

Electron Transfer Reaction of Iron(III)-bipyridyl Complex with Diphenyl Sulfide

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The oxidation of diphenyl sulfide in aqueous methanol at constant $[H^+]$ and ionic strength with iron(III)-bipyridyl complex has been investigated under pseudo first order condition by spectrophotometric technique. The reaction follows first order kinetics with respect to substrate and oxidant and proceeds through rate determining electron transfer (ET) from organic sulfide to iron(III). The rate constant values are observed for organic sulfide with oxidant $Fe(bpy)_3^{3+}$. The product of oxidation is sulfoxide.

Key Words: Electron transfer reaction, Iron(III)-bipyridyl complex, Diphenyl sulfide.

INTRODUCTION

The important role of sulfur compounds and, in particular, sulfur centered radicals in biological systems is now well established^{1,2}. As a consequence much attention has been paid to the chemistry of these species. Organic sulfides are interesting substrates. The electron transfer reaction of biologically important organic sulfides with several metal ions to generate sulfide radical cations has been extensively studied³⁻¹⁴. This sulfide radical cation in the presence of water produces sulfoxide as one of the major products. The formation of a sulfide radical cation as an intermediate during sulfide oxidation to sulfoxide has been identified by flash photolysis¹⁵⁻¹⁸. In biological systems the reduction of Fe(III)-Fe(II) by biological reductants is a well known phenomenon^{19,20}. Porphyrin and polypyridyl complexes of Fe(III) have been synthesized as model compounds and used as electron acceptors from biological reductants²¹⁻²⁴. Electron transfer reaction is highly sensitive to the structure of aromatic sulfide as well as the structure of the ligand of the Fe(III)-polypyridyl complexes³. In order to understand the role of organic sulfides as electron donors towards Fe(III) complexes, we have extended the study of electron transfer reaction to iron(III)-bipyridyl complex with diphenyl sulfide by spectrophotometric technique and the observed results are presented in this studies.

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EXPERIMENTAL

The ligand 2,2'-bipyridine and iron(II)-sulfate were obtained from Aldrich and used as such. Tris(2,2'-bipyridine)iron(II) was prepared by known procedures^{3,25,26}. The iron(III) complex was obtained by the oxidation of iron(II) complex with lead dioxide in 1 M H₂SO₄. The iron(III) complex was precipitated as perchlorate salts. The purity of the iron(II) and iron(III) complexes were checked by IR and UV-visible spectra and compared with the literature data. Stock solutions of the iron(III) complex was made up in concentrated HClO₄. Such solutions were diluted with aqueous methanol to the desired acid strength immediately before each kinetic run. All other reagents used were of Analar grade and solvents (methanol and water) were purified by known procedures before use²⁷.

Kinetic measurement: The iron(II)-bipyridyl complex have molar extinction coefficients of the order of $1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in the wavelength region 522 nm. On the other hand, the corresponding iron(III) complex is practically transparent at this wavelength region^{3,25,26}. The kinetics of Fe(bpy)₃³⁺ oxidation of diphenyl sulfide was followed spectrophotometrically under pseudo first order condition at 298 K by measuring the increase in absorbance of Fe(bpy)₃²⁺ with time³. A sample kinetic run is shown in Fig. 1. The absorption spectral studies were carried out on ELICO SL-164 Double Beam UV-visible spectrophotometer. The plots of $\log(A_\infty - A_t)$ versus time were linear and the pseudo first order rate constant, k_1 values were calculated by least squares method. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 5\%$. Here A_∞ is the final absorbance at the completion of the reaction and A_t is the absorbance at time t . The second order rate constant, k_2 , values were obtained from the equation, $k_2 = k_1/[\text{substrate}]$.

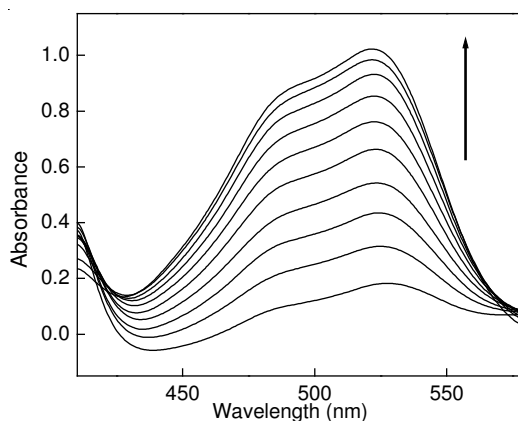


Fig. 1. Increase in absorbance

Product analysis: The inorganic product under kinetic conditions was confirmed to be Fe(bpy)₃²⁺ from the increase in absorbance at 522 nm characteristic of Fe(bpy)₃²⁺. To identify the organic product, the solution after the completion of the

reaction was extracted with chloroform and dried with anhydrous sodium sulfate. After evaporating the solvent, the sample was subjected to GC analysis and the product was found to be the corresponding sulfoxide. This was also confirmed from the analysis of the product with IR spectroscopy and ¹H NMR. In IR spectroscopy, the peak at wavelength 1082 cm⁻¹ (Fig. 2) confirms the presence of sulfoxide. In the ¹H NMR study the aromatic protons appear as multiplets centered at 7.34 and 7.45 ppm this is the case with sulfoxide. If sulfone is the product, the aromatic proton will show a multiplet centre at 8 and at 8.1 ppm. The result of the study confirms sulfoxide as the product.

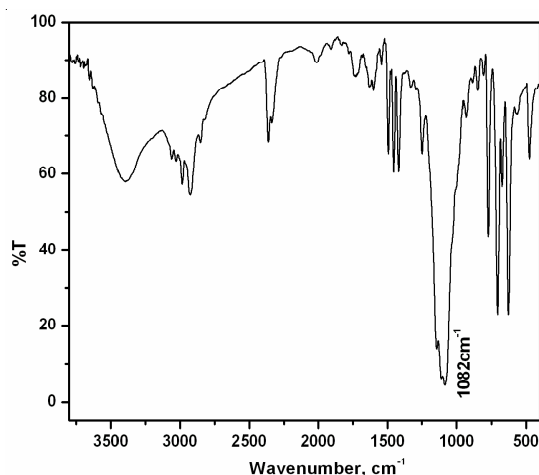


Fig. 2. IR spectrum of the product

Stoichiometry: The stoichiometry of the reaction was determined by taking different ratios of oxidant and substrate concentrations. The study indicated that 1 mol of sulfide was consumed/2 mol of Fe(bpy)₃³⁺ in accordance with eqn. 1.



RESULTS AND DISCUSSION

Pseudo first order (k₁) and second order rate constants (k₂) for the oxidation of diphenyl sulfide by Fe(bpy)₃³⁺: The kinetics of electron transfer from diphenyl sulfide to Fe(bpy)₃³⁺ complex has been studied spectrophotometrically by taking diphenyl sulfide (DPS) as the substrate. A sample run is shown in Fig. 1. The reaction is found to be first order in the substrate and first order in the oxidant. The plots of the log (A_∞ - A_t) versus time for different concentrations of diphenyl sulfide are shown in Fig. 3. The constancy in the k₂ values in Table-1 and the linear plot of log k₁ versus log [DPS] with a slope of 0.997 ± 0.01 (Fig. 4) indicate the first order dependence of the reaction on diphenyl sulfide. The plot of 1/k₁ versus 1/[DPS] is linear (Fig. 5: r = 0.999) and passes through the origin. This result excludes the

TABLE-1
PSEUDO FIRST ORDER AND SECOND ORDER RATE CONSTANTS
FOR THE OXIDATION OF DIPHENYL SULFIDE (DPS) BY $\text{Fe}(\text{bpy})_3^{3+}$
[$\text{Fe}(\text{bpy})_3^{3+}$] = 1×10^{-4} M, H^+ = 0.5 M, μ = 0.7 M, CH_3OH = 60 % (v/v), Temp = 30 °C

[DPS] 10^3 (M)	$k_1 \times 10^3$ (S^{-1})	$k_2 \times 10$ ($\text{M}^{-1} \text{S}^{-1}$)
1.5	0.694 ± 0.04	0.463 ± 0.03
3.0	1.400 ± 0.93	0.465 ± 0.31
4.5	2.100 ± 0.13	0.466 ± 0.03
6.0	2.790 ± 0.18	0.464 ± 0.03
7.5	3.500 ± 0.19	0.467 ± 0.03
9.0	4.190 ± 0.21	0.466 ± 0.02
15.0	6.910 ± 3.82	0.461 ± 0.26
18.0	8.310 ± 0.24	0.462 ± 0.02

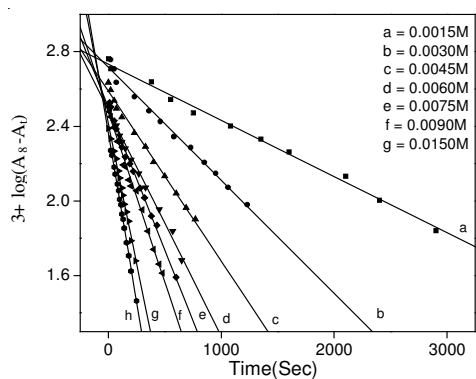


Fig. 3. Variation of [DPS] on the reaction rate

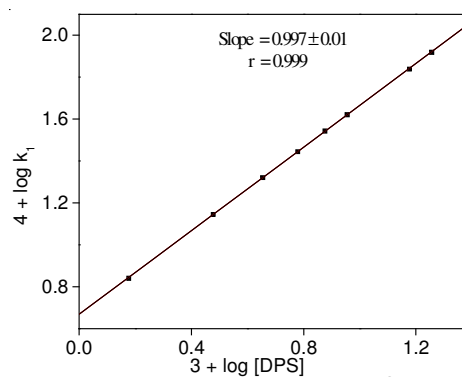


Fig. 4. Plot of log k versus log [DPS]

formation of complex between diphenyl sulfide and $\text{Fe}(\text{bpy})_3^{3+}$. When the concentration of oxidant is varied the k_1 values obtained remain constant indicating first order dependence in the $\text{Fe}(\text{bpy})_3^{3+}$ (Table-2). This is confirmed from the straight lines obtained for $\log(A_\infty - A_t)$ versus time plot (Fig. 6).

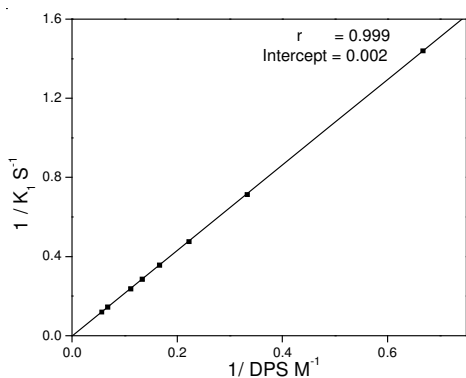
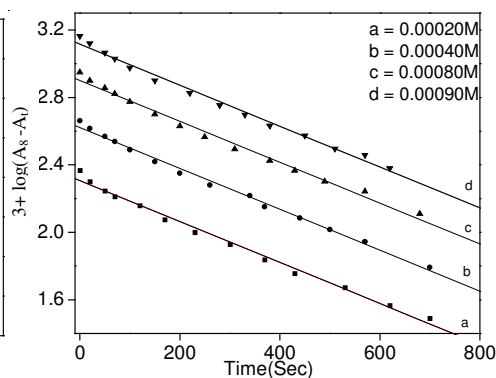
Fig. 5. $1/k_1$ versus $1/[\text{DPS}]$ Fig. 6. $[\text{Fe}(\text{bpy})_3]^{3+}$ Variation

TABLE-2
EFFECT OF CHANGING [Fe(bpy)₃³⁺]
[DPS] = 9 × 10⁻³ M, H⁺ = 0.5 M, μ = 0.7 M, CH₃OH = 60 % (v/v), Temp = 30 °C

[Fe(bpy) ₃ ³⁺] × 10 ⁴ M	k ₁ × 10 ³ (S ⁻¹)
2.0	2.79 ± 0.17
4.0	2.79 ± 0.13
7.0	2.78 ± 0.18
8.0	2.79 ± 0.14
9.0	2.79 ± 0.17

Effect of changing [H⁺], solvent composition, ionic strength, [bpy], [Fe(bpy)₃²⁺]: The results of changing [H⁺], solvent composition, ionic strength and the addition of bpy and Fe(bpy)₃²⁺ are given in Table-3. The rate of the reaction is affected by the change in [H⁺]. As [H⁺] increases the rate of the reaction decreases. This is expected as explained in the mechanism where H⁺ is released in the reaction process. Therefore any increase in [H⁺] will hinder the rate of the reaction. The increase in the methanol content of the reaction mixture favours the reaction. This indicates that the amount of solvent plays an important role in the rate of the reaction. The transient sulfur cation radical may be stabilized by the solvent. The increase in the ionic strength of the medium slightly decreases the rate of the reaction. Also the rate of the reaction slightly increases with the addition of the ligand bipyridine and the product Fe(bpy)₃²⁺.

TABLE-3
EFFECT OF CHANGING THE SOLVENT COMPOSITION, [H⁺], IONIC STRENGTH, bpy, Fe(bpy)₃²⁺ ON THE OXIDATION OF Fe(bpy)₃³⁺ WITH DIPHENYL SULFIDE (DPS)
[DPS] = 9 × 10⁻³ M, [Fe(bpy)₃³⁺] = 6 × 10⁻⁴ M, Temp = 30 °C

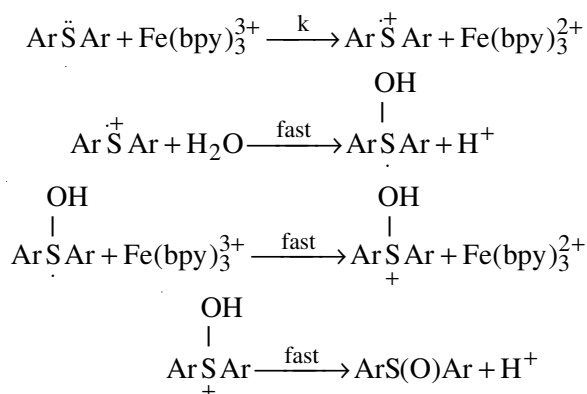
[H ⁺] (M)	k ₁ × 10 ³ (S ⁻¹)	CH ₃ OH (%) (v/v)	k ₁ × 10 ³ (S ⁻¹)	μ (M)	k ₁ × 10 ³ (S ⁻¹)	bpy (10 ³) (M)	k ₁ × 10 ³ (S ⁻¹)	Fe(bpy) ₃ ²⁺ × (10 ⁶) (M)	k ₁ × 10 ³ (S ⁻¹)
0.5	2.33 ± 0.07	40	2.11 ± 0.18	0.9	2.67 ± 0.16	1.0	2.83 ± 0.10	0.8	2.79 ± 0.18
0.6	2.27 ± 0.10	50	2.33 ± 0.12	1.1	2.33 ± 0.07	5.0	2.85 ± 0.06	1.0	2.83 ± 0.10
0.7	2.21 ± 0.07	55	2.53 ± 0.15	1.3	1.87 ± 0.05	7.0	2.88 ± 0.09	3.0	2.88 ± 0.13
0.8	2.13 ± 0.17	65	3.57 ± 0.16	1.5	1.72 ± 0.10	10.0	2.99 ± 0.09	5.0	3.09 ± 0.15
0.9	2.05 ± 0.10	70	4.17 ± 0.18			12.0	3.16 ± 0.10	7.5	3.10 ± 0.13
1.0	1.87 ± 0.04	75	4.47 ± 0.21			15.0	3.25 ± 0.12		
		80	4.79 ± 0.19						

Effect of temperature: The electron transfer reaction of diphenyl sulfide with Fe(bpy)₃³⁺ is studied at four different temperatures and the values of rate constants are given in Table-4. The enthalpy of activation ΔH[#] and the entropy of activation ΔS[#] are evaluated from the linear Eyring's plot of log k₂/T versus 1/T. The activation parameters are presented in Table-4. The positive ΔH[#] value and negative ΔS[#] value shows that the reaction is thermodynamically feasible.

TABLE-4
PSEUDO FIRST ORDER AND SECOND ORDER RATE CONSTANTS
FOR THE OXIDATION OF DIPHENYL SULFIDE (DPS) BY $\text{Fe}(\text{bpy})_3^{3+}$
[DPS] = 9×10^{-3} M, $[\text{Fe}(\text{bpy})_3^{3+}] = 6 \times 10^{-4}$ M, $\text{H}^+ = 0.5$ M, $\mu = 0.7$ M, $\text{CH}_3\text{OH} = 60\%$ (v/v)

Temperature (°C)	$k_2 \times 10^3 \text{ M}^{-1}\text{S}^{-1}$	ΔH^\ddagger (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)
20	0.871 ± 0.12		
25	1.290 ± 0.05	65.86 ± 5.76	78.97 ± 20.1
35	3.850 ± 0.28		
40	4.910 ± 0.32		

To account for the above results a mechanism shown in **Scheme-I**, similar to the study of Balakumar *et al.*³ for the reaction of $\text{Fe}(\text{bpy})_3^{3+}$ with organic sulfides, has been proposed. Generally the outer sphere oxidants, $\text{Fe}(\text{bpy})_3^{3+}$, undergo reaction with electron donors by first order kinetics with rate limiting electron transfer to generate an organic radical ion. In the presence of strong oxidants like $\text{Fe}(\text{bpy})_3^{3+}$, the driving force for back electron transfer is diminished resulting in the long lifetime of the radical cation ArS^+Ar .



Scheme-I

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