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A paradigm shift in rate determining step from single electron transfer between phenylsulfinylacetic acids and iron(III) polypyridyl complexes to nucleophilic attack of water to the produced sulfoxide radical cation: a non-linear Hammett

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Mechanism of oxidative decarboxylation of phenylsulfinylacetic acids (PSAAs) by iron(III) polypyridyl complexes in aqueous acetonitrile medium has been investigated spectrophotometrically. An initial intermediate formation between PSAA and $[Fe(NN)_3]^{3+}$ is confirmed from the observed Michaelis–Menten kinetics and fractional order dependence on PSAA. Significant rate retardation with concentration of $[Fe(NN)_3]^{3+}$ is rationalized on the basis of coordination of a water molecule at the carbon atom adjacent to the ring nitrogen of the metal polypyridyl complexes by nucleophilic attack at higher concentrations. Electron-withdrawing and electron-releasing substituents in PSAA facilitate the reaction and Hammett correlation gives an upward 'V' shaped curve. The apparent upward curvature is rationalized based on the change in the rate determining step from electron transfer to nucleophilic attack, by changing the substituents from electron-releasing to electron-withdrawing groups. Electron-releasing substituents in PSAA accelerate the electron transfer from PSAA to the complex and also stabilize the intermediate through resonance interaction leading to negative reaction constants (ρ). Conversely, electron-withdrawing groups, while retarding the electron transfer exert an accelerating effect on the nucleophilic attack of H_2O which leading to low magnitude of ρ^+ compared to high ρ^- values of electron-releasing groups. Marcus theory is applied, and a fair agreement is seen with the experimental values. Copyright © 2016 John Wiley & Sons, Ltd.

Keywords: electron transfer reaction; iron(III) polypyridyl complex; Marcus theory; non-linear Hammett; phenylsulfinylacetic acid; substituent effect

INTRODUCTION

Organo sulfur compounds, widely distributed in food,[1] are functioning as antiseptics, antibiotics, antithrombotics, antioxidants etc.[2] Sulfur containing compounds play an important role in cellular biochemistry. Among the organic sulfur compounds, organic sulfoxides are biphilic in nature, act either as electrophile or nucleophile.[3] But still they resemble organic sulfides in many oxidation reactions.[4–6] Some of the phenylsulfinyl compounds have found to possess high therapeutic effects. They are used for combating parasitic disorders with broad spectrum of action, treating Alzheimer's disease[7] and enhancing memory activities. They also show antibacterial activities.[8]

Iron is omnipresent on earth and is responsible for vital biological reactions. The reduction of Fe(III) to Fe(II) by biological reductants in biological systems is a well-known phenomenon.[6] For clear understanding of these ET reactions, porphyrin and polypyridyl complexes of Fe(III) have been synthesized as model compounds and used as electron acceptors.[9–11] Recently iron polypyridyl complexes have been identified as potential anticancer drug by inhibiting the cancer cell proliferation.[12] The iron(III) polypyridyl complexes are well-known one electron acceptors,[13] and several interactions of these complexes with inorganic and organic reductants have been reported.[6,13–17] Many of the reactions are rationalized in terms of the outer-sphere mechanism, supported by Marcus-type dependence of rate.

In recent years, much attention has been paid to the chemistry of sulfur-centred radicals and radical cations because of their importance as intermediates in organic synthesis, environmental and biological studies. As these intermediates are reported in

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most of the sulfoxidation reactions, and there is no systematic mechanistic study on the oxidation of phenylsulfinylacetic acid (PSAA) in the literature except our recent publications,[18–21] a systematic mechanistic investigation on the reaction between biologically active iron(III) polypyridyl complexes and therapeutically active PSAA is undertaken in the present work. On the basis of the observed spectral, kinetic, thermodynamic and substituent effects a suitable mechanistic path is proposed.

EXPERIMENTAL SECTION

General

The ligands 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (dmbpy), 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (dmphen) and 5-chloro-1,10-phenanthroline (Clphen) were obtained from Sigma-Aldrich and used as such. Fe(III) polypyridyl complexes $[Fe(NN)_3]^{3+}$ were prepared by the oxidation of corresponding Fe(II) tris(pyridyl) complexes with lead dioxide in sulphuric acid medium.[6] The preparation of $[Fe(NN)_3]^{3+}$ must be done in highly acidic medium in order to get better yield. Finally, Fe(III) complexes were precipitated as perchlorate salts. The purity of the complexes was checked from their IR and absorption spectra. The tris(pyridyl) complexes of Fe(II) were obtained by known procedure.[22] The structure of $[Fe(NN)_3]^{3+}$ complexes used in the present study and their abbreviations are shown in Fig. 1.

Stock solutions of Fe(III) complexes were made up in concentrated perchloric acid and were diluted with aqueous acetonitrile just before initiating the kinetic run. In order to avoid the decomposition of complexes, stock solutions were kept in refrigerator and no solution samples older than 12 h were used. CAUTION: As metal perchlorates have a potential to explode, they should be handled with utmost care, including working with as small amounts as possible and preventing exposure to elevated temperatures.

PSAA, *meta*- and *para*-substituted PSAAs were prepared from the corresponding phenylthioacetic acid (PTAA) by the controlled oxidation with hydrogen peroxide.[17] The PTAAs were prepared by condensing thiophenols and chloroacetic acid in alkaline medium by known procedure.[23] PSAAs were purified by recrystallization from ethyl acetate–benzene mixture and their purities were checked by m.p. and LC-MS. The recrystallized samples were stored in vacuum desiccator in order to avoid the decomposition with moist air.

Kinetic measurements

The polypyridyl iron(II) complexes have absorbance at 522 nm for $[Fe(bpy)_3]^{2+}$, 529 nm for $[Fe(dmbpy)_3]^{2+}$, 510 nm for $[Fe(phen)_3]^{2+}$, 513 nm for $[Fe(dmphen)_3]^{2+}$ and 510 nm for $[Fe(Clphen)_3]^{2+}$. As the iron(II) polypyridyl complexes have high molar extinction coefficients of the order $1 \times 10^4\ M^{-1}\ cm^{-1}$ and the corresponding iron(III) complexes are transparent in the above absorption regions,[6,22] the reactions of PSAAs with $[Fe(NN)_3]^{3+}$ complexes were monitored by measuring the increase in absorbance with time as shown in Fig. 2.

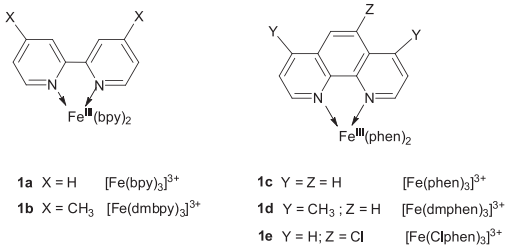


Figure 1. Structure of $[Fe(NN)_3]^{3+}$ complexes and their abbreviations

The kinetics of the reaction was followed spectrophotometrically under pseudo first order conditions with excess of PSAA over $[Fe(NN)_3]^{3+}$ in 50% aqueous acetonitrile (*v/v*) medium. The absorption spectral studies were carried out on a double beam BL 222 Elico UV–vis bio spectrophotometer with an inbuilt thermostat. The pseudo-first-order rate constants were calculated from the linear plots of $\log(A\alpha - A_t)$ versus time by least squares method,[6] where $A\alpha$ is the maximum absorbance obtained by the completion of the reaction and A_t is the absorbance at time t. The overall rate constants (k_{ov}) were calculated from the relation, $k_{ov} = k_1/[PSAA]^{order}$. The error in the rate constants is given according to 95% of the Student's *t*-test.

Product analysis

The reaction mixtures containing PSAA and $[Fe(bpy)_3]^{3+}$ / $[Fe(phen)_3]^{3+}$ in 1:2 molar ratio under the experimental conditions were kept aside for two days. After completion of the reaction the organic solvent was removed under reduced pressure, extracted with chloroform and dried over anhydrous sodium sulfate. The sample obtained after the removal of the solvent was characterized by GC-MS and FT-IR spectral methods and the product was identified as diphenyl disulfone.

The FT-IR spectrum (Fig. 3) shows strong characteristic bands at 1143 cm^{-1} and 1294 cm^{-1} which confirms the existence of $\rangle SO_2$ group in the product and the absorption bands are assigned to symmetric and asymmetric stretching vibrations of $\rangle SO_2$ respectively. The absorption bands at 2924 cm^{-1} show aromaticity, 1570 cm^{-1} show C=C stretching, 737 cm^{-1}, 685 cm^{-1} and 630 cm^{-1} show C—H bending vibrations of phenyl rings. GC-MS spectral analysis (Fig. 4) was done using Thermo GC-Trace ultra ver : 5.0, Thermo MS DSQ II mass spectrometer using DB 35-MS capillary standard non-polar column of length 30 m and internal diameter of 0.25 mm. The sample was dissolved in benzene and 1 μL of the solution was injected into the column. Helium gas was used as the car-

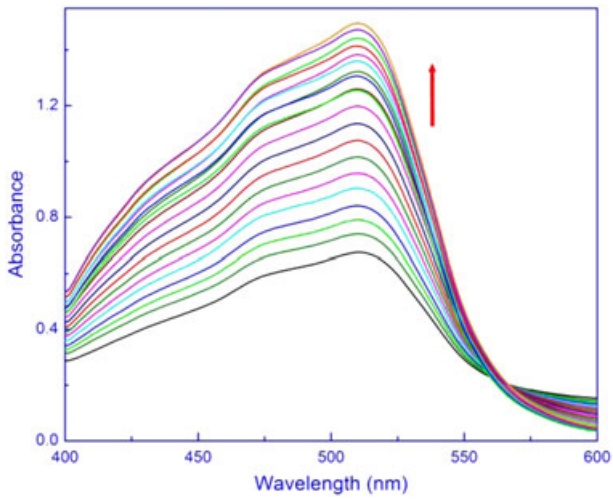


Figure 2. Increase in the absorbance of $[Fe(phen)_3]^{2+}$ during the reaction with the isobestic point

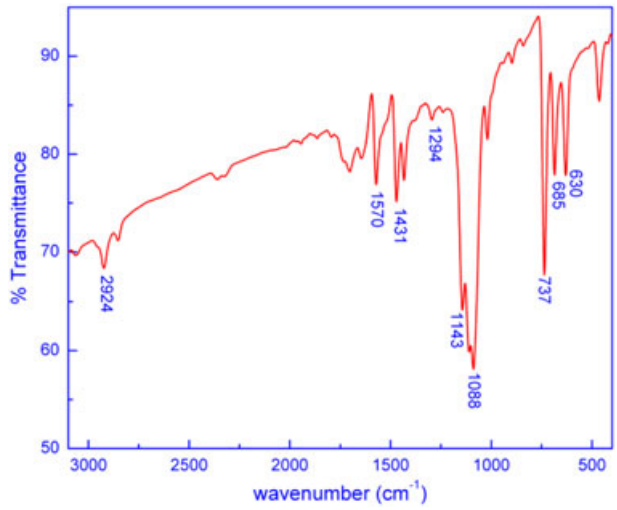


Figure 3. FT-IR spectrum of the product

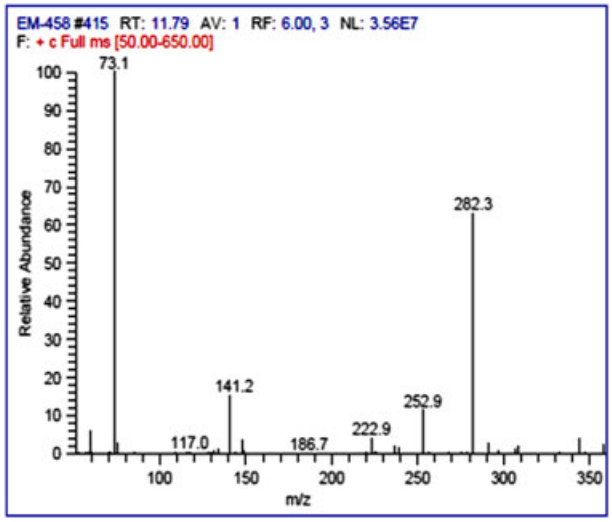


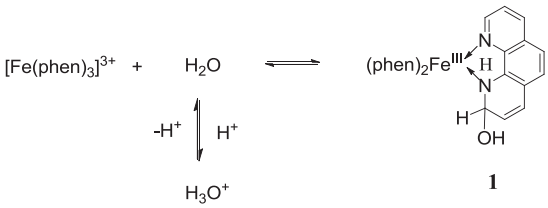
Figure 4. GC-MS spectrum of the product

rier gas. The parent peak eluted at a retention time of 11.79 min at $m/z = 282.3$ in GC-MS confirms the formation of diphenyl disulfone as the product in the reaction. The other product was confirmed as $[Fe(NN)_3]^{2+}$ from the formation of new peak in the absorption spectra where the characteristic absorption increases with time during the course of the reaction.

RESULTS AND DISCUSSION

The pseudo-first-order rate constants for all the reactions investigated at various concentrations of PSAA with iron(III) polypyridyl complexes (**1a–e**) increase progressively with [PSAA] but not in a proportionate manner (Supporting Information—Table S1). The order with respect to PSAA is determined from the slope value of double logarithmic plot of k_1 and [PSAA]. The plots of log k_1 versus log [PSAA] for complexes (**1a–e**) gave a slope of non-integral, fractional values of 0.890, 0.366, 0.661, 0.389 and 0.598 respectively. Further the second order rate constants, k_2 calculated using the expression $k_2 = k_1/[PSAA]$ for different [PSAA] are not constant in a particular complex. Alternatively, the relation $k_1/[PSAA]^{order}$ gave a constant value. These show fractional order dependence of rate on PSAA. The double reciprocal plots of k_1 versus [PSAA] are linear with finite intercept on the rate axis indicating an intermediate formation between PSAA and $[Fe(NN)_3]^{3+}$ in the reaction mechanism before the rate determining step, i.e. Michaelis–Menten kinetics.

Although the pseudo-first-order plots are found to be linear up to 60% completion in all the experimental conditions the rate of reaction decreases considerably with increase in $[Fe(NN)_3^{3+}]$ (Supporting Information Table S2). A possible explanation for the observed decrease in rate would be coordination of a water molecule by nucleophilic attack at the carbon atom adjacent to the ring nitrogen of the iron(III) polypyridyl complexes (Eqn 1) at higher concentrations making them inactive towards oxidation.[24] The coordination of water to metal polypyridyl complexes was proved by Burchett and Meloan[25] by infrared studies and the possibility of attack of water at 2 and 9 positions was shown by Schmid and Han[26] using CNDO calculations. The formation of **1** during the course of the reaction in a parallel reaction is ascertained by the tremendous magnitude of rate retardation observed with complex **1e,** containing electron-withdrawing group (EWG), than other complexes. The chloro substituent in **1e** drains away the electron density from the ring thus favouring the nucleophilic water attack and facilitating the formation of **1**.



Another possibility for the decrease in pseudo-first-order rate constant with increase in $[Fe(NN)_3^{3+}]$ may be due to the conversion of complex into oxo-bridged diiron complex (Fig. 5) as proposed by Hey et al.[27,28] in the aqueous medium at higher concentrations of $[Fe(NN)_3]^{3+}$. As the $[Fe(NN)_3]^{3+}$ increases the rate of Eqn (1) and the formation of species (**2**) may be facilitated, resulting in decrease in stoichiometric concentration of $[Fe(NN)_3]^{3+}$ in the reaction mixture. Thus the decrease in rate constant with increase in $[Fe(NN)_3]^{3+}$ is explained on the basis of deactivation of active species, $[Fe(NN)_3]^{3+}$ into inactive species (**1**) and (**2**) in parallel reactions.

The increase in the concentration of acid favours the rate of reaction (Supporting Information Table S3). The addition of bpy increases the rate of reaction enormously in the case of iron(III) bipyridyl complex (**1a**), whereas in iron(III) phenanthroline complex (**1c**) the effect of phen is only marginal (Supporting Information Table S4). The reason may be explained as follows: In the absence of bpy, majority of $[Fe(bpy)_3]^{3+}$ may exist as less active dimer form (**2**). As the [bpy] increases the dimer formation

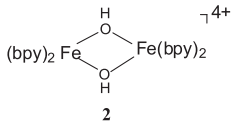


Figure 5. Structure of oxo-bridged diiron complex

is prevented followed by enhancement of rate. This may not be the case in $[Fe(phen)_3]^{3+}$ complex. This is also supported from the oxidant variation studies, where appreciable rate retardation is seen with increase in concentration of iron(III) bipyridyl complexes compared to iron(III) phenanthroline complexes. The ionic strength variation by the addition of $NaClO_4$ has a considerable influence on the rate of reaction. The rate increases steadily upon increasing the ionic strength of the medium (Supporting Information Table S4).

As an extension of the present investigation, the effect of substituents on the reactivity has been studied at three temperatures ranging between 293 K and 313 K for complexes **1a** and **1c** and at 303 K for complexes **1b**, **1d** and **1e** by utilizing several *meta*- and *para*-substituted PSAAs. The overall rate constants obtained with different complexes (**1a–e**) and PSAAs at 303 K are given in Table 1. The rate data in Table 1 show that both electron-withdrawing and electron-releasing substituents in the phenyl ring of PSAA have accelerating effect on the rate. In contradiction, the introduction of electron-withdrawing substituents in the polypyridyl complexes tremendously accelerates the reaction while electron-releasing substituents retard the rate significantly and a direct relation between reduction potential of the complex and its reactivity is found.

Failure of the Hammett linear free energy relationship

On applying Hammett equation between substituent constant σ and log k_{ov} of *meta*- and *para*-substituted PSAAs, a non-linear correlation is observed. The Hammett plots on the reactivity for the reactions of **1a–e** with PSAAs exhibit concave upward curves consists of two intersecting straight lines with a break point at the unsubstituted PSAA (Fig. 6). The electron releasing substituents fall on one side of the curve with a large reaction constant ($\rho = -3.28$ to -7.47) and the electron withdrawing substituents fall on the other side of the curve with a small positive reaction constant ($\rho = +0.351$ to $+0.836$) except in complex **1a**. The unsubstituted PSAA has the least reactivity in this series. The values of ρ^+ and ρ^- obtained for complexes **1a** and **1c** at different temperatures are given in Table 2.

From these ρ values it is clear that the accelerating effect shown by the electron releasing groups (ERG) is significantly higher than that of the electron withdrawing groups. Such type of high ρ^- value is already reported in electron transfer reaction between anilines and oxo(salen)-chromium(V) ($\rho = -3.8$),[29] sulfoxidation of thioanisoles by Ce^{IV} ($\rho = -3.3$)[30] and polypyridyl complexes ($\rho = -3.2$)[31] and the reactions of oxygen atom transfer from aryl sulfoxides to alkyl sulfides catalysed by rhenium(V) monoxo complex ($\rho = -4.6$).[32] High ρ value is also observed in the oxidation reactions of organic sulfides by chloramine-T ($\rho = -4.25$),[33,34] N-chlorosaccharin ($\rho = -3.33$),[35] bromine ($\rho = -3.2$),[36] N-bromobenzamide ($\rho = -3.18$)[37] and PTAAs by N-chlorosaccharin ($\rho = -3.12$)[38] and ammonium meta vanadate ($\rho = -3.64$)[39] where electrophilic attack of the oxidizing species on the sulfur centre has been proposed as the rate-determining step.

In general, the non-linear Hammett correlation is diagnostic of a change in the reaction mechanism or free radical mechanism or a change in the rate determining step with change in the nature of substituents. The involvement of free radical like transition state in the oxidation of alcohols by ruthenate and perchlorate ions,[40] the change in the relative importance of bond formation and bond fission in the Cr(VI) oxidation of benzylamines[41] and competition between the rates of complex formation and its decomposition in the oxidation of benzaldehydes by quinolinium chlorochromate[42] have been given as explanation for the observed V-shaped Hammett plots. V-shaped Hammett plots observed in manganese(V) oxocorrolazine[43] and manganese(V) (imido)(corrole)[44] complexes towards organic sulfur compounds were rationalized by change in mechanism from electrophilic to nucleophilic

Table 1. Overall rate constants for the oxidation of para- and meta-substituted PSAAs by 1a–1e[1]

No.	X	10^2 k_{ov} ($M^{-1}s^{-1}$)				
		1a	1b	1c	1d	1e
1.	p-F	7.43 ± 0.05	0.144 ± 0.01	1.76 ± 0.01	0.168 ± 0.01	6.47 ± 0.04
2.	p-Cl	14.9 ± 0.03	0.171 ± 0.01	2.12 ± 0.01	0.198 ± 0.01	7.24 ± 0.06
3.	p-Br	18.0 ± 0.01	0.189 ± 0.12	2.24 ± 0.01	0.219 ± 0.01	7.57 ± 0.02
4.	m-F	29.4 ± 0.09	0.212 ± 0.02	2.59 ± 0.01	0.243 ± 0.01	7.98 ± 0.09
5.	m-Cl	34.7 ± 0.04	0.218 ± 0.01	2.74 ± 0.01	0.246 ± 0.01	8.74 ± 0.11
6.	m-Br	38.5 ± 0.03	0.222 ± 0.01	2.92 ± 0.01	0.249 ± 0.01	8.65 ± 0.08
7.	H	6.03 ± 0.01	0.137 ± 0.01	1.49 ± 0.01	0.158 ± 0.01	6.09 ± 0.02
8.	m-Me	12.2 ± 0.01	0.209 ± 0.06	2.37 ± 0.01	0.343 ± 0.04	22.7 ± 0.22
9.	p-Et	56.9 ± 0.01	0.348 ± 0.01	6.73 ± 0.03	0.424 ± 0.01	54.7 ± 0.29
10.	p-Me	93.6 ± 0.01	0.525 ± 0.02	9.63 ± 0.03	0.586 ± 0.01	73.8 ± 0.38
11.	p-t.Bu	163 ± 0.01	0.711 ± 0.01	11.9 ± 0.03	0.722 ± 0.01	107 ± 0.01
12.	p-OEt	338 ± 0.03	1.13 ± 0.03	19.2 ± 0.02	1.02 ± 0.06	172 ± 0.12
13.	p-OMe	485 ± 0.03	1.63 ± 0.03	23.9 ± 0.01	1.39 ± 0.02	195 ± 0.23
	ρ^+	2.18 ± 0.11	0.583 ± 0.06	0.652 ± 0.05	0.534 ± 0.06	0.391 ± 0.04
	R	0.995	0.982	0.989	0.978	0.975
	ρ^-	7.47 ± 0.34	4.02 ± 0.32	4.71 ± 0.22	3.28 ± 0.25	5.58 ± 0.33
	R	0.995	0.985	0.995	0.986	0.992

[1] $[H^+] = 0.5$ M, $\mu = 0.55$ M, $CH_3CN–H_2O = 50–50\%$ (*v/v*), [X-PSAA] = 3×10^{-3} M, [**1a**] = [**1b**] = [**1c**] = [**1d**] = [**1e**] = 3×10^{-4} M, T = 303 K.

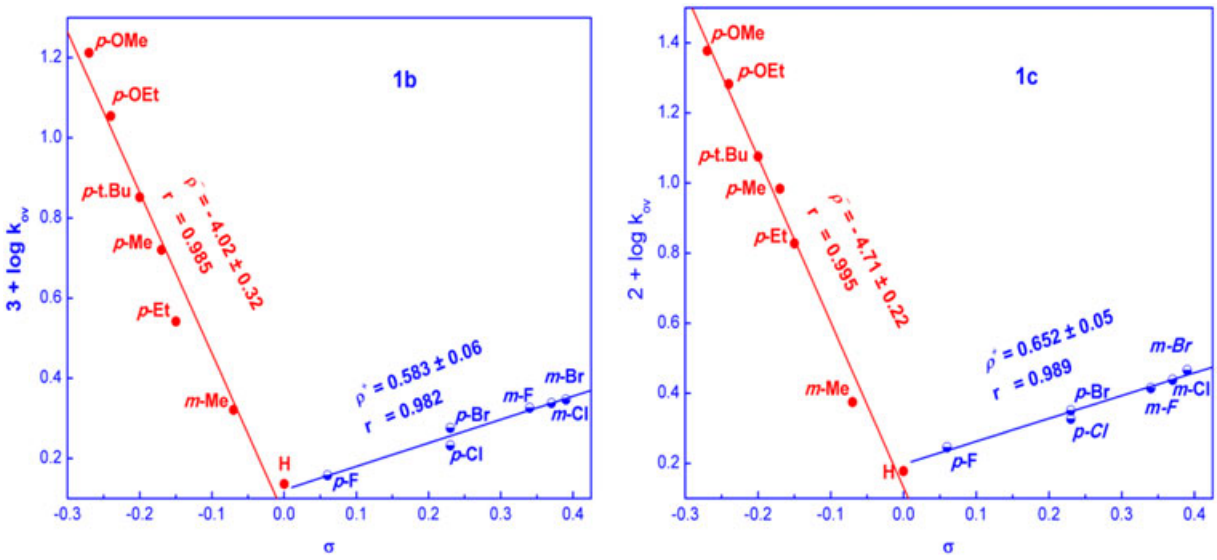


Figure 6. Hammett plots for substituted PSAAs with 1b and 1c at 303 K

Table 2. Thermodynamic parameters for the oxidation of *para*- and *meta*-substituted PSAAs by 1a and 1c[1]

No.	X	1a				1c			
		10^2 k_2 ($M^{-1}s^{-1}$)		$\Delta^{\ddagger}H$ kJ mol^{-1}	$-\Delta^{\ddagger}S$ J K^{-1} mol^{-1}	10^2 k_2 ($M^{-1}s^{-1}$)		$\Delta^{\ddagger}H$ kJ mol^{-1}	$-\Delta^{\ddagger}S$ J K^{-1} mol^{-1}
		293 K	313 K			293 K	313 K		
1.	p-F	2.47 ± 0.01	15.6 ± 0.01	69.6 ± 0.29	43.1 ± 1.02	1.04 ± 0.01	4.19 ± 0.02	51.6 ± 0.01	111 ± 0.02
2.	p-Cl	5.88 ± 0.01	39.2 ± 0.06	71.3 ± 0.13	30.9 ± 0.47	1.35 ± 0.01	4.82 ± 0.01	46.9 ± 0.01	125 ± 0.01
3.	p-Br	7.16 ± 0.02	49.3 ± 0.02	72.7 ± 0.09	24.6 ± 0.34	1.47 ± 0.04	5.23 ± 0.04	46.8 ± 0.01	125 ± 0.03
4.	m-F	11.3 ± 0.01	68.9 ± 0.05	68.0 ± 0.12	36.2 ± 0.42	1.70 ± 0.01	5.74 ± 0.02	44.7 ± 0.01	130 ± 0.01
5.	m-Cl	15.8 ± 0.01	87.2 ± 0.04	64.1 ± 0.06	46.6 ± 0.20	1.79 ± 0.01	6.36 ± 0.03	46.7 ± 0.01	123 ± 0.01
6.	m-Br	18.4 ± 0.02	103 ± 0.04	64.5 ± 0.06	44.2 ± 0.20	2.07 ± 0.04	6.73 ± 0.01	43.2 ± 0.01	134 ± 0.02
7.	H	1.66 ± 0.01	12.7 ± 0.02	77.0 ± 0.24	21.4 ± 0.83	0.839 ± 0.01	3.55 ± 0.02	53.6 ± 0.01	106 ± 0.02
8.	m-Me	6.25 ± 0.04	46.9 ± 0.08	75.8 ± 0.23	16.2 ± 0.80	1.98 ± 0.03	6.53 ± 0.02	43.6 ± 0.01	133 ± 0.02
9.	p-Et	25.1 ± 0.01	162 ± 0.06	70.1 ± 0.02	23.0 ± 0.08	4.36 ± 0.01	11.4 ± 0.04	34.9 ± 0.01	155 ± 0.01
10.	p-Me	39.5 ± 0.03	216 ± 0.03	63.9 ± 0.03	39.6 ± 0.09	5.63 ± 0.01	15.9 ± 0.04	37.9 ± 0.01	142 ± 0.01
11.	p-t.Bu	56.6 ± 0.05	261 ± 0.07	57.3 ± 0.03	57.8 ± 0.11	8.35 ± 0.04	18.5 ± 0.01	28.4 ± 0.01	171 ± 0.01
12.	p-OEt	119 ± 0.04	629 ± 0.06	62.6 ± 0.01	34.3 ± 0.05	12.6 ± 0.01	24.8 ± 0.01	23.9 ± 0.01	182 ± 0.01
13.	p-OMe	169 ± 0.05	869 ± 0.03	61.5 ± 0.01	34.8 ± 0.04	16.1 ± 0.01	29.7 ± 0.01	21.4 ± 0.01	189 ± 0.01
	ρ^+	2.57 ± 0.15	2.31 ± 0.17			0.836 ± 0.08	0.602 ± 0.08		
	r	0.987	0.991			0.980	0.969		
	ρ^-	7.51 ± 0.19	6.79 ± 0.18			4.78 ± 0.10	3.46 ± 0.13		
	r	0.999	0.996			0.999	0.997		

[1] $[H^+] = 0.5$ M, $\mu = 0.55$ M, CH_3CN–H_2O = 50–50% (*v/v*), [X-PSAA] = 3×10^{-3} M, [**1a**] = [**1c**] = 3×10^{-4} M

attack of complexes. Besides, similar V-shaped Hammett plots were reported during the oxidative decarboxylation of PSAA by oxo(salen)-chromium(V),[20] oxidation of trans cinnamic acid by pyridinium chlorochromate[45] and chloramine-T,[46] styrene derivatives by quarternary ammonium permanganate[47] and sulfoxidation by titanium complex.[48]

The thermodynamic parameters were calculated from the linear Eyring's plots[49] of log (k_{ov} /T) versus 1/T and the calculated values are given in Table 2. The negative values of the entropy of activation ($\Delta^{\ddagger}S$) suggest extensive solvation and disorder arrangement of the products over the reactants in the rate determining step. As no linear relationship exists between $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$ in the present series of reactions, a linear isokinetic relationship is established from the rate constants at two different temperatures as proposed by Exner[50] using the following equation.

$$\log k_{ov}(T_2) = a + b \log k_{ov}(T_1) \quad (2)$$

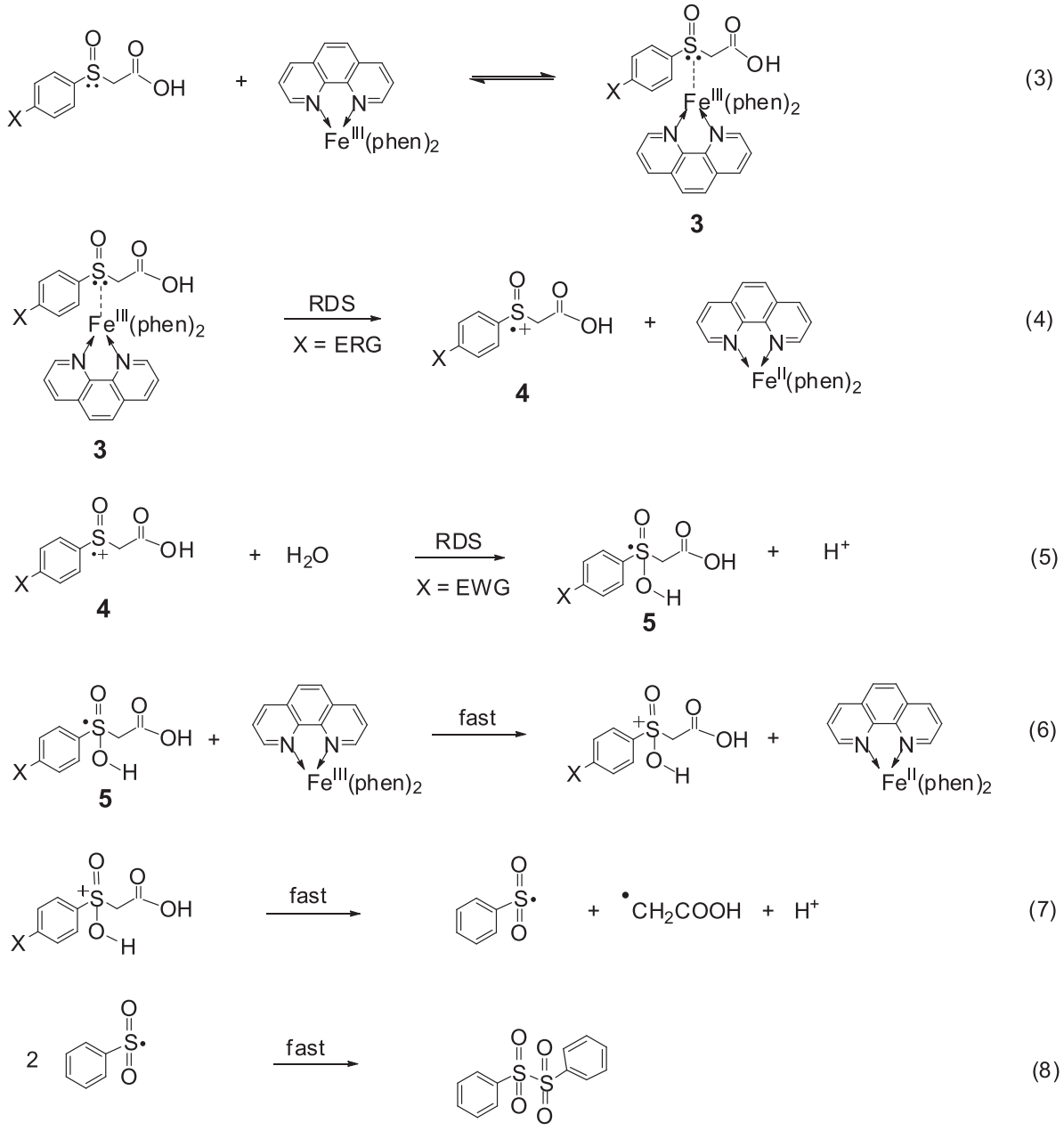
where $T_2 > T_1$

Excellent linear plots ($r = 0.993$ for **1a** and $r = 0.997$ for **1c**) of log k_{ov} (313 K) versus log k_{ov} (293 K) not only prove a unified mechanism[51] in all the PSAAs studied but also rule out the possibility of change in the reaction mechanism with substituent.

Mechanism

When $[Fe(NN)_3]^{3+}$ is added to PSAA during the reaction, a substantial increase in the absorbance is noted in the reaction mixture. This increase in absorbance is taken as spectral evidence for the formation of new adduct (**3**) between PSAA and polypyridyl complex in the initial stage of the mechanism.[52] It is also shown that the increase in absorbance is more pronounced in Phen complexes than in Bpy complexes. The observed Michaelis–Menten kinetics[53] with PSAA can be taken as the kinetic evidence for the formation of adduct (**3**). The strong one electron nature of the oxidant $[Fe(NN)_3]^{3+}$ and formation of a new peak characteristic of $[Fe(NN)_3]^{2+}$ as one of the products of the reaction clearly confirm the formation of sulfoxide radical cation (**4**) as the transient species by electron transfer from PSAA to Fe(III). Similar type of sulfoxide radical cation formation has already been advocated by Rajagopal and co-workers[54] in ruthenium(III) polypyridyl complexes and Adaikalasamy et al.[6] in iron(III) polypyridyl complexes. Based on these facts, a mechanism involving sulfoxide radical cation in the rate determining step (RDS) as shown in Scheme 1 has been proposed for the reactions of PSAAs with $[Fe(NN)_3]^{3+}$.

Electron-withdrawing substituents in the phenanthroline ligand of $[Fe(phen)_3]^{3+}$ and electron-releasing substituents in the phenyl ring of PSAA are found to enhance the rate of reaction. These observations strongly favour the formation of sulfoxide cation radical by internal transfer of an electron from PSAA to $[Fe(NN)_3]^{3+}$ within the adduct (**3**) in the rate determining step (Eqn 4). This is further supported by the rate retardation effect observed with electron-releasing substituents in $[Fe(NN)_3]^{3+}$ (Table 1). The electron-withdrawing chlorine in **1e** decreases its electron density at Fe(III) centre and favours the electron



Scheme 1. Mechanism for the reaction between PSAAs and $[Fe(NN)_3]^{3+}$

accepting tendency from PSAA. The replacement of chlorine by methyl makes the Fe(III) complex less electrophile and decreases the electron accepting ability. Similarly the observed increase in rate with acid concentration is explained on the basis of protonation of $[Fe(NN)_3]^{3+}$ to form $[HFe(NN)_3]^{4+}$ as postulated by Sutin[55] and Kmura[56] co-workers, which makes the oxidant more electrophile thus favouring the formation of (**3**) and ET from PSAA to the complex. In addition, H^+ ions also stabilize the sulfonium cation radical (**4**) formed in the rate determining step. It has been shown that[57] the sulfur radical cation is more stabilized by $[H^+]$. Thus the rate enhancement by the addition of acid gave additional evidence for the formation of sulfonium cation radical. As charged species are more easily formed in high ionic medium, an enhancement of rate observed with ionic strength also supports the proposed mechanism. The insignificant effect observed in the rate constant by the addition of $[Fe(NN)_3]^{2+}$ to the reaction mixture indicates that the conversion of Fe^{3+} to Fe^{2+} is not a reversible process. The existence of isobestic point in the overlay spectrum of kinetic runs (Fig. 2) during the reduction of $[Fe(NN)_3]^{3+}$ to $[Fe(NN)_3]^{2+}$ clearly demonstrates that the conversion of Fe(III) to Fe(II) proceeds via simple kinetics without any intermediate form.

The formation of sulfone as the final product of PSAA leads to the conclusion that the major portion of sulfoxide cation radical is consumed by the solvent, water. Thus formation of sulfoxide radical (**5**) is proposed as a result of nucleophilic attack of water on sulfonium cation intermediate (**4**) (Eqn 5) which then transfers its electron to another $[Fe(NN)_3]^{3+}$ (Eqn 6) that leads to the formation of sulfoxide cation. Such type of attack by water followed by second electron transfer to another $[Fe(NN)_3]^{3+}$ is already shown in the oxidation of sulfur compounds by polypyridyl complexes.[6,53] The sulfoxide cation then undergoes rearrangement to form phenylsulfonyl free radical via cleavage of a C-S bond β to the aromatic ring.[58] Srinivasan et al.[59] showed a fairly intense peak corresponding to $C_6H_5SO_2^{\bullet}$ radical in the mass spectrum of phenylsulfonylacetic acid by the loss of $^{\bullet}CH_2COOH$. The same radical is also reported in the photolysis study of PTAA by Filipiak et al.[60] Finally phenylsulfonyl free radicals undergo dimerization leading to the formation of diphenyl disulfone as the product, and such type of dimerization reaction has been reported earlier by Green et al.[61] If the formation of cation radical is the one and only rate determining step and the electronic effect is the deciding factor, then the rate would be decreased by EWGs on the phenyl ring of PSAA. In contradiction, the observed rate acceleration with EWG points out that electronic effect alone does not decide the reaction rate.

The apparent upward curvature in the Hammett plots (Fig. 6) observed in the present case is rationalized based upon the change in the rate determining step in the proposed mechanism (Scheme 1) upon changing the substitutes in PSAA. Electron releasing substituents in PSAA accelerate the electron transfer from sulfur atom to iron in adduct (**3**) (Eqn 4) and also stabilize the intermediate (**4**) through resonance interaction leading to negative reaction constants (ρ). At the same time, they retard the nucleophilic attack of OH^- on the sulfoxide cation radical (Eqn 5). Conversely, the EWGs while retarding the electron transfer (Eqn 4) not only exert an accelerating effect on the nucleophilic attack of H_2O (Eqn 5) but also stabilize the intermediate (**5**) in the mechanism. From the observed increase in rate with EWG one could expect a change in rate determining step from electron transfer to nucleophilic attack, by changing the substituents from electron donating to electron withdrawing groups. The strong evidence for the nucleophilic attack of water on intermediate (**4**) (Eqn 5) as the rate determining step for EWG comes from enormous increase in rate with increase in water content of the medium for PSAA containing EWG. Interestingly no such solvent effect is observed with PSAA and PSAA containing ERG (Table 3) which indicates the non-involvement of water molecule in these PSAAs. The observed low magnitude of ρ^+ (Table 1 and Fig. 6) with electron-withdrawing substituents compared to ρ^- of electron-releasing groups is because of opposite substituent effects of EWG on reaction rates, i.e. electron-withdrawing substituents simultaneously retard the electron transfer step (Eqn 4) and exert accelerating effect in the nucleophilic attack of H_2O (Eqn 5). Thus, the observed non-linear Hammett behaviour with upward curvature in the present reaction can be visualized to a change in the rate determining step on changing the substituents in PSAA.

Application of Marcus theory of electron transfer

Marcus analysis[62] has been successfully applied to many thermal, photochemical and electrochemical reactions where single electron transfer takes place in the rate determining step. In order to confirm the proposed single electron transfer in the present reaction, it is subjected to the theoretical work of Marcus cross-relation. According to this concept, the rate constant (k_{12}) for an ET reaction (Eqn 9) depends on intrinsic reactivity of the redox couples involved, i.e. self-exchange rate constants at zero driving force, k_{11} and k_{22} and the thermodynamics of the couples.

$$PSAA + [Fe(NN)_3]^{3+} \xrightarrow{k_{12}} PSAA^{+\bullet} + [Fe(NN)_3]^{2+} \quad (9)$$

$$[Fe(NN)_3]^{3+} + e^- \xrightarrow{k_{11}} [Fe(NN)_3]^{2+} \quad (10)$$

$$PSAA \xrightarrow{k_{22}} PSAA^{+\bullet} + e^- \quad (11)$$

The rate constant, k_{12} for an ET cross reaction obtained from Marcus cross-relation in its simple form is given as

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

$$\ln f_{12} = [\ln(K_{12})]^2 / [4 \ln k_{11}k_{22}/z^2]. \quad (13)$$

Table 3. Effect of water on the oxidation of PSAAs with 1c

CH_3CN–H_2O (*v/v*)	10^4 k_1 (s^{-1})		
	p-Cl PSAA	PSAA	p-Et PSAA
10–90	315 ± 0.07	6.88 ± 0.04	69.8 ± 0.05
20–80	283 ± 0.08	8.53 ± 0.05	71.4 ± 0.01
30–70	248 ± 0.02	7.83 ± 0.02	64.2 ± 0.04
50–50	174 ± 0.07	6.21 ± 0.03	68.6 ± 0.09
60–40	121 ± 0.08	7.18 ± 0.05	67.9 ± 0.02
80–20	33.4 ± 0.05	8.12 ± 0.06	62.3 ± 0.03

[PSAA] = 1×10^{-2} M, [p-Cl PSAA] = [p-Et PSAA] = 3×10^{-2} M, [**1c**] = 3×10^{-4} M, $[H^+]$ = 0.5 M, μ = 0.6 M, T = 303 K.

Equations 12 and 13 have been successfully applied to a variety of inorganic, organic and organometallic and biochemical ET reactions that have a wide range of structural types including hetero atom substituted aromatics. In the above equations, K_{12} and z are the equilibrium constant for the cross reaction and collision frequency for the uncharged reactant molecules in solution respectively. The value of z is the pre exponential factor which is often taken as $1\times10^{11}\,m^{-1}s^{-1}$. The value of self-exchange rate (k_{11}) of $[Fe(NN)_3]^{3+}/[Fe(NN)_3]^{2+}$ couple is taken from the previous studies of Sutin and co-workers[63] as $3.3\times10^{8}\,M^{-1}\,s^{-1}$. The value of K_{12} is calculated from the redox potential of the couples $[Fe(NN)_3]^{3+}$ / $[Fe(NN)_3]^{2+}$ and $\rangle SO^{\bullet+}/\rangle SO$ using the following equations

$$K_{12} = \exp\left(-\Delta G^{o}/RT\right) \tag{14}$$

where

$$\Delta G^{o} = nF\left(E^{o}_{S^{+}O/SO} - E^{o}_{Fe^{3+}/Fe^{2+}}\right). \tag{15}$$

The value of k_{22} for $\rangle SO^{\bullet+}/\rangle SO$ couple can be determined from an iterative procedure, i.e. a value of k_{22} is guessed and plugged into Eqn 12 to calculate f. A plot of log k_{12} – 0.5 (log k_{11} – log f_{12}) versus log K_{12} is made, and from mean least-square 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 $k_{22}=1.3\times10^{7}\,M^{-1}\,s^{-1}$ for Fe(III) complexes as oxidant. It is pertinent to point out that similar treatment of the oxidation of organic sulfoxides with $[Fe(NN)_3]^{3+}$ has given the same value of k_{22}. The value of k_{22} is then used to get the rate constant for ET (k_{12}) from PSAA to $[Fe(bpy)_3]^{3+}$ and $[Fe(phen)_3]^{3+}$. The calculated values, $12.3\times10^{-4}\,s^{-1}$ and $19.4\times10^{-4}\,s^{-1}$ are in fair agreement with the experimental values $3.43\times10^{-4}\,s^{-1}$ and $3.24\times10^{-4}\,s^{-1}$. In order to account for the dynamics of ET reactions it is essential to include the solvation energy in the calculation. Thus we presume that if the solvation energy had been included, the agreement between the experimental and calculated values would have been better. The fair agreement between the experimental and calculated rate constant values confirms the involvement of single electron transfer from PSAA to $[Fe(NN)_3]^{3+}$.

CONCLUSIONS

The electron transfer between substituted PSAAs and iron(III) polypyridyl complexes was studied in aqueous acetonitrile medium. PSAAs were converted to diphenyl disulfones as products. The effect of acid concentration, ionic strength and solvent variation on the rate of ET was studied. The observed substituent effect and non-linear Hammett behaviour with upward curvature are explained based upon the change in the rate determining step in the mechanism from electron transfer to nucleophilic attack of water upon changing the substitutes in PSAA. A satisfactory mechanism incorporating all the effects was proposed. Marcus relation has been successfully applied.

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