

Kinetic Study on the Oxidation of Phenyl Vinyl Sulfide with Iron(III)-Polypyridyl Complexes in the Presence of Non-Ionic Micelle

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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.¹⁻¹⁰ As micelles are considered to mimic the cellular membranes, the redox process occurring in the micellar system is considered as a model to obtain an insight into the redox process prevailing in body systems. The kinetics and mechanism of oxidation of benzyl alcohol by Cr (VI) has been studied in the presence of SDS, TX-100 and cetyl pyridinium chloride (CPC) medium. CPC was found to retard the rate while SDS and TX-100 show the rate acceleration effect.¹¹ The kinetics of oxidation of ascorbic acid by hexacyanoferrate(III) in acidic (HClO₄) medium and in the presence of a non-ionic surfactant (Brij-35) are reported by Shukla et al.⁸ In the present study, a detailed kinetic investigation has been made on the oxidation of phenyl vinyl sulfides by iron(III)- polypyridyl complexes in the presence of TX-100, a non-ionic micelle.

Experimental

The kinetics of the reaction between Phenyl Vinyl Sulfide with $[\text{Fe}(\text{NN})_3]^{3+}$ in the presence of non-ionic micelle, TX-100, was followed spectrophotometrically by measuring the increase in absorbance of $[\text{Fe}(\text{NN})_3]^{2+}$ with time. The reported critical micellar concentration of TX-100 is $3 \times 10^{-4} \text{M}$. Therefore the reactions were carried out above their CMC values i.e., in the range of 0.001 M to 0.15 M. All 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 of non-ionic micelle. As the reactions of PVS with $[\text{Fe}(\text{NN})_3]^{3+}$ is too fast to measure at room temperature, the reactions were carried out at 295 K.

Determination of binding constants

The values of the binding constant K_s of phenyl vinyl sulfide with non-ionic micelle were determined spectrophotometrically. The calculated binding constant obtained for PVS is 115 M^{-1} with TX-100. Bunton and coworkers^{12,13} have also reported the same range of binding constants, 80–340 M^{-1} for the organic sulfides with cationic micelle.

Results and Discussion

The kinetic study has been carried out by the oxidation of phenyl vinyl sulfide with $[\text{Fe}(\text{NN})_3]^{3+}$ in the presence of non-ionic micelle. The rate constant decreases with increase in [TX-100]. The pseudo first-order rate constant (k_1) for kinetic run was evaluated from the slope of $\log(A_\infty - A_t)$ vs time by the method of least

squares. The linearity of fit is confirmed from the values of correlation coefficient (r) and standard deviation (s). The second order rate constant (k_2) is evaluated from the relation, $k_2 = k_1 / [\text{PVS}]$. The precision of k values in the kinetic runs is given in terms of 95% confidence limits of the Student 't' test. The formation of product is phenyl vinyl sulfoxide has been proved by GC-MS analysis.

Table 1: Effect of changing [TX-100] on the rate of $[\text{Fe}(\text{phen})_3]^{3+}$ oxidation of phenyl vinyl sulfide $\text{CH}_3\text{OH} = 5\%$, $[\text{H}^+] = 1.5 \text{ M}$

[TX-100]	$[\text{Fe}(\text{Phen})_3]^{3+}$	$[\text{Fe}(\text{bpy})_3]^{3+}$
0	118 ± 1.67	132 ± 8.78
0.005	69.9 ± 1.77	45.0 ± 7.22
0.008	55.2 ± 2.67	39.9 ± 5.44
0.01	45.0 ± 3.22	37.7 ± 7.33
0.03	34.0 ± 2.89	36.9 ± 5.78
0.05	31.4 ± 2.44	35.8 ± 4.89
0.07	30.4 ± 1.00	33.2 ± 5.22
0.09	30.9 ± 1.11	31.4 ± 3.22
0.1	29.8 ± 1.30	29.4 ± 3.00
0.12	29.3 ± 1.78	-----
0.15	28.7 ± 1.78	

Evidence for the oxidation of sulfides is obtained from the GC-MS analysis of the product. A GC-MS product obtained for the oxidation of PVS with iron(III)-polypyridyl complexes is shown in Figure 1. The GC-MS data shows distinct peaks at m/z values 136 and 156 formed during the oxidation of PVS by iron(III)-polypyridyl complexes. It strongly confirms the conversion of phenyl vinyl sulfide ($m/z = 136$) to phenyl vinyl sulfoxide ($m/z = 156$).

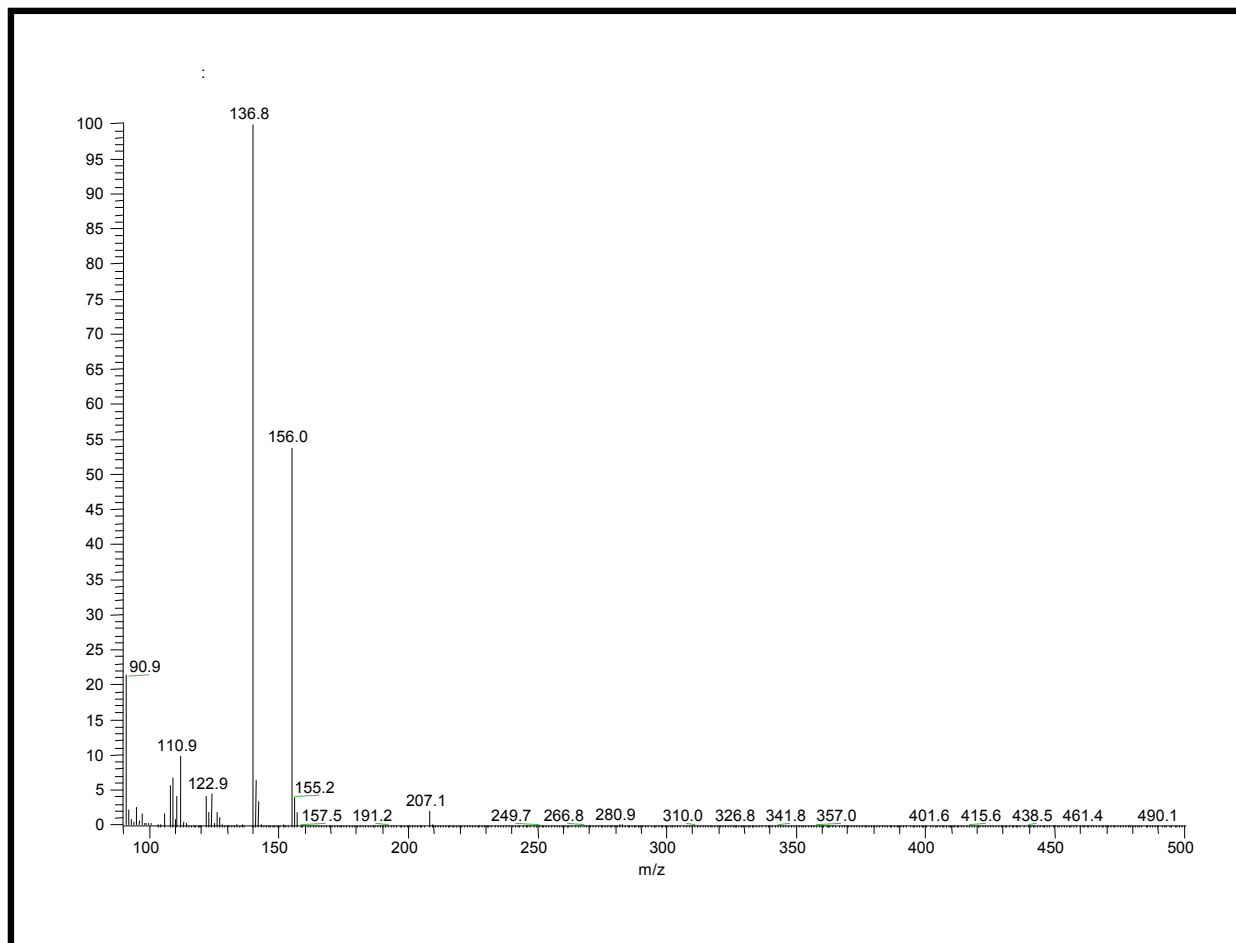


Figure 1: GC-MS data of products observed for the oxidation of PVS with $[\text{Fe}(\text{NN})_3]^{3+}$

The rate retardation has been observed in PVS oxidation as given in Table 1. The micellar inhibition by non-ionic micelle for PVS can be treated quantitatively in terms of the pseudo phase model that includes distribution of reactants between the aqueous and micellar phases. According to this model the first order rate constant in the micellar phase k_1 , is given by the eq. 1.

$$k_1 = [k_w + k_m K_s [D_n]] / (1 + k_s [D_n]) \quad (1)$$

where k_w and k_m are the first order rate constants in aqueous and micellar pseudo phases and K_s is the substrate binding constant written in terms of the concentration of micellized surfactant, $[D_n] = \{[TX-100] - CMC\}$.

In the present study in PVS oxidation, it is assumed that the cationic oxidant is totally excluded from the non-ionic micellar phase, $k_m \rightarrow 0$, then eq. 1 becomes

$$k_1 = k_w / (1 + k_s [D_n]) \quad (2)$$

By inverting eq.2

$$1 / k_1 = 1 / k_w + (K_s + k_w) [D_n] \quad (3)$$

The plots of $1 / k_1$ vs $[D_n]$ are given in Figure 2. If no reaction occurs in the micellar phase, the plots should be linear. Though the plot is linear at low $[TX-100]$, the values deviate significantly from linearity at higher $[D_n]$ values, i.e., greater than 0.03M. This deviation may be attributed to the reaction at micellar surface that is non-negligible at higher micellar concentrations.

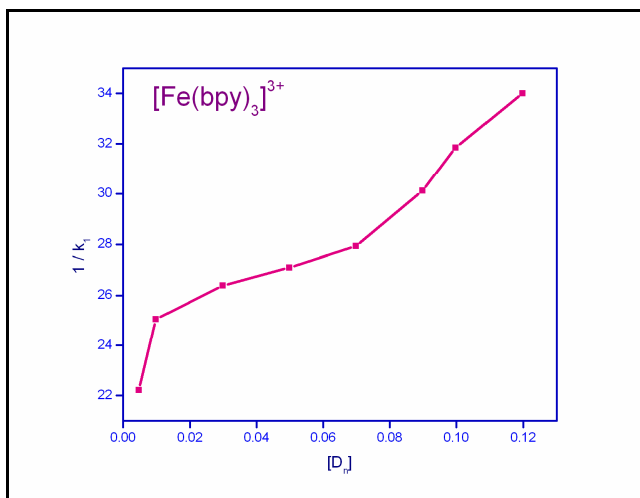
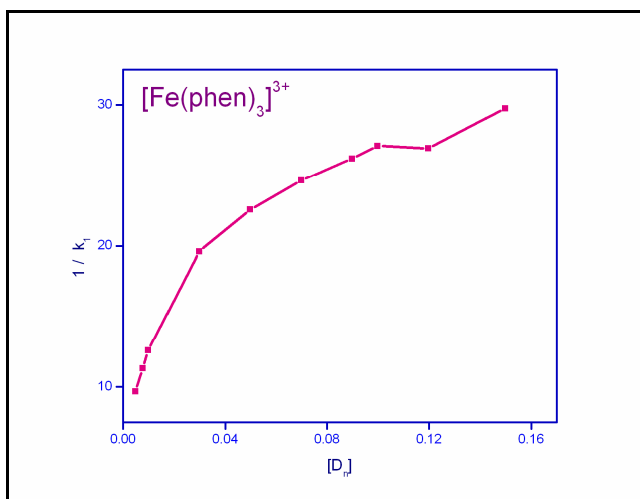


Figure 2: Plot of $1 / k_1$ vs $[D_n]$ for the $[Fe(NN)_3]^{3+}$ oxidation of PVS

Conclusion

The reason for the less reactivity of non-ionic micelle is the observed rate acceleration in the absence and presence of micelle is due to the favourable reaction condition in the micellar phase, where both substrate and the oxidant are preferably accumulated. Anionic micelle owing to the electrostatic attraction between the positively charged oxidant and negatively charged micellar head groups; the oxidant gets easily attached to the Stern layer of the micelle. In the case of TX-100, the amount of oxidant attached to the Stern layer is less compared to anionic micelle, as TX-100 is a non-ionic and there is no electrostatic attraction.

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