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Kinetic study on the Oxidation of Dibenzyl Sulfide with iron(III) polypyridyl complexes in the presence of Cationic micelle

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Abstract : The kinetics of the reaction between DBS with $Fe(NN)_3^{3+}$ was followed spectrophotometrically by measuring the increase in absorbance of $[Fe(NN)_3]^{2+}$ with time. The article describes a detailed kinetic investigation on the oxidation of DBS by iron(III)-polypyridyl complexes in the presence of CTAB, cationic micelle. The kinetics in micellar medium is governed by both electrostatic interactions and hydrophobic between micelles and reactants, transition states and product¹⁻⁴. The increase in rate with increase in [CTAB] demonstrates the importance of hydrophobic interactions in the binding of positively charged metal complexes to micelles.

Introduction

The study of the effect of organized assemblies such as micelles on the rates of reactions is a topic of increased attraction in recent years. This interest is based on the realization that many biochemical processes proceed in a microheterogeneous system which contains an aqueous and a lipophilic moiety.⁵ The growth in the chemistry of organic sulphide and sulfoxides during last decade was due to their importance as synthetic intermediates for the production of a wide range of chemically and biologically active molecules. They often perform a major function as therapeutic agents such as anti-ulcer (proton pump inhibitor), antibacterial, antifungal, anti atherosclerotic, antihypertensive and cardiotoxic agents. Surface-active agents are amphiphilic compounds which form micelles in solution. Micelles possess distinct regions of hydrophobic (water-repelling) and hydrophilic (water-attracting) character. Increased reactant concentrations at the surfaces of the micelle are of major importance and various attempts⁶ have been made to measure these concentrations. As micelles are considered to mimic the cellular membranes, the redox process occurring in the micellar system is considered as a model to obtain insight in to the redox process prevailing in body systems. The interest in examining micellar effects upon rates of oxidation of DBS by Iron (III) polypyridyl complexes. These studies are useful when discussing the effects of micelles on electron transfer reactions⁷. In the present study, a detailed kinetic investigation has been made on the oxidation of DBS by Iron(III)polypyridyl complexes in cationic micellar medium.

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Materials and Methods

The details of the synthesis of $[\text{Fe}(\text{NN})_3]^{2+}$ and $[\text{Fe}(\text{NN})_3]^{3+}$ (NN = 2,2'-bipyridine; 1,10-phenanthroline) and DBS have been synthesized as per the standard procedure. The rate of formation of $[\text{Fe}(\text{NN})_3]^{2+}$ complex was followed using the UV-Vis spectrophotometer by measuring the change in the absorbance at wavelengths 522nm and 510nm corresponding to $[\text{Fe}(\text{bpy})_3]^{2+}$, $[\text{Fe}(\text{phen})_3]^{2+}$ respectively. The increase in absorbance with time for the oxidation of DBS with $[\text{Fe}(\text{bpy})_3]^{3+}$ is given in Figure 1.

The pseudo first order rate constant for each kinetic run was evaluated from the slopes of linear plots of $\log(A_\infty - A_t)$ vs time by the method of least squares. The precision of k values in all the kinetic runs is given in terms of 95% confidence limits of the Student 't' test. The activation parameters ΔH^\ddagger and ΔS^\ddagger are calculated by the least-squares analysis of a linear plot of $\log k / T$ vs $1/T$. The details on the determination of stoichiometry of the reaction, binding constants of substrates with micelle and product analysis are also given.

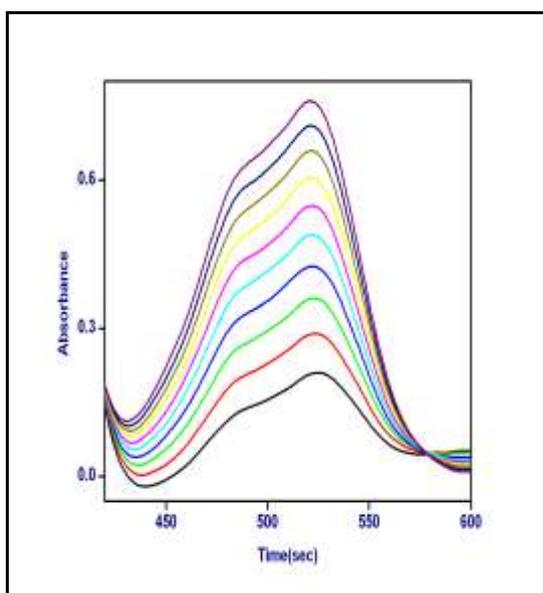


Fig. 1: Absorbance of $[\text{Fe}(\text{bpy})_3]^{2+}$ at 10 seconds time intervals for the $[\text{Fe}(\text{bpy})_3]^{3+}$ oxidation of DBS

The wavelength of maximum absorption (λ_{max}) and molar extinction coefficients (ϵ) estimated from the absorption spectra and IR spectra of $[\text{Fe}(\text{NN})_3]^{3+}$ complexes.

Rate measurements

The kinetic studies were carried out under pseudo first order conditions with DBS, $[\text{Fe}(\text{NN})_3]^{3+}$ complex ratio of at least 15:1 in perchloric acid medium. The substrate with all additives except the oxidant was allowed to attain the experimental temperature by keeping them separately in the constant temperature bath. A known volume of $[\text{Fe}(\text{NN})_3]^{3+}$ complex was then transferred to the reaction mixture at zero time and shaken well. The rate of formation of $[\text{Fe}(\text{NN})_3]^{2+}$ complex was followed using the UV-Vis spectrophotometer by measuring the change in the absorbance at wavelengths 522nm, 510 nm corresponding to $[\text{Fe}(\text{bpy})_3]^{2+}$, $[\text{Fe}(\text{phen})_3]^{2+}$ respectively.⁹ The $[\text{Fe}(\text{NN})_3]^{2+}$ complexes had molar extinction coefficients of the order of $\sim 1 \times 10^4 \text{ cm}^{-1}\text{M}^{-1}$ in the observed region while the corresponding iron(III) complexes were practically transparent at this wavelength region. The reaction was followed at definite time intervals by following the increase in absorbance of $[\text{Fe}(\text{NN})_3]^{2+}$ till maximum absorbance (A_∞) was reached. For the cationic micelle, CTAB, perchloric acid is used instead of sulfuric acid in the reaction mixture because of solubility problem. A set of duplicate runs were carried out to ensure the reproducibility of the rate constants.

The pseudo first order rate constant for each kinetic run was evaluated from the slopes of linear plots of $\log(A_\infty - A_t)$ vs time according to the first-order rate equation 1, by the method of least squares. The linearity of each fit is confirmed in terms of the values of correlation coefficient and standard deviation.

$$k_1 = \frac{2.303}{t} \log_{10} \frac{A_\infty - A_0}{A_\infty - A_t} \quad (1)$$

$$k = 2.303 \times \text{slope expressed in } s^{-1} \quad (2)$$

where k_1 is the pseudo first-order rate constant and 't' is the time in seconds. A_0 , A_t and A_∞ denote the absorbance at zero time, time 't' and absorption maximum respectively of the $[\text{Fe}(\text{NN})_3]^{2+}$ complex. The second order rate constant is evaluated from the relation $k_2 = k_1/[\text{DBS}]$. It is expressed in $M^{-1} s^{-1}$. The precision of k values in all the kinetic runs is given in terms of 95% confidence limits of the Student 't' test.

Kinetics of the reaction in the absence of cationic surfactant

The reaction of $[\text{Fe}(\text{NN})_3]^{3+}$ with DBS follows simple second order kinetics first order each in iron(III) complex and the DBS- first order in the DBS and first order in the oxidant. The rate of oxidation is accelerated by an increase in methanol content of the medium and this has been accounted for the formulation of a charge separated complex in the rate determining step. The electron transfer mechanism has been confirmed from the linear plots observed, when $\log k_2$ values are plotted against oxidation potentials of sulfides. Again involvement of electron transfer from DBS to $[\text{Fe}(\text{NN})_3]^{3+}$ in the rate determining step has been proved by the successful application of Marcus theory to this reaction. The observed 2:1 between $[\text{Fe}(\text{NN})_3]^{3+}$ and DBS and the product, Dibenzylsulfoxide are similar to non-micellar medium.

Stoichiometry

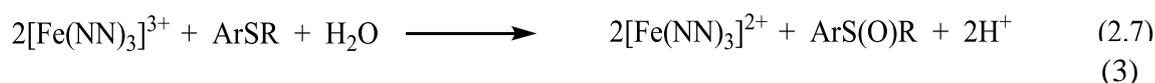
The stoichiometry of the reaction was determined by taking different ratios of oxidant and DBS concentrations. The investigation was first carried out with the oxidant, tris(2,2'-bipyridine)iron(III) and the DBS. A known excess of $[\text{Fe}(\text{bpy})_3]^{3+}$ was mixed with a known concentration of DBS under the experimental conditions of $[\text{H}^+] = 0.5\text{M}$ in 50% aqueous CH_3OH at 305K. The reaction was followed by measuring the change of absorbance of $[\text{Fe}(\text{bpy})_3]^{2+}$ at 522nm. The amount of $[\text{Fe}(\text{bpy})_3]^{2+}$ formed must be equal to the amount of $[\text{Fe}(\text{bpy})_3]^{3+}$ consumed during the reaction. After the reaction was complete, the concentration of the product, $[\text{Fe}(\text{bpy})_3]^{2+}$ was calculated from its absorbance maximum and the known value of molar extinction coefficient and this gave the amount of $[\text{Fe}(\text{bpy})_3]^{3+}$ consumed in the reaction. The results are presented in Table 1.

Table 1: Stoichiometry of the reaction

$[\text{Fe}(\text{bpy})_3]^{3+}$ $\times 10^3, \text{M}$	$[\text{DBS}]$ $\times 10^4, \text{M}$	$[\text{Fe}(\text{bpy})_3]^{3+}_{\text{reac}}$ $\times 10^4, \text{M}$	$\frac{[\text{Fe}(\text{bpy})_3]^{3+}_{\text{reac}}}{[\text{DBS}]_{\text{initial}}}$
1.0	1.0	2.04	2.04
2.0	1.0	1.96	1.96
2.0	2.0	4.16	2.08

$[\text{H}^+] = 0.5 \text{ M}$; solvent = 80% CH_3OH – 20% H_2O (v/v); temp. = 32° C

These results indicate that one mole of DBS was consumed per two moles of $[\text{Fe}(\text{bpy})_3]^{3+}$. Similar studies were also carried out with other oxidants $[\text{Fe}(\text{phen})_3]^{3+}$ and again in the presence of micelle. All these studies confirm the above conclusion that one mole of DBS was consumed per two moles of oxidant, $[\text{Fe}(\text{NN})_3]^{3+}$ in accordance with the eq. 3.



where



Kinetics of the reaction in the presence of CTAB

As the reported critical micellar concentration of SDS is $8 \times 10^{-3} \text{ mol dm}^{-3}$ and for CTAB is $9.2 \times 10^{-4} \text{ mol dm}^{-3}$, the reactions were carried out in the concentration range of 0.001 M - 0.15 M, i.e., above the CMC value. All kinetic measurements were performed under pseudo-first order conditions with DBS 15 folds in excess over the iron(III)-polypyridyl complexes in the presence and in the absence of cationic surfactant at 303K. Due to the low solubility of aryl sulfides in aqueous media, the reactions in the presence of surfactants were carried out in 2% CH₃OH-98% H₂O (v/v). The ionic strength was maintained in all the runs using NaClO₄. In the case of CTAB micelle, the kinetic studies were carried out in sulphuric acid medium and at constant ionic strength maintained by the addition of potassium sulphate under pseudo first-order conditions. The reactions were followed spectrophotometrically by measuring the increase in the absorbance of [Fe(NN)₃]²⁺ with time. The iron(II)-polypyridyl complexes have maximum molar extinction coefficients of the order of $1 \times 10^4 \text{ M}^{-1} \text{ cm}^2$ in the wavelength region of 510-530 nm; [Fe(bpy)₃]²⁺(522nm), [Fe(phen)₃]²⁺(510nm),⁸⁻⁹ while the corresponding iron(III)complexes are practically transparent at this wavelength region.¹⁰⁻¹¹ The plots of log(A_∞ - A_t) versus time were linear and the pseudo first order rate constant, k₁ values were calculated by the method of least squares.

Measurement of binding constant

The values of the binding constant K_s of DBS with cationic surfactant was determined spectrophotometrically from the variation of absorbance, A, at their respective λ_{max} by using the following equation

$$\frac{A_s - A_w}{[D_n]} = A_m k_s - A_s k_s \quad (4)$$

where A_w and A_m are the absorbance in the absence of surfactant and the limiting absorbance upon complete incorporation into the micellar phase respectively. A_s is the absorbance in the presence of micelle. From the spectral data a plot of A_s-A_w / [D_n] vs A_s has been made. The plot gave the straight line with negative slope = -k_s and from this k_s can be evaluated. The calculated binding constant for DBS is 340 with CTAB. Bunton and co-workers,¹²⁻¹³ have used similar method for measuring the binding constant of organic sulfide with micelle. The authors have established that organic sulfides bind efficiently with anionic as well as cationic surfactants and the binding constants are in the range of 80–340 M⁻¹.

Results & Discussion

The kinetic has been carried out by the oxidation of DBS with [Fe(NN)₃]³⁺ in the presence of cationic micelle. The pseudo-first order rate constant increases and is greater than that observed in the absence of micelle. For example, in the oxidation of DBS with [Fe(phen)₃]³⁺ when the concentration of CTAB is changed from 0.001 M to 0.12 M the rate constant increases from $0.019 \times 10^{-3} \text{ s}^{-1}$ to $0.460 \times 10^{-3} \text{ s}^{-1}$, while in the absence of micelle the rate constant is only $0.015 \times 10^{-3} \text{ s}^{-1}$ (Table 2). In general the increase in rate is more pronounced in [Fe(phen)₃]³⁺ compared to [Fe(bpy)₃]³⁺ in micellar medium.

Table 2: Effect of changing [CTAB] on the rate of [Fe(NN)₃]³⁺ oxidation of DBS DBS : 2% CH₃OH, 0.5M [H⁺]

[CTAB]	DBS $k_2, M^{-1}s^{-1}$	
	[Fe(phen) ₃] ³⁺	[Fe(bpy) ₃] ³⁺
0	0.015 ± 0.01	0.047± 0.04
0.001	0.019 ± 0.01	0.101± 0.01
0.005	0.020 ± 0.04	0.108± 0.01
0.01	0.025 ± 0.09	0.119± 0.06
0.03	0.037 ± 0.01	0.123± 0.05
0.05	0.055 ± 0.01	0.130± 0.05
0.07	0.076 ± 0.02	0.157± 0.01
0.09	0.157 ± 0.03	0.170± 0.01
0.1	0.233 ± 0.02	0.247± 0.02
0.12	0.460 ± 0.05	0.293± 0.02

The rate enhancement demonstrates the importance of hydrophobic interactions in the binding of positively charged metal complexes to micelles. In the positively charged CTAB micellar surface, the hydrophobic interactions of the ligands of the [Fe(NN)₃]³⁺ complexes with the micelle are apparently sufficient to overcome the coulombic repulsion between [Fe(NN)₃]³⁺ and the cationic micelle. Similar explanation has been given for the aryl methyl sulfide oxidation by [Fe(NN)₃]³⁺ complexes in the presence of cationic micelle.¹⁴⁻¹⁶

There is decrease in polarity of the medium with increase in methanol content or surfactant concentration. In the absence of micelle, the rate of the reaction increases with increase in methanol content of the medium. i.e. decrease in polarity.

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