Pergamon

SCIENCE DIRECT®

TETRAHEDRON

Tetrahedron 59 (2003) 3613–3619

Electron transfer reactions of iron(III)-polypyridyl complexes with organic sulfoxides

Kulandai John Adaikalasamy,[a] Natarajan Sathiyamoorthy Venkataramanan[b] and Seenivasan Rajagopal[b,*]

[a]*Department of Chemistry, The American College, Madurai 625002, India*
[b]*School of Chemistry, Madurai Kamaraj University, Palkalai Nagar, Madurai 625021, India*

Received 13 December 2002; revised 6 March 2003; accepted 27 March 2003

Abstract—The redox reactions of four iron(III)-polypyridyl complexes with six aryl methyl sulfoxides have been investigated by spectrophotometric technique. The reaction follows clean second order kinetics and proceeds through rate determining electron transfer (ET) from organic sulfoxides to iron(III). The Marcus cross-reaction relation has been applied to obtain the self exchange rate constant for the ArSOR/ArS$^{\cdot+}$(O)R couple as 1.3×10^7 M^{-1} s^{-1}. The application of Marcus theory to this ET reaction shows that the contribution of inner sphere reorganization energy is 0.4 eV. The rate constant and reaction constant values observed with organic sulfoxides are small compared with organic sulfides towards the same oxidant $Fe(NN)_3^{3+}$. © 2003 Published by Elsevier Science Ltd.

1. 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. The electron transfer (ET) reaction of biologically important organic sulfides with several metal ions to generate sulfide radical cations has been extensively studied.[3–14] This sulfide radical cation in the presence of water produces sulfoxide as one of the major products. On the other hand little attention has been paid to the next stage of oxidation i.e. one electron oxidation of organic sulfoxides to the corresponding sulfoxide radical cation. The formation of a sulfide radical cation as an intermediate during sulfide oxidation to sulfoxide has been recently identified by flash photolysis.[15–18] As far as we know, no report is available on the detection of the sulfoxide radical cation by flash photolysis. However EPR has been extensively applied for the detection of sulfoxide radical cations.[1] Recently we have studied the oxidation of organic sulfoxides with powerful one electron oxidants, Ru(III)-polypyridyl complexes, and detected the formation of the sulfoxide radical cation by conventional flash photolysis.[9]

In biological systems the reduction of Fe(III) to Fe(II) by biological reductants is a well known phenomenon.[19,20] For example the detailed study on the reduction of Fe(III) bound to transferrin at low pH is of considerable importance in gaining an understanding of the physiological activity of the iron transport protein, transferrin. In order to understand the mechanism of this ET reaction, Fe(III)→Fe(II), porphyrin and polypyridyl complexes of Fe(III) have been synthesized as model compounds and used as electron acceptors from biological reductants.[21–24] Realizing the importance of organic sulfides and sulfoxides as reductants in biological systems we have investigated the ET reaction of iron(III)-polypyridyl complexes with organic sulfides and this ET reaction is highly sensitive to the structure of aromatic sulfide as well as the structure of the ligand of the Fe(III)-polypyridyl complexes.[3] The experimentally determined rate constants for this ET reaction agree well with the rate constants estimated from the Marcus cross-reaction relationship. In order to understand the role of organic sulfoxides as electron donors towards Fe(III) complexes, we have extended the study of ET reactions to several iron(III)-polypyridyl complexes with six *para*-substituted phenyl methyl sulfoxides by spectrophotometric technique and the observed results are presented in this article.

2. Results

The structure of the ligands and the abbreviations of iron(III) complexes used in the present study are shown in Chart 1.

The kinetics of ET from six aryl methyl sulfoxides to four iron(III) complexes, $Fe(NN)_3^{3+}$ (NN=2,2′-bipyridine,4,4′-dimethyl-2,2′-bipyridine,1,10-phenanthroline, and 4,7-

---

Keywords: iron(III)-polypyridyl complexes; methylphenyl sulfoxides; Marcus cross-reaction.

* Corresponding author. Tel.: +91-0452-2458246; fax: +91-0452-2459139; e-mail: seenirajan@yahoo.com

0040–4020/03/$ - see front matter © 2003 Published by Elsevier Science Ltd.
doi:10.1016/S0040-4020(03)00509-X

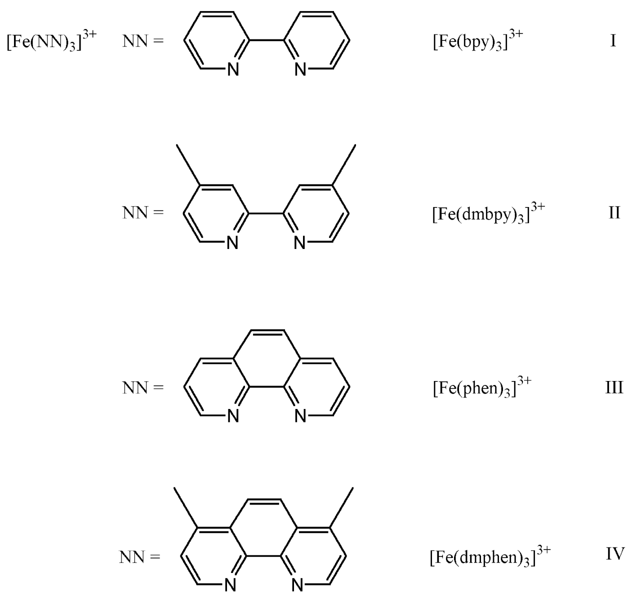


Chart 1. Structure of the ligands and abbreviations of iron(III) complexes.

dimethyl-1,10-phenanthroline), $Fe(bpy)_3^{3+}$, $Fe(dmbpy)_3^{3+}$, $Fe(phen)_3^{3+}$ and $Fe(dmphen)_3^{3+}$, respectively, has been studied spectrophotometrically by taking methyl phenyl sulfoxide MPSO) as the sample substrate. A sample run is shown in Figure 1.

The reaction is of total second order, first order in the oxidant and in the substrate. The first order dependence in the oxidant is understood from the linear $\log(A_\infty - A_t)$ vs time plots. The first order dependence in the substrate is confirmed from the linear k_1 vs [substrate] plot (Fig. 2).

The rate of the reaction is little affected by the change in [H^+] but the increase in the ionic strength of the medium decreases the rate slightly. The increase in the methanol content of the H_2O–CH_3OH mixture favors the reaction (Table 1). The study of substituent effect with several *para*-substituted phenyl methyl sulfoxides shows that the rate of the reaction is accelerated by electron donating groups and retarded by electron withdrawing substituents present in the phenyl ring of PhS(O)Me (Table 2). The Hammett plot drawn for the kinetic data obtained for the oxidation p-$XC_6H_4S(O)Me$ with $Fe(phen)_3^{3+}$ shows satisfactory correlation (r=0.92) with sigma values and the ρ value is -1.0. However the correlation is improved if $\log k_2$ values are plotted against Brown–Okamoto's σ^+ values and the sample plot is shown in the Figure 3 and ρ^+ value is -0.8. The negative ρ^+ value indicates that the sulfoxides is partially positively charged in the transition state.

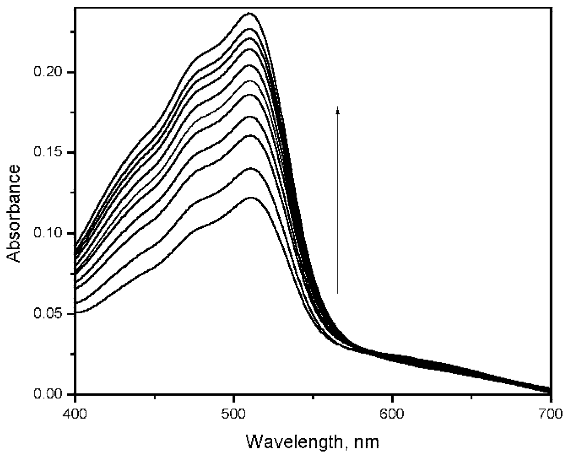


Figure 1. Increase in the absorbance of $Fe(phen)_3^{2+}$ formed from the reaction of $Fe(phen)_3^{3+}$ (2×10^{-4} M) with MPSO (2×10^{-3} M) in aqueous methanol (50% v/v) at 298 K at a time interval of 50 s.

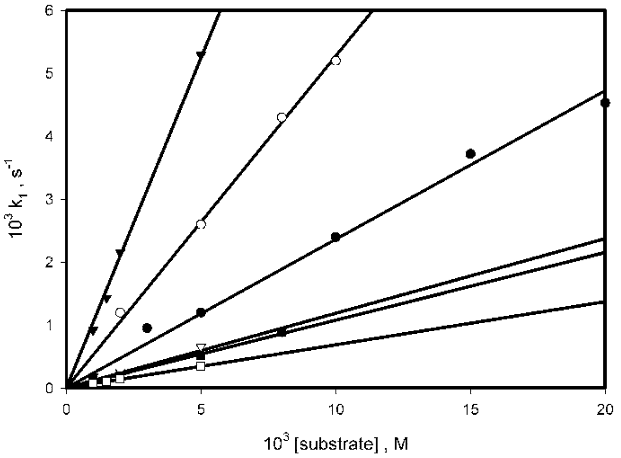


Figure 2. Plot of k_1 vs [sulfoxide] for the oxidation of p-$XC_6H_4S(O)Me$ with $Fe(phen)_3^{3+}$ in aqueous methanol (50% v/v) at 298 K.; ●=H; ○=–Me; ▼=–OMe; △=–Cl; ■=–Br; □=–NO_2.

Similar linear $\log k_2$ vs σ^+ plots were obtained for the oxidation of sulfoxides with other $Fe(NN)_3^{3+}$ complexes and the ρ^+ values are given in Table 2.

3. Discussion

The Fe(III)-polypyridyl complexes are well established one electron oxidants.[25,26] The observation of sulfoxide radical cation as a transient species in our recent study[9] with Ru(III)-polypyridyl complexes prompts us to postulate that the same sulfoxide cation radical would have been formed during the one electron oxidation of sulfoxides with Fe(III)-polypyridyl complexes. Further, the observation of isobestic point at 580 nm for the reduction of Fe(III) to Fe(II) (Fig. 1) points out that the conversion proceeds neatly without any intermediate and confirms that the reaction follows simple kinetics without involving any complex mechanism. These experimental observations are strongly in favor of ET from sulfoxide to Fe(III)-complex in the rate determining step. The additional support for the ET mechanism comes form the substituent effect study. The ρ^+ observed here (-0.8) is just one fourth of the ρ^+ value (-3.2) observed for the $Fe(NN)_3^{3+}$ oxidation of aryl methyl sulfides. An ET mechanism involving rate determining ET from sulfide to $Fe(NN)_3^{3+}$ has been proposed in our previous study.[3] This low ρ^+ value obtained with aryl methyl sulfoxides is understandable as sulfoxides are less powerful nucleophiles compared to sulfides, because of polar S–O bond.

To account for the above spectral and kinetic results a mechanism shown in Scheme 1, (Eqs. (1)–(4)) similar to the one postulated, in our previous report,[3] for the reaction of $Fe(NN)_3^{3+}$ with organic sulfides, has been proposed.

Table 1. Effect of changing the solvent composition, $[H^+]$ and ionic strength on the $Fe(NN)_3^{3+}$ oxidation of $C_6H_5S(O)Me$ at 298 K

% CH_3OH	$k_1\times10^4$ (s^{-1})[a]		$[H^+]$ (M)	$k_1\times10^4$ (s^{-1})[b]		μ (M)	$k_1\times10^4$ (s^{-1})[a]	
	$Fe(bpy)_3^{3+}$	$Fe(phen)_3^{3+}$		$Fe(bpy)_3^{3+}$	$Fe(phen)_3^{3+}$		$Fe(bpy)_3^{3+}$	$Fe(phen)_3^{3+}$
10	3.8±0.03	3.5±0.06	0.5	3.3±0.05	4.0±0.02	0.5	5.4±0.04	6.0±0.16
20	4.2±0.02	5.0±0.08	0.6	3.0±0.09	3.9±0.03	0.6	5.2±0.08	5.3±0.04
40	6.6±0.04	7.0±0.01	0.7	2.7±0.03	3.8±0.03	0.7	4.3±0.06	4.8±0.03
50	7.4±0.04	8.1±0.16	0.8	2.7±0.03	3.8±0.03	0.8	3.9±0.06	4.4±0.03
60	10.6±0.17	9.9±0.18	0.9	2.6±0.04	3.7±0.02	0.9	3.4±0.05	4.2±0.03
80	13.1±0.23	14.2±0.17	–	–	–	1.0	3.3±0.05	4.0±0.02

[a] General conditions: $[MPSO]=2\times10^{-3}$ M; $[Fe(NN)_3^{3+}]=1\times10^{-4}$ M; solvent=50% (v/v) aqueous methanol $[H^+]=0.5$ M.
[b] General conditions: $[MPSO]=2\times10^{-3}$ M; $[Fe(NN)_3^{3+}]=1\times10^{-4}$ M; solvent=50% (v/v) aqueous methanol $[\mu]=1.0$ M.

Table 2. Second order rate constant ($10k_2$, M^{-1} s^{-1}) values for the oxidation of *p*-$XC_6H_4S(O)Me$ by $Fe(NN)_3^{3+}$ in 50% (v/v) aqueous methanol at 298 K

p-$XC_6H_4S(O)Me$ (X=)	E_{ox} V(SCE)	$Fe(phen)_3^{3+}$		$Fe(bpy)_3^{3+}$		$Fe(dmphen)_3^{3+}$		$Fe(dmbpy)_3^{3+}$	
		Obs	Cal	Obs	Cal	Obs	Cal	Obs	Cal
H	1.73	3.0±0.08	5.0	2.7±0.02	4.1	0.1±0.01	0.48	0.08±0.00	0.41
Me	1.62	6.0±0.18	42.0	4.2±0.10	34.9	0.3±0.02	4.09	0.28±0.04	3.47
OMe	1.51	9.8±0.14	361	8.6±0.11	297	0.5±0.03	34.9	0.36±0.01	29.5
Cl	1.81	1.4±0.02	1.3	1.3±0.09	1.1	0.1±0.01	0.12	0.07±0.01	0.10
Br	1.81	1.0±0.01	1.3	1.2±0.08	1.1	0.1±0.01	0.12	0.09±0.01	0.10
NO_2	–	0.7±0.01	–	0.7±0.01	–	0.08±0.0	–	0.06±0.01	–
ρ^+		−0.80±0.23		−0.80±0.19		−0.58±0.10		−0.56±0.09	
r		0.95		0.97		0.97		0.92	

$[Fe(NN)_3^{3+}]=1\times10^{-4}$ M.

Generally the outer sphere oxidants, $Fe(NN)_3^{3+}$, undergo reaction with electron donors by second order kinetics with rate limiting ET to generate an organic radical ion. In the presence of strong oxidants like $Fe(NN)_3^{3+}$, the driving force for back ET is diminished resulting in the long lifetime of the radical cation $ArS^{+\cdot}(O)Me$. Consequently, the sulfoxide radical cation may undergo other types of reactions, either fragmentation or reaction with $Fe(NN)_3^{3+}$ or solvent in competition with back ET.[27–30] The formation of sulfone as the major product helps us to conclude that the major portion of sulfoxide radical cation is consumed by the solvent, water, though fragmentation and back ET may be competing processes. Further, a good agreement between the experimentally observed second-order rate constants and the values calculated by Marcus theory also supports the proposed mechanism (vide infra).

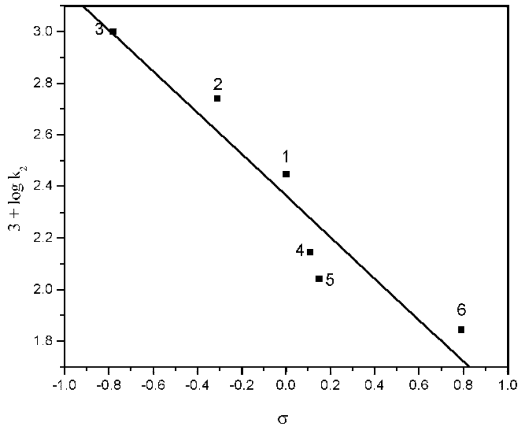
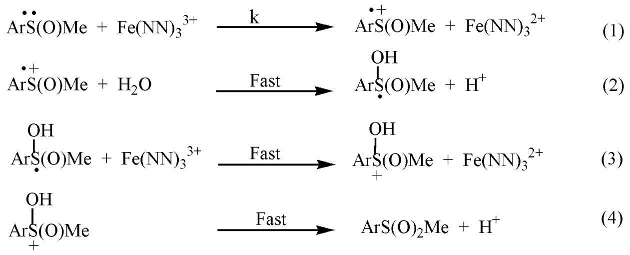


Figure 3. Hammett plot for the oxidation of *p*-$XC_6H_4S(O)Me$ by $Fe(phen)_3^{3+}$ in aqueous methanol (50% v/v) at 298 K; 1=H; 2=–Me; 3=–OMe; 4=–Cl; 5=–Br; 6=–NO$_2$.



Scheme 1.

3.1. Application of Marcus cross-reaction relation

Marcus[31] introduced the concept that the rate constant for ET from the electron donor (S) to the acceptor (M^+) (Eq. (5)), k_{12}, could be calculated from the intrinsic reactivity of the redox couples involved, the self-exchange rate constants, k_{11} ($M^+\rightarrow M$) and k_{22} ($S\rightarrow S^+$) at zero driving force and the thermodynamics for ET between the couples.

$$S + M^+ \xrightarrow{k_{12}} S^+ + M \tag{5}$$

Here M^+ represents $Fe(NN)_3^{3+}$, the oxidant, and S represents ArS(O)Me, the substrate undergoing oxidation.

The thermodynamic data for the reaction can be estimated from the redox potentials of M^+ and S when the couples are stable enough that k_{12} can be experimentally measured. The simple form of Marcus's cross-reaction relation is given in Eqs. (6a) and (6b)

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \tag{6a}$$

$$\ln f_{12} = [\ln(K_{12})]^2/[(4 \ln k_{11}k_{22})/Z^2] \tag{6b}$$

The self-exchange rate constants, k_{11} and k_{22} and the

Table 3. Second order rate constant (k_2) values and activation parameters for the oxidation of p-$XC_6H_4S(O)Me$ by $Fe(phen)_3^{3+}$ in aqueous methanol (50% v/v) at three different temperatures

No.	p-$XC_6H_4S(O)Me$ (X=)	$10k_2$ ($M^{-1}\ s^{-1}$)			$\Delta H^{\neq}$ (kJ mol^{-1})	$-\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
		298 K	308 K	318 K			
1	H	3.0±0.08	6.2±0.20	11.0±0.28	48.5±1.2	91.2±0.9	76.6±0.9
2	Me	6.0±0.18	10.0±0.31	22.0±0.41	48.5±3.6	86.6±2.5	74.9±2.7
3	Cl	1.4±0.02	2.5±0.07	6.0±0.15	57.3±3.8	69.0±2.7	79.1±2.9
4	Br	1.0±0.00	2.2±0.07	4.1±0.10	54.8±1.4	79.0±1.0	79.1±0.3
5	NO_2	0.7±0.01	1.2±0.02	2.0±0.06	38.9±0.1	137±1.0	80.7±0.1

equilibrium constant K_{12} are the principal parameters determining k_{12}. The term Z is the pre-exponential factor which is often taken as $10^{11}\ M^{-1}\ s^{-1}$ (Table 3).

The more general form of Eqs. (6a) and (6b) including work terms has successfully been applied to a variety of inorganic, organic, organometallic and biochemical reactions.[27–35]

Eqs. (6a) and (6b) were derived assuming that ET reactions are adiabatic which requires the pre-exponential factor in the expression $k_{12}=Z\,e^{-\Delta G\#/RT}$ to be a constant and the rate constant to be controlled by the activation barrier. The fundamental assumption in deriving Eqs. (6a) and (6b) was that averaging the activation barriers for self-exchange reactions produced the proper activation barrier for the cross-reaction.[30] Recently, it has been established that the great majority of ET reactions are non-adiabatic.[36] Non-adiabatic reaction rate constants are controlled by activation barriers as well as by the widely varying pre-exponential factors (Eqs. (7a) and (7b))

$$k_{12} = |H_{DA}|^2 e^{-s}\ \nu_n \exp[-\Delta G^{\neq}/k_B T] \tag{7a}$$

where

$$\Delta G^{\neq} = (\Delta G^0 + \lambda)^2/4\lambda \tag{7b}$$

In Eqs. (7a) and (7b) $|H_{DA}|^2$ is the ET orbital overlap integral squared and s is the vibronic coupling constant which is the ratio of $h\nu_v$ to the internal vibrational component of λ, λ_v where λ is the reorganization energy.[30] The terms ΔG^0 and $\Delta G^{\neq}$ are the standard free energy change and free energy of activation, respectively. Eq. (7b) is called the Marcus equation. In addition to the vertical reorganization energy (λ) that controls the rate constant for adiabatic ET, the size of the electronic interaction between the reactants at the ET transition state (also called the electronic coupling matrix element, H_{DA}) and the energy corresponding to the inherent barrier-crossing frequency (ν_v) are important in determining the rate constant for non-adiabatic reactions. Despite the predictions of modern theory by Bixon and Jortner,[36] Nelsen et al.[30,37] have applied Eqs. (6a) and (6b) successfully for the calculation of rate constants, k_{12}, for 141 reactions having couples of a wide range of structural types. Since Eqs. (6a) and (6b) are successful in accounting for ET reactions for couples that have a wide range of structural types including heteroatom substituted aromatics we have attempted to apply this equation to the titled reaction to get the self-exchange rate of $>S^+O/>SO$ couple. The value of self-exchange rate of $Fe(NN)_3^{3+}/Fe(NN)_3^{2+}$ couple is known from previous studies of Sutin et al.[27] as $3.3\times10^8\ M^{-1}\ s^{-1}$. The high self-exchange rates observed with $[M(NN)_3]^{3+/2+}$ (M=Fe, Ru and Os) complexes is accounted for by Sutin et al.[27] and others. On taking logarithms Eq. (6a) becomes Eq. (8)

$$\log k_{12} - 0.5 \log k_{11} - 0.5 \log f_{12} = 0.5 \log k_{22} + 0.5 \log K_{12} \tag{8}$$

In Eqs. (6a) and (6b), the value of K_{12} is calculated from the redox potentials of the couples $Fe(NN)_3^{3+}/Fe(NN)_3^{2+}$ and $>S^+O/>SO$ using Eqs. (9) and (10).

$$\Delta G^0 = nF(E_{S^+O/SO} - E^0_{Fe^{3+}/Fe^{2+}}) \tag{9}$$

$$K_{12} = \exp(-\Delta G^0/RT) \tag{10}$$

The value of k_{22} for $>S^+O/>SO$ couple can be estimated from an iterative procedure i.e. a value of k_{22} is guessed and plugged into Eq. (8) to calculate f. With the calculated value of $\log f$, a plot of left hand side of Eq. (8) vs $\log K_{12}$ is made and from mean least squares calculations, the intercept and slope of such plots are determined. From the intercept a new estimated value of k_{22} is obtained and this is then used to calculate a new $\log f$. The entire iterative process was repeated until successive estimates of k_{22} differed by less than 10%. The final result gives $k_{22}=1.3\times10^7\ M^{-1}\ s^{-1}$ if we use all four Fe(III) complexes as oxidants and the plot is shown in Figure 4.

This seems to be the first report for the self-exchange rate constant for the sulfoxide/sulfoxide radical cation couple. It is pertinent to point out that similar treatment of the oxidation of organic sulfides with $Fe(NN)_3^{3+}$ has given the same value of k_{22}, the self exchange rate constant for the sulfide/sulfide radical cation couple. After calculating the value of k_{22}, it is then used to get the rate constant for ET, k_{12}, from organic sulfoxides to $Fe(NN)_3^{3+}$ and the values are collected in Table 2. These calculated values are in fair

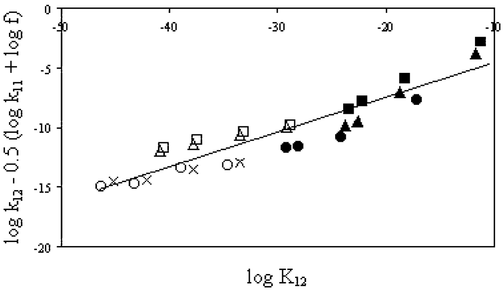


Figure 4. Plot of $\log k_{12}-0.5$ ($\log k_{11}+\log f$) vs $\log K_{12}$: X=sulfoxides vs Fe(dmphen); ○=sulfoxides vs Fe(dmbpy); △=sulfoxides vs Fe(bpy):□=sulfoxides vs Fe(phen); ■=sulfide vs Fe(phen); ▼=Sulfide vs Fe(bpy); ●=sulfide vs Fe(dmbpy).

agreement with the experimental values, supporting our arguments presented above. However, a difference of 1–2 orders of magnitude is observed between the experimental and calculated values for sulfoxides carrying an electron donating group on the phenyl ring of ArS(O)Me. It is important to point out that solvation of the reactants and transition state play an important role in deciding the reactivity and course of the reactions particularly when polar solvents are used in reactions involving charge development. The presence of electron donating and withdrawing groups leads to a different solvation energy ΔH^0_{solv}. Recently it has been established[38,39] that p-OCH$_3$-C$_6$H$_4$S$^{\cdot}$ involves a solvation energy of 42 kJ mol^{-1} and p-NO$_2$C$_6$H$_5$S$^{\cdot}$ −96 kJ mol^{-1} in CH$_3$CN. Thus in order to account for the dynamics of ET reactions it is essential to include the solvation energy in the calculation of driving force of the reaction. Thus, we presume that if the solvation energy is also included, the agreement between the experimental and calculated values will be better. In the case of p-OCH$_3$C$_6$H$_4$S(O)CH$_3$ if solvation energy of 16.7 kJ M^{-1} is included in the calculation of rate constant using Marcus equation the agreement between the experimental and calculated value becomes good. The solvation energies of benzene thiols containing p-Cl and p-Br substituents do not vary significantly from the parent thiols.[38,39] After establishing successful application of Marcus cross-reaction relation of the ET reaction between Fe(NN)$_3^{3+}$ and organic sulfides and sulfoxides we can apply Eq. (11) to calculate the value of the reorganization energy, λ, of the reaction.

$$k_{12} = \nu_n \, e^{-(\Delta G^0+\lambda)^2/4\lambda RT} \qquad (11)$$

The value of ν_n is taken as 1.0×10^{11} s^{-1} and ΔG^0 as 0.96 eV for the reaction of Fe(bpy)$_3^{3+}$ with PhS(O)CH$_3$. Substitution of the values of k_{12}, ν_n and ΔG^0, gives the value of λ as 1.4 eV. This value is the sum of two terms, λ_o and λ_i, the outer and inner-sphere reorganization energy. We have estimated the value of λ_o using Eq. (12) as 1.0 eV.

$$\lambda_o = [(\Delta e)^2/4\pi\varepsilon_o]\,(1/2r_{Fe} + 1/2r_S - 1/r)(1/D_{op} - 1/D_S) \qquad (12)$$

In Eq. (12) Δe, D_{op} and D_S are the number of electrons transferred, the optical and static dielectric constant respectively and ε_o is the permittivity of vacuum. The radii of Fe(bpy)$_3^{3+}$ and MPSO are represented by r_{Fe} and r_S, respectively, and the sum of the radii is r.[40] The values of D_{op} and D_S are available in the literature and the radii of Fe(bpy)$_3^{3+}$ and MPSO are 7 and 4 Å, respectively.[27,28]

From this analysis we understand that the contribution from the inner-sphere reorganization energy, λ_i to the overall λ value is 0.4 eV. It is well known that λ_i value for reactions involving M(bpy)$_3^{3+}$ complexes (M=Fe, Ru and Os) is negligible.[27] Thus we understand that during ET from ArS(O)Me to Fe(NN)$_3^{3+}$ the change in the bond length in sulfoxide is significant leading to appreciable λ_i value. This is understandable because during ET the S–O bond length may vary substantially leading to appreciable λ_i value. In recent years attempts have been made to evaluate λ_i value theoretically and for benzyl system the value is ~0.6 eV.[41]

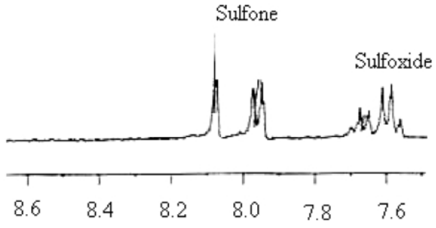


Figure 5. ^{1}H NMR spectrum of the reaction solution.

3.2. Identity of the product of the reaction using ^{1}H NMR

The oxidation of MPSO with Fe(bpy)$_3^{3+}$ was monitored by ^{1}H NMR to determine the identity of the product. Recently Pecoraro et al.[42] used ^{1}H NMR to identify products in the vanadium haloperoxidase model complexes oxidation of organic sulfides. The aromatic protons from MPSO appear as multiplets centered at 7.58 and 7.68 ppm. With two equivalents of Fe(bpy)$_3^{3+}$ per equivalent of MPSO NMR spectrum was recorded after 1 h. The spectrum is shown in Figure 5. After 1 h just one half of the sulfoxide appears to be oxidized to sulfone. The protons from sulfone appear as multiplets centered at 8 and at 8.1 ppm. Similar results were reported by Pecoraro et al. The formation of proton signals for the sulfone confirms that the sulfone is the major product of the reaction.

3.3. Comparison with Fe(NN)$_3^{3+}$ oxidation of organic sulfides

To compare the nucleophilicity of organic sulfides and sulfoxides it is useful to compare the kinetic data observed for the ET reactions of organic sulfides and sulfoxides towards the one electron oxidant Fe(NN)$_3^{3+}$. If we compare the kinetic data observed in the present study with data obtained for organic sulfides in our previous report[3] we realize that the second order rate constants measured for the oxidation of organic sulfides are larger by one to three orders of magnitude compared to the k_2 values observed for organic sulfoxides. To know the range of k_2 values the data obtained for the parent, p-Cl, p-Me and p-OMe phenyl methyl sulfides and sulfoxides are given in the order 1.4, 0.27; 1.01, 0.13; 16.9, 0.42 and 398, 0.86 M^{-1} s^{-1}, respectively. Further, the reaction constant value obtained for the oxidation of organic sulfoxides is small compared to the value calculated with organic sulfides. These rate constant and reaction constant data prompt us to conclude that not only the reactivity, but the selectivity is also less with organic sulfoxides compared to organic sulfides. From this observation, we presume that the transition state is similar in both oxidation reactions. These results are in contrary to our recent observation with oxo(salen)manganese(V) oxidation of organic sulfides and sulfoxides,[43] wherein we have postulated an early transition state for the oxidation of organic sulfides and a late transition state for sulfoxides based on the ρ values. We wish to recall that the oxo(salen)manganese(V) oxidation of organic sulfides and sulfoxides proceeds through a common mechanism involving an electrophilic attack of oxidant at the sulfur center of the substrate. Thus the reactions in the present study proceeding through an ET mechanism fail to obey the reactivity–selectivity principle (RSP). To have selectivity the reactants should orient suitably with definite structure in the transition state. The implicit assumption in the outer-sphere ET reactions is that little interaction exists between the electron donor and acceptor in the transition state[44] i.e. there is no definite structure for the transition state. As the titled reaction proceeds through outer sphere ET mechanism the failure of RSP is understandable.

4. Experimental

4.1. Materials

The ligands, 2,2′-bipyridine,4,4′-dimethyl-2,2′-bipyridine,1,10-phenanthroline and 4,7-dimethyl-1,10-phenanthroline and iron(II)-sulfate were obtained from Aldrich and used as such. Tris(2,2′-bipyridine)iron(II), tris(4,4′-dimethyl-2,2′-bipyridine)iron(II), tris(1,10-phenanthroline)iron(II) and tris(4,7-dimethyl-1,10-phenanthroline)-iron(II) were prepared by known procedures.[3,25,26] The iron(III) complexes were obtained by the oxidation of iron(II) complexes with either lead dioxide in 1 M H_2SO_4 or ceric ammonium nitrate. The iron(III) complexes were precipitated as perchlorate salts. The purity of the iron(II) and iron(III) complexes were checked by IR and UV–Vis spectra and compared with the literature data. Stock solutions of the iron(III) complexes were made up in concentrated H_2SO_4 or $HClO_4$ solutions. Such solutions were diluted with aqueous methanol to the desired acid strength immediately before each kinetic run. MPSO, and substituted phenyl methyl sulfoxides were synthesized by established procedures[43,45] and purity checked by GC. All other reagents used were of AnalaR grade and solvents (methanol and water) were purified by known procedures before use.[46]

4.2. Kinetic measurement

The iron(II)-polypyridyl complexes have molar extinction coefficients of the order of $1\times10^4\ \mathrm{M^{-1}\,cm^{-1}}$ in the wavelength region 510–530 nm, $[\mathrm{Fe(bpy)_3}]^{2+}$ (522 nm); $[\mathrm{Fe(phen)_3}]^{2+}$ (510 nm); $[\mathrm{Fe(dmbpy)_3}]^{2+}$ (529 nm); $[\mathrm{Fe(dmphen)_3}]^{2+}$ (513 nm); on the other hand, the corresponding iron(III) complexes are practically transparent at this wavelength region in aqueous acetonitrile.[3,25,26] (for the explanation of abbreviations see Chart 1). The kinetics of $\mathrm{Fe(NN)_3^{3+}}$ oxidation of aryl methyl sulfoxides were followed spectrophotometrically under pseudo first order conditions at 298 K by measuring the increase in absorbance of $\mathrm{Fe(NN)_3^{2+}}$ with time.[3] A sample kinetic run is shown in Figure 1. The absorption spectral studies were carried out on an analytik-jena Specord-diode array photometer (Specord S100). The plots of $\log(A_\infty - A_t)$ vs 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 ±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, $k_2 = k_1/[\text{substrate}]$.

4.3. Stoichiometry

The stoichiometry of the reaction was determined by taking different ratios of oxidant and substrate concentrations. These studies indicated that one mole of sulfoxide was consumed per two moles of $\mathrm{Fe(NN)_3^{3+}}$ in accordance with Eq. (13).

$$2\mathrm{Fe(NN)_3^{3+}} + \mathrm{ArS(O)R} + \mathrm{H_2O} \rightarrow 2\mathrm{Fe(NN)_3^{2+}} + \mathrm{ArSO_2R} + 2\mathrm{H^+} \tag{13}$$

4.4. Product analysis

The inorganic product under kinetic conditions was confirmed to be $\mathrm{Fe(NN)_3^{2+}}$ as the rate of the reaction was followed by measuring the increase in the concentration of $\mathrm{Fe(NN)_3^{2+}}$ spectrophotometrically. 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 sulfone. This was also confirmed from the analysis of the product with ^{1}H NMR (vide supra).

Acknowledgements

The authors thank Professor C. Srinivasan, Emeritus Scientist, Department of Materials Science, Madurai Kamaraj University, for his constant encouragement, and K. J. A. thanks University Grants Commission, New Delhi for providing FIP study leave and the Principal and the Management of The American College, Madurai, for their support.

References

1. *Sulfur-Centered Reactive Intermediates in Chemistry and Biology. NATO ASI Series*; Chatgilialoglu, C., Asmus, K. D., Eds.; Plenum: New York, 1990.
2. *S-Centered Radicals*; Alfassi, Z. B., Ed.; Wiley: Chichester, 1999.
3. Balakumar, S.; Thanasekaran, P.; Rajagopal, S.; Ramaraj, R. *Tetrahedron* **1995**, *51*, 4801.
4. Baciocchi, E.; Intini, D.; Pimermattei, A.; Rol, C.; Ruzziconi, A. *Gazz. Chim. Ital.* **1989**, 119.
5. (a) Srinivasan, C.; Chellamani, A.; Rajagopal, S. *J. Org. Chem.* **1985**, *50*, 1201. (b) Srinivasan, C.; Rajagopal, S.; Chellamani, A. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1939.
6. (a) Ganesan, T. K.; Rajagopal, S.; Bosco Bharathy, J. R.; Md. Sheriff, A. I. *J. Org. Chem.* **1998**, *63*, 21. (b) Ganesan, T. K.; Rajagopal, S.; Bosco Bharathy, J. R. *Tetrahedron* **2000**, *56*, 5885.
7. Gilmore, J. R.; Mellor, J. M. *Tetrahedron Lett.* **1971**, 3977.
8. Acquaze, J. H.; Miller, J. G.; Takeuchi, K. J. *Inorg. Chem.* **1993**, *32*, 160.
9. Ganesan, M. Ph.D Thesis, Madurai Kamaraj University, 2002.
10. Baciocchi, E.; Ioele, M.; Lanzalunga, O.; Malandrucco, M.; Steenken, S. *J. Am. Chem. Soc.* **1996**, *118*, 8973.
11. Miller, A. E.; Biscoff, J. J.; Cheryl, B.; Luminoso, P.; Smiley, S. *J. Am. Chem. Soc.* **1986**, *108*, 7773.

12. Kamata, M.; Miyashi, T. *J. Chem. Soc. Chem. Commun.* **1989**, 557.
13. Adam, S.; Gonzalez Nunez, E. *Tetrahedron* **1991**, *47*, 3773.
14. Bosch, E.; Kochi, J. K. *J. Org. Chem.* **1995**, *60*, 3172.
15. Engman, L.; Lind, J.; Merenyi, G. *J. Phys. Chem.* **1994**, *98*, 3174.
16. (a) Ioele, M.; Steenken, S.; Baciocchi, E. *J. Phys. Chem. A* **1997**, *101*, 2979. (b) Baciocchi, E.; Biethi, M.; lanzalunga, O. *Acc. Chem. Res.* **2000**, *33*, 243.
17. Yokoi, H.; Hatta, A.; Ishiguro, K.; Sawaki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 12728.
18. Giacco, T. D.; Elisei, F.; Lanzalunga, O. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1701.
19. Aisen, P. In *Iron-Metabolism in Health and Disease*; Brock, J. H., Halliday, A. W., Pipperd, M. J., Powell, L. W., Eds.; W. B. Saunders: London, 1994; p 1.
20. Kraiter, D. C.; Zak, O.; Aisen, P.; Crumbliss, A. L. *Inorg. Chem.* **1998**, *37*, 964–968.
21. Fukuzumi, S.; Nakanishi, I.; Tanak, K.; Suenobu, T.; Tabard, A.; Guilard, R.; Caemelbecke, E. V.; Kadish, K. M. *J. Am. Chem. Soc.* **1999**, *121*, 785.
22. Meunier, B.; Sorokin, A. *Acc. Chem. Res.* **1997**, *30*, 470.
23. Hamachi, I.; Tsukiji, S.; Shinkai, S.; Oishi, S. *J. Am. Chem. Soc.* **1999**, *121*, 5500.
24. Batinic-Haberle, I.; Spasojevic, I.; Hambright, P.; Benov, L.; Crumbliss, A. L.; Fridovich, I. *Inorg. Chem.* **1999**, *38*, 4011.
25. Rollick, K. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 1319.
26. Braterman, P. S.; Song, J. I.; Peacock, R. D. *Inorg. Chem.* **1992**, *31*, 555.
27. (a) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615. (b) Brown, G. W.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883. (c) Macartney, D. H.; Sutin, N. *Inorg. Chem.* **1985**, *24*, 3403.
28. (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. (b) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.
29. (a) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer: Berlin, 1987. (b) Kochi, J. K. *Acta Chem. Scand.* **1990**, *44*, 409.
30. Nelson, S. F.; Pladziewicz, J. R. *Acc. Chem. Res.* **2002**, *35*, 247.
31. (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966. (b) Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21. (c) Marcus, R. A. *J. Chem. Phys.* **1963**, *853*, 2889. (c) Marcus, R. A.; Sutin, N. *Inorg. Chem.* **1975**, *14*, 213. (d) Marcus, R. A. *Angew. Chem. Int. Ed.* **1993**, *32*, 1111.
32. Ghosh, P. K.; Brunschwig, B. S.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1984**, *106*, 4772.
33. (a) Wherland, S. *Coord. Chem. Rev.* **1999**, *123*, 169. (b) Brunschwig, B. S.; Sutin, N. *Coord. Chem. Rev.* **1999**, *187*, 233. (c) *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinhein, 2001.
34. (a) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148. (b) Gray, H. B.; Winkler, J. R. *Ann. Rev. Biochem.* **1996**, *65*, 537.
35. (a) Fukuzumi, S.; Nakanishi, I.; Tanaka, K. *J. Phys. Chem. A.* **1999**, *103*, 11212. (b) Roth, J. P.; Lovell, S.; Mayer, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 5486.
36. Bixon, M.; Jortner, J. *Adv. Chem. Phys.* **1999**, *106*, 35.
37. Nelson, S. F.; Trieber, D. A., II.; Nagy, M. A.; Konradsson, A.; Halfen, D. T.; Splan, K. A.; Pladziewicz, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 5940 and references cited therein.
38. Brinck, T.; Carlqvist, P.; Holm, A. H.; Dassbjerg, K. *J. Phys. Chem. A* **2002**, *106*, 8827.
39. Larsen, A. G.; Holm, A. H.; Roberson, M.; Daasbjerg, K. *J. Am. Chem. Soc.* **2001**, *123*, 1723.
40. Reynolds, L.; Gardecki, J. A.; Frankland, S. J. V.; Horng, M. L.; Maroncelli, *J. Phys. Chem.* **1996**, *100*, 10337.
41. (a) Mikkelsen, K. V.; Pedersen, S. U.; Lund, H.; Swanstrom, P. *J. Phys. Chem.* **1991**, *95*, 8892. (b) Amashukeh, X.; Winkler, J. R.; Gray, H. B.; Gruhn, N. E.; Lichtenberger, D. L. *J. Phys. Chem. A* **2002**, *106*, 7593.
42. Smith, T. S., II.; Pecoraro, V. I. *Inorg. Chem.* **2002**, *41*, 6754.
43. (a) Chellamani, A.; Alhaji, N. M. I.; Rajagopal, S.; Sevvel, R.; Srinivasan, C. *Tetrahedron* **1995**, *51*, 12677. (b) Chellamani, A.; Alhaji, N. M. I.; Rajagopal, S. *J. Chem. Soc., Perkin Trans. 2* **1997**, 299. (c) Chellamani, A.; Kulanthaipandi, P.; Rajagopal, S. *J. Org. Chem.* **1999**, *64*, 2232.
44. Zipse, H. *Angew Chem. Int. Ed. Engl.* **1997**, *36*, 1697.
45. Price, C. C.; Hydock, J. J. *J. Am. Chem. Soc.* **1952**, *74*, 1943.
46. Perrin, D. D.; Armargo, A. L. F.; Perrin, D. R. *Purifications of Laboratory Chemicals*; Pergamon: New York, 1980.