the reactions in aqueous as well as acidic medium. Where nucleophile resides predominantly in Stern layer of the micelle, Menger and Portnoy treatment for unimolecular reaction should hold good for bimolecular reaction also.

Conclusion

The interpreted results based on this study shows that the micelle substrate interactions are specific and depend on both electrostatic and hydrophobic forces. The investigation suggests that rate of reduction of azo compounds by SnCl_2 carried out in the acidic medium is faster in the presence of cationic micelles. The utility of micellar media for preparative and analytical purposes is expected to be enhanced, due to these studies. Many methods can be developed to reduce the pollution in waste waters of industries dealing with azo dyes due to the catalytic effect of micelles on the redox reactions of azo compounds.

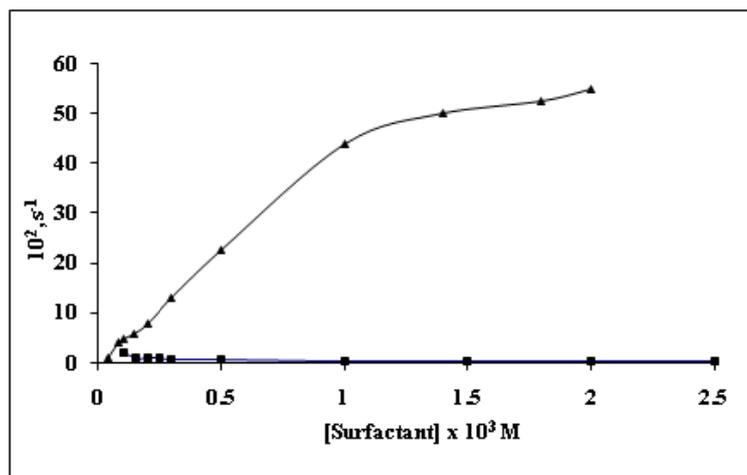


Figure 1: Variation of rate constant with ▲CTAB concentration and ■SDS concentration for the reduction of dithizone by SnCl₂ in acidic medium.

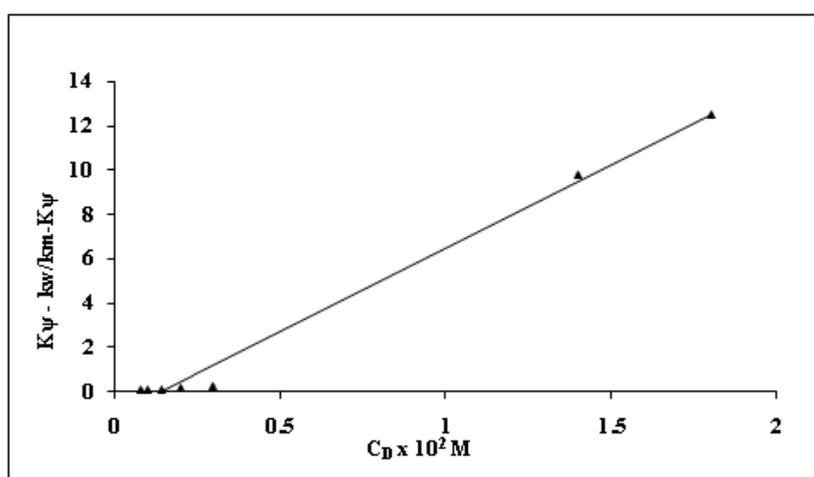
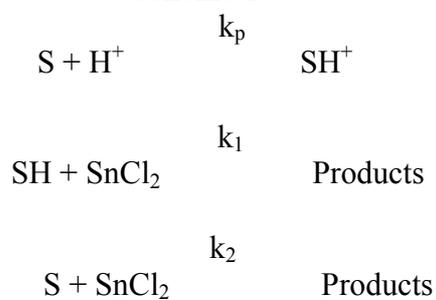
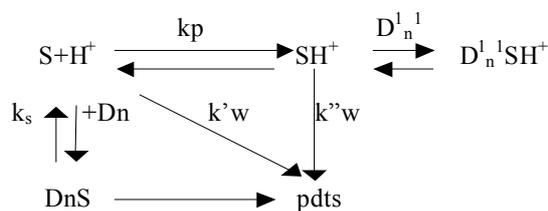


Figure 2: Analysis of effect of CTAB on the rate of reduction of dithizone using SnCl₂ in acidic medium.

Scheme 1



Scheme 1



Scheme 2

Table I: Effect of $[\text{SnCl}_2]$, [dithizone] and $[\text{Cl}^-]$ on the rate of reduction of dithizone by SnCl_2 in acidic medium at room temperature $[\text{SnCl}_2] = 2 \times 10^{-3}$ [dithizone] = 2×10^{-4} .

[dithizone] $10^4, \text{M}$	$k \times 10^3, \text{s}^{-1}$		$[\text{SnCl}_2]$ $10^3, \text{M}$	$k \times 10^3, \text{s}^{-1}$		$[\text{Cl}^-]$ $10^2, \text{M}$	$k \times 10^3, \text{s}^{-1}$	
	No surfactant	CTAB		No surfactant	CTAB		No surfactant	CTAB
2	0.0106	7.9	0.5	0.023	3.1	1	4.4	6.9
2.5	0.0107	8.7	1	0.045	6.7	1.5	3.98	7.4
3	0.0101	7.4	1.5	0.067	9	2	4.39	8.5
3.5	0.0093	8.5	2	0.094	13.5	2.5	4.6	9.2
4	0.009	9.1	3	0.16	16.72	3	4.7	9.6
4.5	0.0103	9.2						
5	0.0089	9.5						

Bibliography

- [1] Fendler, J. H.; Fendler, E. S. Catalysis in micellar and macromolecular systems; Academic: New York, 1975.
- [2] Rosen, M. Surfactants and Interscience. New York, 1978.
- [3] Rafiquee, M. D. Z.; Shah R. A.; Kabir-ud-Din; Khan, Z. Kinetics of the Interaction of Cd(III)-histidine complex with ninhydrin in absence and presence of cationic and anionic micelles. *Int J Kinet* 1997, 29:13.
- [4] Isa, R. M.; Ghonium, A. K.; Dessouk, H. A.; Mustafa, H. M. *J. Chem. Soc.*, 1984, 61, 286.
- [5] Lurieju, S. *Hand Book of Analytical Chemistry*; Mir Publishers, Moscow, 1367, 196.
- [6] Gaind, K.N.; Gulati, S. K. *Indian J. Pharm.*, 1996, 28, 272.
- [7] Goodman, L.S.; Gilman, A. *The Pharmacological Basis of Therapeutics*; McMillan: New York, 1970, 111.
- [8] Brown, H. C.; Weissman, P. M. *J. Am. Chem. Soc.*, 1965, 87, 5614.
- [9] Brown, H. C.; Weissman, P. M.; Yoon, N. M. *J. Am. Chem. Soc.*, 1966, 88, 1458.

- [10] Ogawa, T.; Shibata, K.; Yotome, C.; Takase, Y.; *Kogyo Kagakuzasshi*, 1971, 74, 720.
- [11] Harrison, G. P.; Haylett, B. J.; King, J. T. *Inorg. Chim. Acta*, 1983, 75, 265 – 270.
- [12] Bunton, C. A. *Prog. Solid Chem.*, 1970, 8, 239; *Micellar Reactions. Chap. IV. Application of Biomedical Systems in Chemistry: Part II*, ed. J. Bryan Jones, Wiley, New York, 1976.
- [13] Radjarejesri, S; Sarada, N. C. *J. Indian Chem. Soc.*, 2007, 84, 554.
- [14] Radjarejesri, S; Sarada, N. C., *Kinetic Studies on the Reduction of Dithizone by Stannous Chloride in Aqueous Medium in Micellar System*, *International Journal of Applied Chemistry*, 2010, Vol. 6, No. 1, 105–112.
- [15] Piszkiwicz, D. *J. Am. Chem. Soc.*, 1977, 99, 1550.
- [16] Hill, A. V. (1910), *The possible effects of the aggregation of the molecules of haemoglobin on its dissociation curve*; *J. Physiol* 40: 4.
- [17] Raghavan, P. S.; Srinivasan, V.S. *Proc Indian Acad Sci (Chem Sci)*., 98 (1987) 199.
- [18] Romsted, L. S. *Micellisation, Solubilisation and Microemulsions*; Vol. 2, ed. K. L. Mittal, Plenum Press: New York, 1977.