



Kinetic study on the oxidation of Phenyl Vinyl Sulfide with Iron(III)-Polypyridyl complexes in the presence of Anionic Micelle

Balakumar P^{1*}, Balakumar S^{*2},
Subramaniam P^{*3}, Sweetlin Rajula Rubavathi D⁴

¹Dr. Sivanthi Aditanar College of Engineering, Tiruchendur 628 215, India

²PSN College of Engineering and Technology, Tirunelveli 627 152, India

³Aditanar College of Arts & Science, Tiruchendur 628 216, India

⁴Loyola College, Nungambakkam, Chennai 600034, India

Abstract: The present study to investigate the effect of anionic surfactant, SDS on the ET reactions of Phenyl vinyl sulfide with $[\text{Fe}(\text{NN})_3]^{3+}$ by spectrophotometric techniques is more helpful to understand the role of electrostatic and hydrophobic interactions.

Keywords: Kinetic study, oxidation, Phenyl Vinyl Sulfide, Iron(III)-Polypyridyl complexes, Anionic Micelle.

Introduction

Several metal ions undergo efficient electron transfer reactions with organic sulfur compounds.¹⁻⁷ These metal ions easily form complexes with ligands like 1,10-phenanthroline and 2,2'-bipyridine. The study using these complexes becomes more interesting because both the electrostatic and hydrophobic interactions can be varied substantially in these ligands. Rajagopal and co-workers⁸ reported that the photo induced electron transfer reactions of Ru(II)-polypyridyl complexes with phenolate ions were highly influenced by the hydrophobic interactions of the reactants with the anionic and cationic surfactants. Balakumar et al⁹ demonstrated that the electron transfer reactions of iron(III)-polypyridyl complexes with alkyl and aryl sulfides were highly influenced by the hydrophobic interactions of the reactants with the anionic and cationic surfactants. The work carried out in a homogeneous aqueous system is far from being a realistic representation of the complexity of the heterogeneous system. So it is better to study the reaction in micelle, to understand the efficiency of redox reactions. Both electrostatic and hydrophobic interactions influence the reactivity and micelles are very good model systems to understand the role of these interactions in the biologically important processes.^{10,11} The present study to investigate the effect of anionic surfactant, SDS on the ET reactions of Phenyl vinyl sulfide with $[\text{Fe}(\text{NN})_3]^{3+}$ by spectrophotometric techniques is more helpful to understand the role of electrostatic and hydrophobic interactions.

Experimental

The reactions were carried out in the presence of SDS. As the reported critical micellar concentration of SDS is $8 \times 10^{-3} \text{ mol dm}^{-3}$ the reactions were carried out in the concentration range of 0.01 M - 0.12 M, i.e.,

above the CMC value. The kinetic measurements were performed under pseudo-first order conditions with Phenyl vinyl sulfide 15 folds in excess over the iron(III)-polypyridyl complexes in the presence and in the absence of anionic surfactant at 295 K. Due to the low solubility of Phenyl vinyl sulfide in aqueous media, the reactions in the presence of anionic surfactants were carried out in 5% CH₃OH-95% H₂O (v/v) for PVS. Bunton and co-workers¹²⁻¹⁴ have also used similar solvent system 1% CH₃CN-99% H₂O (v/v) to study the micellar effect on the IO₄⁻, and HSO₅⁻ oxidation of organic sulfides. Since the stability of iron(III) complexes are more in higher acid concentrations, 1.5 M HClO₄ was used in this study. The ionic strength was maintained using NaClO₄. 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 x 10⁴ M⁻¹ cm² in the wavelength region of 510-530 nm; [Fe(bpy)₃]²⁺(522nm), [Fe(phen)₃]²⁺(510nm),^{15,16} while the corresponding iron(III) complexes are practically transparent at this wavelength region.¹⁷ 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.

Results and Discussion

In the oxidation of PVS, retardation has been observed with increase in concentration of micelle as shown in Figure 1 and Table 1. The rate constant decreases with the increase in [SDS], reaches a minimum and then begins to increase at high [SDS]. The retardation of rate in micellar medium in the oxidation of PVS may be explained as follows.

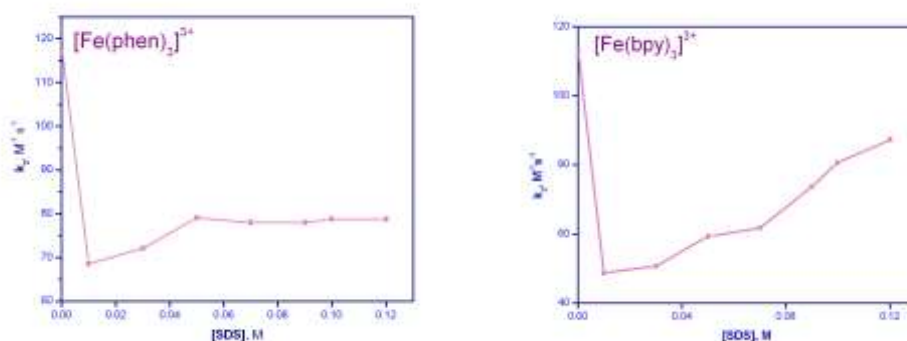


Fig. 1: Effect of [SDS] on [Fe(NN)₃]³⁺ oxidation of PVS

Table 1: Effect of changing [SDS] on the rate of [Fe(NN)₃]³⁺ oxidation of PVS CH₃OH- 5%, [H⁺]-1.5 M

[SDS]	k ₂ , M ⁻¹ s ⁻¹	
	[Fe(Phen) ₃] ³⁺	[Fe(bpy) ₃] ³⁺
0	118± 1.67	113± 8.78
0.01	68.6± 4.00	48.7± 8.67
0.03	72.1± 0.67	50.7± 7.56
0.05	79.1± 0.56	59.3± 1.41
0.07	78.0± 0.78	61.7± 1.17
0.09	78.0± 0.67	73.7± 1.71
0.1	78.8± 6.0	80.6± 1.13
0.12	78.8± 5.89	87.2± 0.67

There will be a competition between H⁺ and [Fe(NN)₃]³⁺ with SDS at high concentration of acid medium (1.5M H⁺). Since the concentration of H⁺ is very high compared to [Fe(NN)₃]³⁺, the binding constant of [Fe(NN)₃]³⁺ with SDS will be less compared to H⁺. The organic sulfides bind efficiently with anionic micelle and [Fe(NN)₃]³⁺ complex does not bind with SDS as both the reactants are present in two different medium.

Conclusion

The kinetics of oxidation of phenyl vinyl sulfide (PVS) with iron(III)-polypyridyl complexes was performed under pseudo-first order conditions in the presence and in the absence of anionic surfactant 295 K. Due to the low solubility of Phenyl vinyl sulfide in aqueous media, the reactions in the presence of anionic surfactants were carried out in 5% CH₃OH-95% H₂O (v/v) for PVS. The reactions were followed spectrophotometrically by measuring the increase in the absorbance of [Fe(NN)₃]²⁺ with time. The reaction of [Fe(NN)₃]³⁺ with PVS follows simple second order kinetics, first order each in iron(III)-polypyridyl complex and PVS. The rate of oxidation is accelerated by an increase in methanol content of the medium. Based on the experimental facts, a suitable mechanism involving single ET in the rate-determining step has been proposed. Marcus theory has been successfully applied to this reaction. The rate constant decreases with the increase in [SDS], reaches a minimum and then begins to increase at high [SDS]. The retardation of rate in micellar medium in the oxidation of PVS may be explained as follows. There will be a competition between H⁺ and [Fe(NN)₃]³⁺ with SDS at high concentration of acid medium (1.5M H⁺). Since the concentration of H⁺ is very high compared to [Fe(NN)₃]³⁺, the binding constant of [Fe(NN)₃]³⁺ with SDS will be less compared to H⁺. The observed rate constant in aqueous phase is always less than that of the reaction in micellar phase. Thus it is assumed that the major portion of the reaction takes place in the micellar pseudo phase. The observed same stoichiometry of 2:1 between [Fe(NN)₃]³⁺ and PVS, and the same product formed during the reactions in aqueous and micellar medium indicate the operation of same mechanism in both media. Phenyl vinyl sulfide radical cations are novel reaction intermediate and some reactions of these cations are attracting interest in organic synthesis.¹⁸The effects of anionic micelle in phenyl vinyl sulfide are useful for enzymatic and catalytic activity.

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