Asian Journal of Chemistry; Vol. 36, No. 8 (2024), 1829-1839

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2024.31880

Triton X-100 Mediated Electron Transfer Reactions between Iron(III) Polypyridyl Complexes and Phenylsulfinylacetic Acids

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Received: 5 May 2024; *Accepted*: 7 June 2024; *Published online*: 25 July 2024; AJC-21704

Oxidative decarboxylation of phenylsulfinylacetic acids (PSAAs) by iron(III) polypyridyl complexes in non-ionic surfactant Triton X-100 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. Applying the Hammett substituent constants to the overall rate constants obtained in TX-100 medium gives non-linear concave upward Hammett plots. A suitable mechanism involving the formation of diphenyl sulphone as product has been proposed. The observed increase in rate with increase in concentration of TX-100 at low concentration range, clearly shows that the reaction takes place in micellar medium and both the reactants are associated or incorporated into micellar phase.

Keywords: Electron transfer reaction, Iron(III) polypyridyl complex, Phenylsulfinylacetic acid, Non-linear Hammett.

INTRODUCTION

Water is considered as an ideal low cost solvent due to the environmental concerns [1,2]. Surfactants are amphipathic molecules having hydrophobic and hydrophilic properties. When these surfactant molecules are dissolved in water they can achieve segregation of their hydrophobic portions from the solvent by self-aggregation. The aggregation products, known as micelles, are responsible for altering the rates of organic reactions in aqueous-surfactant solutions. Aqueous micellar solutions can alter the kinetics [3], yield [4] as well as the selectivity [5,6] of many organic reactions to a higher extent compared to the reactions carried out in organic solvents. The substrates attain a suitable orientation in a micelle due to the dual nature of micelles. The hydrophobic core of micelles solubilizes sparingly soluble substrates, Intermediates and products in water [7-9]. Additions of surfactant to a mixture of chemical reactants are used to understand the factors that influence the rates and course of reactions, to gain additional insight into the exceptional catalysis, which is a characteristic of enzymatic reactions.

Non-ionic detergents have neutral and hydrophilic head groups. They are considered as mild surfactants due to their ability to break protein-lipid, lipid-lipid associations but not protein-protein interactions. Most of them do not denature proteins, therefore, proteins are solubilized and isolated in their native and active form, retaining their protein interactors. Triton X-100 is a typical non-ionic surfactant and is a perfect choice for the most immune precipitation experiments. TX-100 has a hydrophilic polyethylene oxide chain and an aromatic hydrocarbon hydrophobic head group, where the hydrocarbon group is 4-(1,1,3,3-tetramethylbutyl)phenyl group.

Recently, Zewail *et al*. [10] reported that the surface of protein is similar to a micellar surface. Protein based miscelles are used as carrier in drug delivery system [11]. Thus, the study of such reactions in a micellar medium is thought to throw more light on the details of electron transfer reaction in the biological systems. The kinetics of the electron transfer reactions between phenylsulfinylacetic acid (PSAA) and $[Fe(NN)_3]^{3+}$ were studied in the absence and presence of nonionic surfactant, (TX-100) in order to gain a better understanding of their oxidizing properties. The aim of this study is to examine the effects of non-ionic surfactant TX-100 at various concentrations on the reaction rate involving PSAA and $[Fe(NN)_3]^{3+}$ and to predict a suitable mechanism for the reaction.

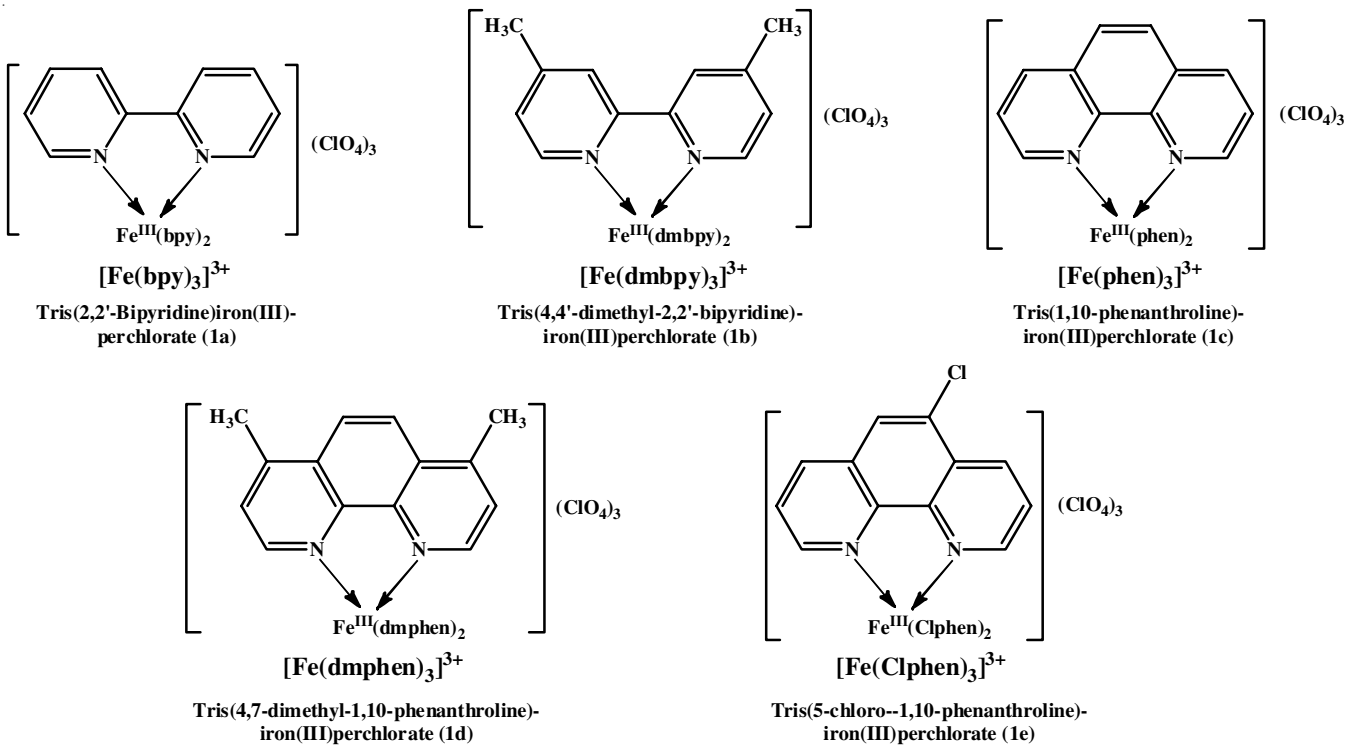


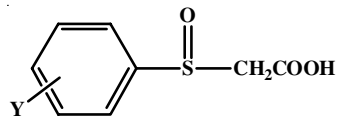
Fig. 1. Structure of iron(III) polypyridyl complexes

EXPERIMENTAL

Synthesis of Fe(III) polypyridyl $[Fe(NN)_3]^{3+}$ complexes and phenylsulfinylacetic acid: 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, USA and used as such. Iron(III) polypyridyl complexes $[Fe(NN)_3]^{3+}$ (Fig. 1) were synthesized by the oxidation of corresponding Fe(II) tris(pyridyl) complexes with PbO_2 in sulphuric acid medium [12]. The synthesis of $[Fe(NN)_3]^{3+}$ must be done in highly acidic medium in order to get better yield and were precipitated as perchlorate salts. Tris(pyridyl) complexes of Fe(II) were obtained by known procedure [13]. The purity of synthesized complexes was checked from their infrared and absorption spectra.

The stock solutions of Fe(III) complexes were prepared in concentrated perchloric acid and diluted with aqueous acetonitrile just before initiating the kinetic run. In order to avoid the decomposition of complexes, the stock solutions were kept in refrigerator. The *meta*- and *para*-substituted phenylsulfinylacetic acids (PSAAs, Fig. 2) were prepared from the corresponding phenylthioacetic acid (PTAA) by the controlled oxidation with H_2O_2 [14]. Phenylsulfinylacetic acids (PSAAs) were purified by recrystallization from ethyl acetate–benzene mixture and their purities were checked by melting point and LC-MS. The recrystallized samples were stored in vacuum desiccator in order to avoid the decomposition with moist air.

Kinetic investigations in the presence of TX-100: The kinetic studies of the reactions between PSAAs and $[Fe(NN)_3]^{3+}$ were carried out in the presence of non-ionic micelle, TX-100 above its CMC value *i.e.*, in the range of 0.001 M to 0.15 M.



where Y = *p*-F, *p*-Cl, *p*-Br, *m*-F, *m*-Cl, *m*-Br, H, *m*-Me, *p*-Et, *p*-Me, *p*-*t*.Bu, *p*-OEt, *p*-OMe

Fig. 2. Structure of substituted phenylsulfinyl acetic acids

All kinetic measurements were performed under pseudo-first-order conditions with PSAA atleast 10 folds in excess over the $[Fe(NN)_3]^{3+}$ in presence of TX-100 at 303 K. Due to solubility problem, the reactions in TX-100 were carried out in 97% H_2O-3% CH_3CN (v/v) medium. Similar solvent systems have been used [15] in several sulfoxidation reactions studies under micellar conditions. Perchloric acid was used to maintain $[H^+]$ and sodium perchlorate was used to maintain the ionic strength. The reactions were followed spectrophotometrically by measuring the increase in absorbance of product, $[Fe(NN)_3]^{2+}$ formed during the reaction. The pseudo-first-order rate constants were calculated from the slope of the linear plots of $\log(A_\infty - A_t)$ *vs.* time.

RESULTS AND DISCUSSION

Rate dependence on [PSAA] in TX-100 medium: In order to know the order with respect to PSAA in TX-100, the concentration was varied from 3×10^{-3} M to 10×10^{-3} M by keeping all other conditions as constant. The pseudo-first-order plots at different initial [PSAA] with **1a** and **1c** are presented in Fig. 3. The pseudo-first-order rate constants computed at different concentrations of PSAA are presented in Table-1 for complexes **1a** and **1c**. The analysis of rate data shows that the pseudo-first order rate constants increase steadily with [PSAA]. The

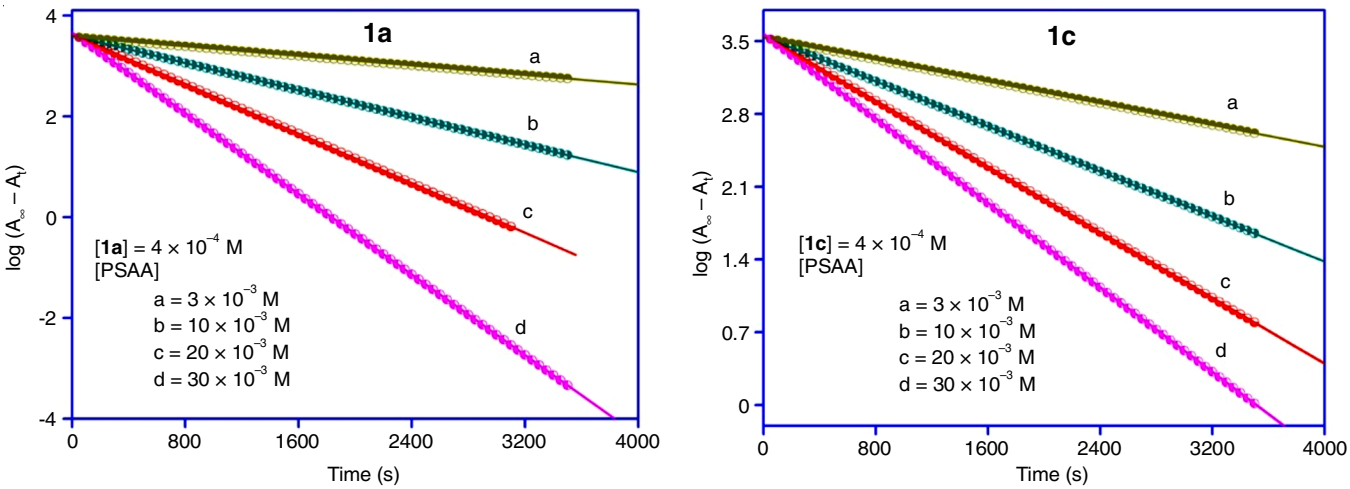


Fig. 3. Progress of the reaction at different [PSAA] in TX-100 medium

TABLE-1
EFFECT OF [PSAA], [**1a**] AND [**1c**] ON THE RATE OF TX-100 MEDIATED REACTIONS

10^3 [PSAA] (M)	$10^4[Fe(NN)_3]^{3+}$ (M)	10^4k_1 (s^{-1})	10^2k_{ov} $(M^{-1})^n$ (s^{-1})
1a			
3.0	4.0	5.65 ± 0.02	7.83 ± 0.03
5.0	4.0	9.12 ± 0.06	8.20 ± 0.05
10.0	4.0	15.8 ± 0.04	7.91 ± 0.02
20.0	4.0	27.5 ± 0.08	7.63 ± 0.02
30.0	4.0	41.7 ± 0.10	8.18 ± 0.02
10.0	2.0	24.5 ± 0.02	12.2 ± 0.01
10.0	8.0	9.71 ± 0.04	4.84 ± 0.02
1c			
3.0	4.0	6.10 ± 0.12	1.74 ± 0.03
5.0	4.0	8.65 ± 0.04	1.84 ± 0.01
10.0	4.0	12.6 ± 0.02	1.80 ± 0.01
20.0	4.0	18.5 ± 0.04	1.76 ± 0.01
30.0	4.0	23.5 ± 0.08	1.78 ± 0.01
10.0	2.0	16.8 ± 0.06	2.39 ± 0.01
10.0	8.0	8.12 ± 0.04	1.16 ± 0.01

$[H^+]$ =0.5 M; μ = 0.6 M; [TX-100] = 5 × 10^{-2} M; solvent =97%H_2O-3%CH_3CN (v/v).

rate constants in TX-100 have higher values as compared to that of in aqueous media [16].

Fig. 4 shows the plots of k_1 *vs.* [PSAA] are linear which are not passing through the origin. Further linear plots are obtained when log k_1 is plotted against log [PSAA] for complexes **1a** and **1c** (Fig. 5). The slope values are found to be fractional values. The slope values are found to be 0.849 for complex **1a** and 0.577 for complex **1c**. The k_2 values calculated using $k_2 = k_1/[PSAA]$ were not constant. Therefore, the overall rate constants were calculated using the relation $k_{ov} = k_1/[PSAA]^{order}$, which are found to be constant. All these facts proved that the order of PSAA for the reactions inTX-100 is fractional.

The linear plots with finite intercept on the rate axis obtained in the double reciprocal plots of k_1 *vs.* [PSAA] (Fig. 6), confirm the Michaelis-Menten kinetics *i.e.* formation of an intermediate between reactant molecules before the rate determining step.

By applying Michaelis-Menten equation:

$$\frac{1}{k_1} = \frac{1}{k} + \frac{K_m}{k[PSAA]}$$

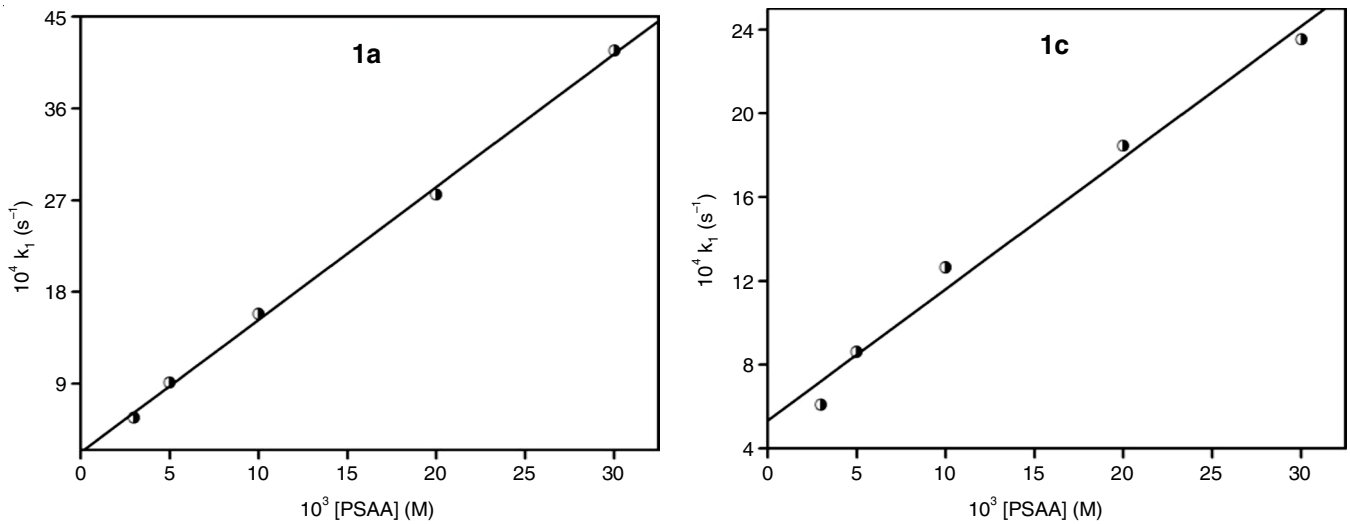


Fig. 4. Plots of k_1 *vs.* PSAA

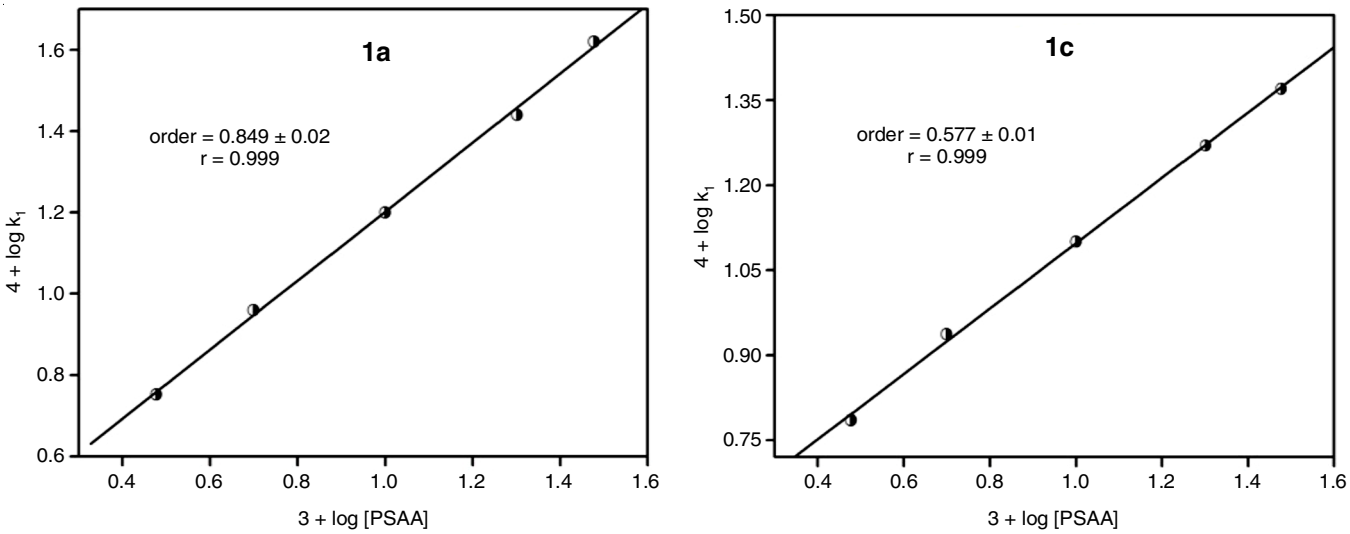


Fig. 5. Order plot for PSAA with **1a** and **1c** in TX-100 medium

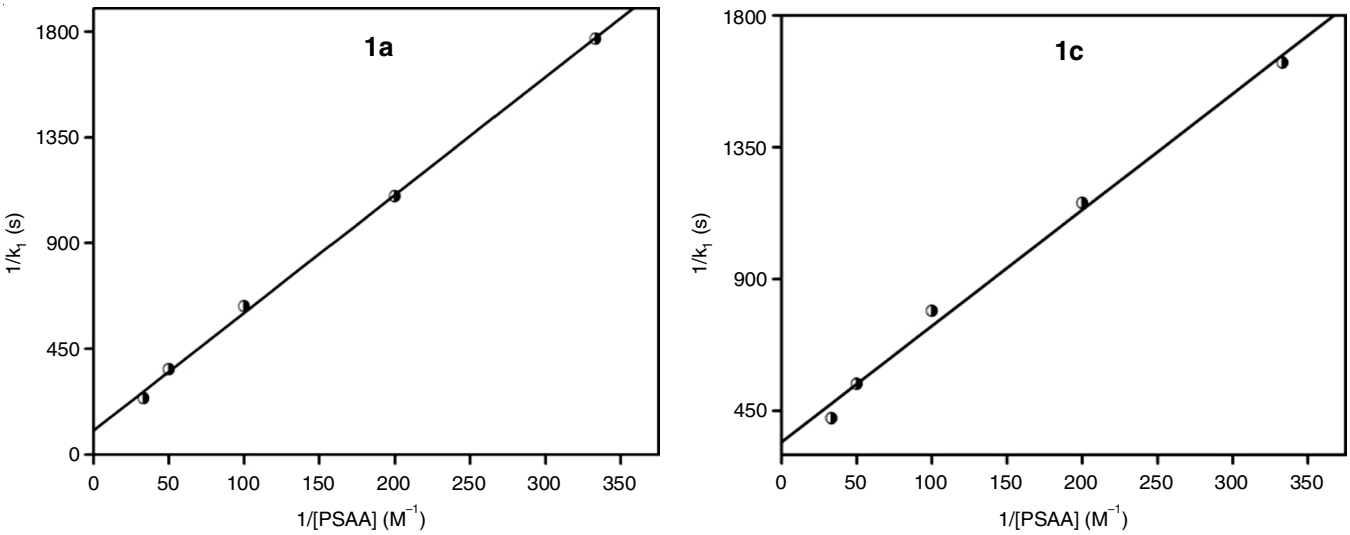


Fig. 6. Michaelis-Menten plot for PSAA with **1a** and **1c** in TX-100 medium

the values of k and K_m were evaluated from the slope and intercept of the double inverse plot of k_1 against [PSAA]. The evaluated K_m values were found to be 5.32×10^{-2} M and 1.33×10^{-2} M for complexes **1a** and **1c**, respectively. The calculated low values of Michaelis-Menten constant ensures the strong binding of PSAA to the iron(III) polypyridyl complexes during intermediate formation in TX-100 medium. Table-2 illustrates the comparative results of binding between the reactants in micellar as well as in aqueous medium.

TABLE-2
COMPARISON OF K_m VALUES IN AQUEOUS AND TX-100 MEDIA

Medium	10^2 K_m (M)	
	1a	**1c**
Aqueous	4.01	0.96
TX-100	5.32	1.33

Among the K_m values obtained in aqueous and TX-100 media, K_m value is found to be low for the reaction in absence of micelles. Usually smaller the binding constant value, greater will be the interaction between the reactants. The observed small K_m value in aqueous medium suggests that the binding is effective in aqueous medium than in micellar medium.

Rate dependence on $[Fe(NN)_3]^{3+}$ in TX-100: The progress of the reaction *i.e.* $\log(A_\infty - A_t)$ against time at different $[Fe(NN)_3]^{3+}$ is shown in Fig. 7. The pseudo-first-order rate constants calculated from the above plots at different initial concentrations of $[Fe(NN)_3]^{3+}$ are tabulated in Table-1. It is concluded that the rate constants decrease with increase in $[Fe(NN)_3]^{3+}$ concentration. The same trend was also observed for the reaction in aqueous medium. As in other cases, the reason for the deceleration in rate may be due to the formation of inactive hydrated complex [17] or oxo-bridged diiron complex [18] followed by the decrease in the concentration of reactive species. The explanations and the formation of the above inactive species are discussed previously [16]. Among the iron(III) polypyridyl complexes, $[Fe(phen)_3]^{3+}$ is less reactive than $[Fe(bpy)_3]^{3+}$.

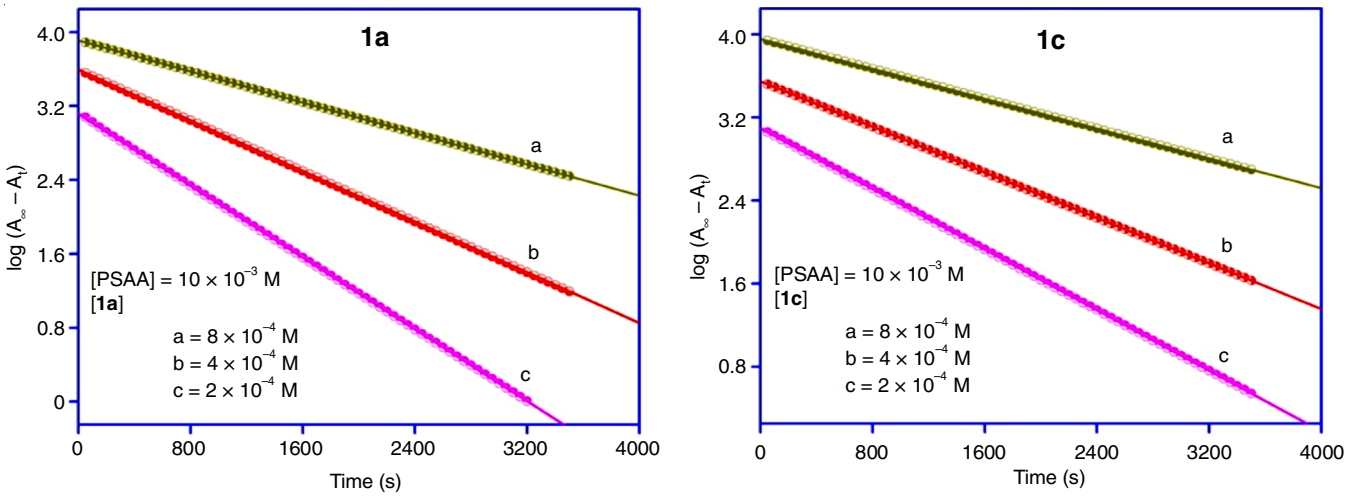


Fig. 7. Progress of the reactions at different [**1a**] and [**1c**] with PSAA in TX-100

Rate dependence on [H$^+$]: The effect of variation of H$^+$ concentration on TX-100 mediated electron transfer reaction between PSAA with complexes **1a** and **1c** were carried out by varying the concentration of perchloric acid. The electron transfer rate increases feebly with an increase in [H$^+$] (Table-3). The mild rate acceleration can be explained by the stabilization of sulfoxide radical cation at high [H$^+$].

TABLE-3
EFFECT OF [H$^+$] ON THE RATE CONSTANT FOR THE REACTION OF PSAA WITH **1a** AND **1c** IN TX-100 MEDIUM

[H$^+$] (M)	$10^2 k_{ov}$ (M^{-1})^n (s^{-1})	
	1a	**1c**
0.5	7.93 ± 0.04	1.83 ± 0.11
0.7	9.03 ± 0.12	2.31 ± 0.08
0.9	9.88 ± 0.02	3.98 ± 0.02
1.0	10.6 ± 0.06	4.45 ± 0.04
1.1	11.2 ± 0.08	5.01 ± 0.05
1.2	12.8 ± 0.06	6.12 ± 0.08

[PSAA] = 1×10^{-2} M; [**1a**] = [**1c**] = 4×10^{-4} M; μ = 1.2 M; [TX-100] = 5×10^{-2} M; solvent = 97% H_2O-3% CH_3CN (v/v)

Dependence of TX-100 on rate: To study the effect of TX-100 on the reaction rate of electron transfer between PSAA and $[Fe(NN)_3]^{3+}$, a series of kinetic runs were carried out with varied concentrations of TX-100 from 3×10^{-3} M to 15×10^{-2} M at constant $[Fe(NN)_3]^{3+}$, [H]$^+$, μ, [PSAA] and temperature. Though the reaction rate is found to be linearly accelerated with increase in concentration of TX-100 at low concentration region, the rate constant reaches a maximum and then decreases at higher concentration of TX-100 for the complexes **1a** to **1d**. However, in case of complex **1e** the rate constant increases continuously irrespective of concentrations studied without any maxima and rate retardation. The results (Table-4) also revealed that the accelerating effect of TX-100 is only marginal in complexes **1a** to **1d**, while in complex **1e**, TX-100 shows a tremendous catalytic effect.

Similar rate acceleration with increase in TX-100 concentration was observed in the oxidation of phenyl vinyl sulfide [19] and diphenyl sulphide [20] with iron(III) polypyridyl complexes in TX-100 medium. The rates of dioxygenase reaction of mononuclear iron(III) complexes were significantly higher in TX-100 [21] due to the binding of cation of iron(III) complex with the neutral head group of TX-100. Rate enhancement was also observed with TX-100 for the chromic acid oxidation of dimethyl sulfoxide to dimethyl sulfone [22] and oxidative degradation of D-sucrose by *N*-bromosuccinimide [23]. Rate acceleration of the reaction at low concentrations and reaching

TABLE-4
EFFECT OF [TX-100] ON THE RATE OF REACTION BETWEEN PSAA AND THE COMPLEXES **1a-e**

10^2[TX-100] (M)	$10^4 k_1$ (s^{-1})				
	1a	**1b**	**1c**	**1d**	**1e**
0	7.14 ± 0.04	3.63 ± 0.08	8.33 ± 0.02	1.69 ± 0.01	13.3 ± 0.06
0.8	7.54 ± 0.08	3.79 ± 0.02	8.34 ± 0.08	1.77 ± 0.01	13.9 ± 0.08
0.9	7.66 ± 0.11	3.89 ± 0.12	8.45 ± 0.04	1.89 ± 0.02	14.7 ± 0.12
1.0	8.25 ± 0.02	4.15 ± 0.04	8.56 ± 0.06	2.13 ± 0.01	16.8 ± 0.08
2.0	8.46 ± 0.01	4.26 ± 0.06	9.40 ± 0.02	2.20 ± 0.04	17.5 ± 0.14
3.0	8.66 ± 0.14	4.31 ± 0.08	10.3 ± 0.05	2.29 ± 0.01	18.6 ± 0.06
4.0	11.4 ± 0.21	5.64 ± 0.14	11.2 ± 0.07	3.23 ± 0.04	47.9 ± 0.18
5.0	15.8 ± 0.03	5.97 ± 0.04	12.6 ± 0.02	3.73 ± 0.02	90.5 ± 0.22
7.0	14.6 ± 0.05	6.44 ± 0.02	13.5 ± 0.01	3.99 ± 0.03	138 ± 0.24
9.0	14.2 ± 0.02	6.15 ± 0.06	14.9 ± 0.06	3.88 ± 0.01	176 ± 0.18
10.0	13.5 ± 0.06	5.64 ± 0.01	17.5 ± 0.03	3.15 ± 0.04	196 ± 0.26
12.0	12.2 ± 0.07	5.04 ± 0.04	16.3 ± 0.01	2.74 ± 0.01	215 ± 0.16
15.0	11.6 ± 0.05	4.42 ± 0.06	15.1 ± 0.03	2.08 ± 0.05	244 ± 0.28

[PSAA] = 1×10^{-2} M; [**1a-e**] = 4×10^{-4} M; [H$^+$] = 0.5M; μ = 0.6 M; [TX-100] = 5×10^{-2} M; solvent = 97% H_2O-3% CH_3CN (v/v).

a plateau at higher concentrations of TX-100 was observed in the oxidation of methionine [24] and glycyl leucine [25] by colloidal MnO_2. Similar rate enhancement at lower concentrations of TX-100 followed by a limiting value at higher concentrations was also observed in the oxidation of dextrose by *N*-bromophthalimide in the presence of mercuric(II) acetate [26].

The retardation of rate in the oxidation of *p*-anisaldehyde by chromic acid inTX-100 medium [27] was explained by the low concentration of protons needed for reaction in the miceller phase and a small concentration of intermediate neutral ester formed in the aqueous phase. The ester enters in to the miceller phase by hydrophobic interaction. Retardation of rate with TX-100 was also recorded in the hydrolysis of thiamine pyrophosphate [28].

Rate dependence of substituted PSAA in TX-100 medium: The substituent effect can give more information about the nature of transition state intermediates and the mechanism of electron transfer, the rate of the reaction was examined with several *meta*- and *para*-substituted PSAAs with complexes **1a** and **1c** at three different temperatures *viz.* 293 K, 303 K and 313 K. On applying the Hammett substituent constants to the overall rate constants obtained in TX-100 medium gave non-linear concave upward Hammett plots.

The electron releasing group (ERG) fall on one side of the curve with large negative ρ value and the electron withdrawing group (EWG) fall on the other side with low positive ρ value. The PSAA with ERG and EWG have higher rate constant values compared to parent PSAA. This indicates that the substituents have accelerating effect on the rate of reaction. The ρ^+ and ρ^- values obtained from Hammett plots (Figs. 8 and 9) along with the overall rate constants for the complexes **1a** and **1c** are tabulated in Tables 5 and 6, respectively.

The observed trend of pronounced rate acceleration by ERG than EWG indicates the involvement of more positively polarized sulfoxide center of PSAA in the transition state than in the reactant. Similar high ρ^- values are obtained for the reactions in aqueous mediated reactions of PSAAs with complexes **1a** and **1c** [16]. Such high ρ^- values were also observed in many sulfoxidation studies [29].

Evaluation of thermodynamic parameters: The rate constants obtained for several PSAAs with complexes **1a** and **1c** at different temperatures were analyzed using Eyring's equation [30]. The overall rate constants for the substituted PSAAs fit Eyring's equation excellently and the thermodynamic parameters calculated from the Eyring's plot (Fig. 10) are given in Tables 5 and 6. The reaction was characterized by low enthalpy of activation and appreciable negative entropy of activation implying that the activated complex has a specific orientation. Further, the large negative entropy values ($\Delta S^{\ddagger}$) and moderate enthalpy ($\Delta H^{\ddagger}$) values observed in present study are of the magnitude, expected for a bimolecular nucleophilic attack of organic sulfur compounds. Such analogous values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are reported in the oxygenation of aromatic sulfides and aryl mercapto acetic acids by peroxomonophosphoric acid and phenylthioacetic acids by chloramines-T where sulfonium ion intermediate has been proposed as a result of bimolecular nucleophilic attack.

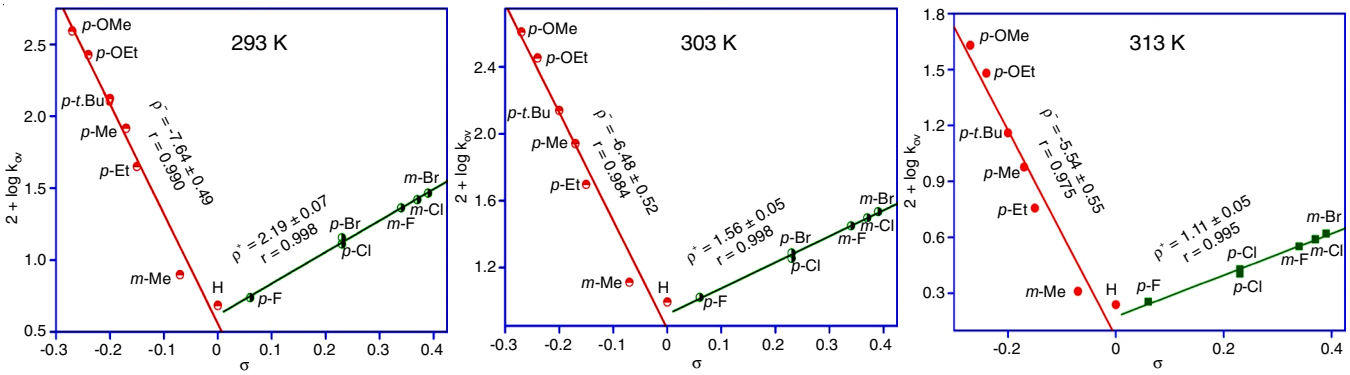


Fig. 8. Non-linear Hammett plot in TX-100 medium for **1a** at different temperatures

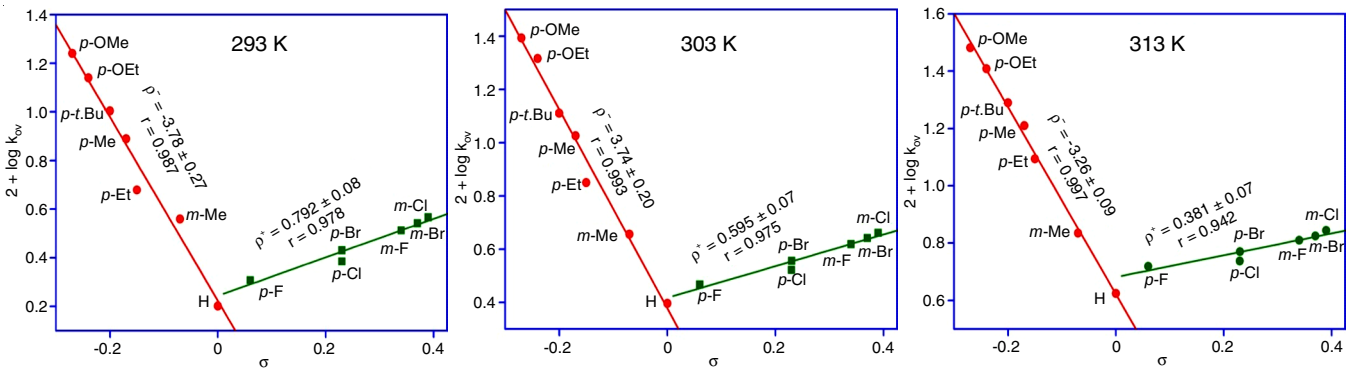


Fig. 9. Non-linear Hammett plot in TX-100 medium for **1c** at different temperatures

TABLE-5
OVERALL RATE CONSTANTS AND THERMODYNAMIC PARAMETERS FOR THE OXIDATION OF *para*- AND *meta*-SUBSTITUTED PSAAs BY **1a** IN TX-100 MEDIUM

X	$10^2 k_{ov}(M^{-1})^n (s^{-1})$			$\Delta H^{\ddagger}$ (kJ mol^{-1})	$-\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})
	293 K	303 K	313 K		
p-F	5.49 ± 0.08	10.5 ± 0.03	18.0 ± 0.12	42.8 ± 0.54	46.4 ± 1.89
p-Cl	12.9 ± 0.12	17.9 ± 0.11	25.5 ± 0.06	23.2 ± 0.45	106 ± 1.59
p-Br	14.3 ± 0.16	19.3 ± 0.10	26.8 ± 0.22	21.4 ± 0.58	111 ± 2.04
m-F	23.1 ± 1.02	28.1 ± 0.15	35.6 ± 0.46	14.3 ± 1.89	132 ± 6.64
m-Cl	26.4 ± 1.04	31.4 ± 0.47	38.9 ± 1.88	11.9 ± 2.50	139 ± 8.79
m-Br	29.2 ± 0.56	34.2 ± 2.05	41.7 ± 0.61	10.6 ± 2.35	142 ± 8.26
H	4.84 ± 0.08	7.91 ± 0.06	17.3 ± 0.22	46.2 ± 0.82	35.7 ± 2.90
m-Me	7.92 ± 0.44	12.9 ± 0.66	20.4 ± 0.74	33.6 ± 3.32	74.6 ± 11.7
p-Et	44.7 ± 0.32	49.6 ± 0.82	57.2 ± 0.64	6.74 ± 0.84	152 ± 2.97
p-Me	82.4 ± 1.36	87.4 ± 2.88	94.9 ± 1.02	2.69 ± 1.61	160 ± 568
ρ^+	2.19 ± 0.07	1.56 ± 0.05	1.11 ± 0.05		
R	0.998	0.998	0.995		
ρ^-	-7.64 ± 0.49	-6.48 ± 0.52	-5.54 ± 0.55		
R	0.990	0.984	0.975		

[PSAA] = 1×10^{-2} M; [**1a**] = 4×10^{-4} M; [H$^+$] = 0.5 M; μ = 0.6 M; [TX-100] = 5×10^{-2} M; solvent = 97% H_2O-3% CH_3CN (v/v)

TABLE-6
OVERALL RATE CONSTANTS AND THERMODYNAMIC PARAMETERS FOR THE OXIDATION OF *para*- AND *meta*-SUBSTITUTED PSAAs BY **1c** IN TX-100 MEDIUM

X	$10^2 k_{ov}(M^{-1})^n (s^{-1})$			$\Delta H^{\ddagger}$ (kJ mol^{-1})	$-\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})
	293 K	303 K	313 K		
p-F	2.03 ± 0.03	2.93 ± 0.03	5.23 ± 0.02	33.4 ± 0.73	68.0 ± 2.58
p-Cl	2.43 ± 0.08	3.33 ± 0.01	5.46 ± 0.06	28.3 ± 1.19	83.8 ± 4.20
p-Br	2.69 ± 0.12	3.59 ± 0.12	5.89 ± 0.02	27.2 ± 2.07	86.6 ± 7.29
m-F	3.26 ± 0.22	4.16 ± 0.05	6.45 ± 0.13	23.5 ± 2.53	97.9 ± 8.92
m-Cl	3.48 ± 0.06	4.38 ± 0.07	6.68 ± 0.08	22.2 ± 1.15	101 ± 4.05
m-Br	3.68 ± 0.04	4.58 ± 0.05	6.98 ± 0.21	21.8 ± 1.32	103 ± 4.64
H	1.59 ± 0.02	1.80 ± 0.06	4.21 ± 0.22	34.7 ± 2.26	65.5 ± 7.96
m-Me	3.63 ± 0.04	4.53 ± 0.16	6.83 ± 0.14	21.5 ± 1.70	104 ± 5.98
p-Et	4.77 ± 0.12	7.08 ± 0.22	12.4 ± 0.04	33.8 ± 1.51	59.3 ± 5.32
p-Me	7.74 ± 0.02	10.6 ± 0.28	16.2 ± 0.02	25.7 ± 0.77	82.9 ± 2.71
p-*t*.Bu	10.1 ± 0.16	12.9 ± 0.26	19.5 ± 0.14	22.5 ± 1.10	91.7 ± 3.86
p-OEt	13.8 ± 0.18	20.7 ± 0.02	25.6 ± 0.22	21.2 ± 0.57	93.2 ± 2.02
p-OMe	17.4 ± 0.16	24.7 ± 0.19	30.3 ± 0.02	18.7 ± 0.47	99.8 ± 1.57
ρ^+	0.792 ± 0.08	0.595 ± 0.07	0.381 ± 0.07		
R	0.978	0.975	0.942		
ρ^-	-3.78 ± 0.27	-3.74 ± 0.20	-3.26 ± 0.09		
R	0.987	0.993	0.998		

[PSAA] = 1×10^{-2} M; [**1c**] = 4×10^{-4} M; [H$^+$] = 0.5 M; μ = 0.6 M; [TX-100] = 5×10^{-2} M; solvent = 97% H_2O-3% CH_3CN (v/v)

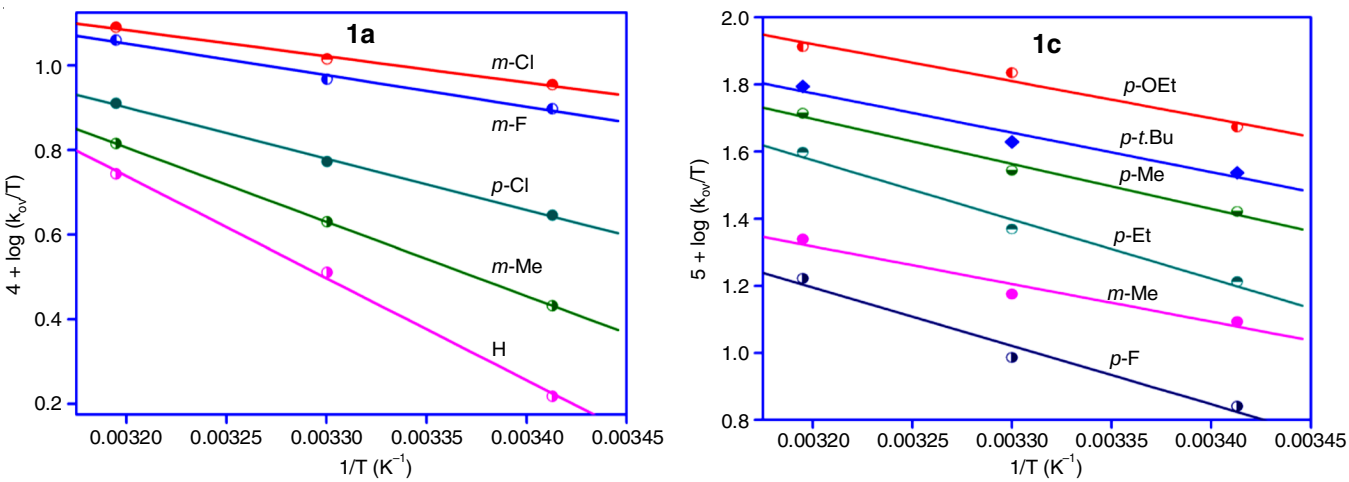


Fig. 10. Eyring's plots for the reaction in TX-100 medium

Isokinetic relationship: As the analysis of kinetic data with respect to linear free energy relationships is indispensable, the validity of isokinetic relationship is tested with the observed $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values as per eqn. 1:

$$\Delta H^{\ddagger} = \Delta H^{\ddagger} + \beta\Delta S^{\ddagger} \quad (1)$$

where β is the isokinetic temperature at which all the substituents in a given series have the same reactivity. Though the Petersen's error criterion for the validity of $\Delta H^{\ddagger} - \Delta S^{\ddagger}$ relationship is satisfied, $\Delta\Delta H^{\ddagger}$ (kJ mol^{-1}) > 2Δ (kJ mol^{-1}), the plot of $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$ gives only a poor correlation. However, Exner's plot of log k_{ov} (313 K) against log k_{ov} (293 K) correlates excellently (Fig. 11; r = 0.987 for **1a** and 0.996 for **1c**) and the slope (b) of the plot affords the isokinetic temperature β. The isokinetic temperature computed is 386 K for complex **1a** and 366 K for complex **1c** which is higher than the experimental temperature.

Mechanism: The results obtained during the variation of [PSAA], $[Fe(NN)_3]^{3+}$ and $[HClO_4]$ in TX-100 medium are identical with the results of the reaction in aqueous medium [16]. These results along with spectral results show that the reaction mechanism in the presence of TX-100 remains the same as that in aqueous medium. The rate enhancement observed in the electron transfer reaction between PSAA and $[Fe(NN)_3]^{3+}$ in TX-100 may be due to the hydrogen bonding and hydrophobic interaction which occurs between the surfactant and reactants (**Scheme-I**).

The iron atom of $[Fe(NN)_3]^{3+}$ complex receives a nucleophilic attack by the sulfur atom of PSAA, incorporating PSAA to form a bimolecular complex. As the reaction follows a non-integral kinetic order for PSAA, it is reasonable to envisage that the reaction follows Michaelis-Menten kinetics. As a result of nucleophilic attack of PSAA on $[Fe(NN)_3]^{3+}$, a positive charge is developed on the sulfur atom of PSAA in the intermediate.

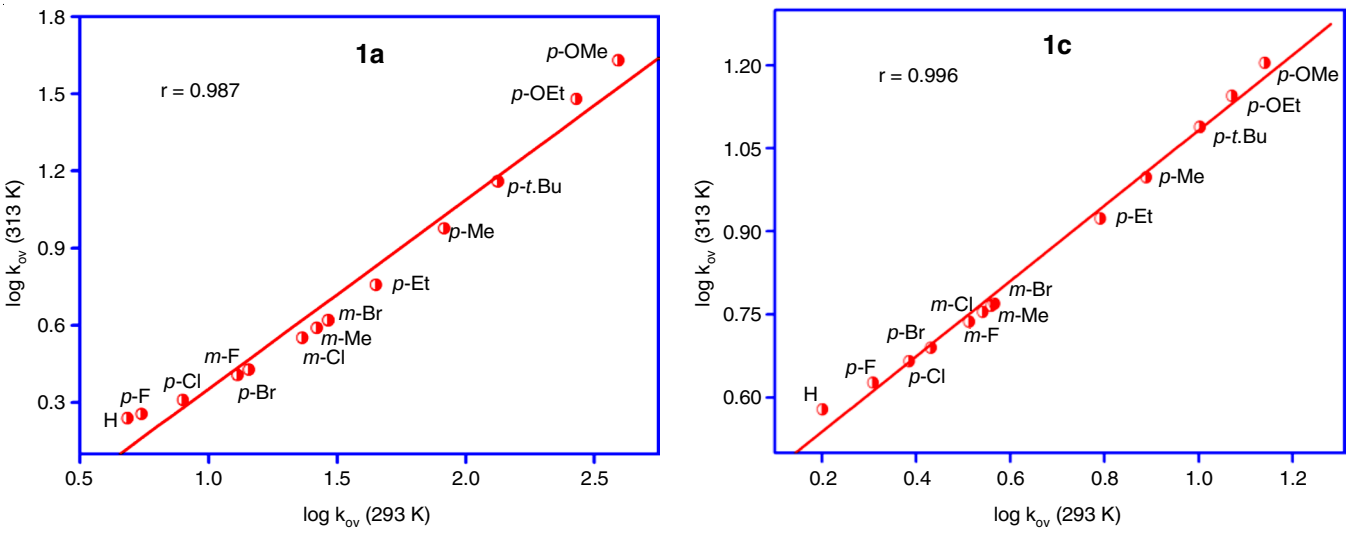
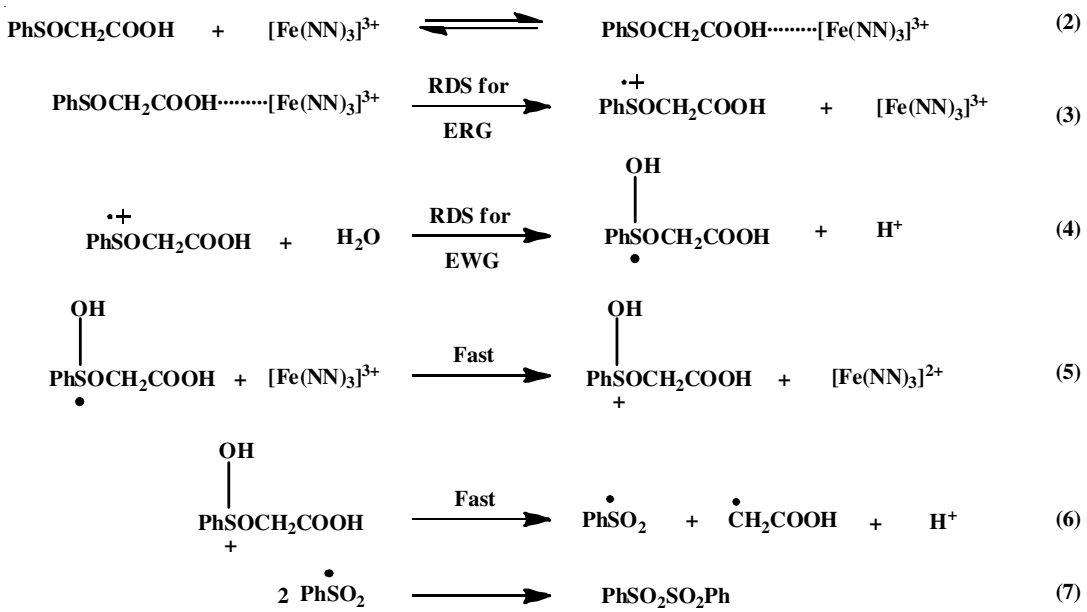


Fig. 11. Exner's plots for the reactions in TX-100 medium



Scheme-I: Mechanism of the reaction in TX-100 medium

The nature of transition state was studied by varying the substituents in *meta*- and *para*-positions of PSAA and $[Fe(NN)_3]^{3+}$. The trend of the reaction with different substituents indicates that the electron releasing substituents in the *para*- and *meta*-positions accelerate the reaction to a greater extent where as electron withdrawing groups accelerate the reaction to a lesser extent. On the basis of above discussion and the observed rate acceleration by both electron withdrawing and electron donating substituents, two different rate determining steps have been proposed on the basis of stabilization of the positive centre on sulfoxide radical cation in the intermediate by electron releasing groups and facilitation of nucleophilic attack of water on the sulfoxide radical cation of PSAA by electron withdrawing groups. Additional evidence for the formation of sulfonium cation radical in the rate determining step *via* electron transfer comes from the rate enhancement by the addition of acid. It has been established that the sulfur radical cation is stabilized by $[H^+]$.

From the formation of diphenyl disulfone as final product, it has been proposed that major portion of sulfoxide cation radical is consumed by the solvent water (eqn. 4) followed by electron transfer and fragmentation. The sulfoxide radical formed as a result of nucleophilic attack of water on sulfoxide cation radical (eqn. 3) is followed by second electron transfer by another $[Fe(NN)_3]^{3+}$ (eqn. 5). This type of electron transfer is already shown in the oxidation of sulfur compounds by polypyridyl complexes. The sulfoxide cation then undergoes a C-S bond cleavage β to the aromatic ring [31] to form phenylsulfonyl free radical which then undergoes dimerization leading to the formation of diphenyl disulfone as product [32].

Interpretation of micellar effect: From Fig. 12, it is clear that the rate constant increases at low concentration of TX-100, reaches a maximum and thereafter, decreases with an increase in concentration of TX-100. The decrease in reaction rate at higher surfactant concentration is seen in most of the micelle catalyzed bimolecular reactions. This may be due to the dilution of the reactant molecules in the micellar medium. At higher [surfactant] though the total number of micelles is increased, the stoichiometric concentrations of the substrate and the oxidant in and around Stern layer of micellar surface are decreased [33]. As a result, the net concentration of the reactants is diluted with the increase in the concentration of surfactants and thereby causing a decrease in the reaction rate.

It is well-established that most of the micellar reactions involving ionic and neutral reactants are believed to take place either inside the Stern layer or at the interface between the micellar surface and the bulk solvent, water. The effect of non-ionic micelles on the reaction rates of bimolecular reactions is due to the association or incorporation of reactants through hydrophobic interaction and hydrogen bonding within a small volume of the self-assemblies. TX-100 contains an average of 9.5 oxyethylene units per molecule, which has been widely used as a dispersing agent for the colloidal suspensions. The TX-100 molecules contain an aromatic nucleus, a highly methylated hydrocarbon chain as the hydrophobic part and an oxyethylene ethereal group, where oxyethylene oxygen atom can make the hydrogen bond.

The observed increase in rate with increase in concentration of TX-100 at low concentrations clearly shows that the

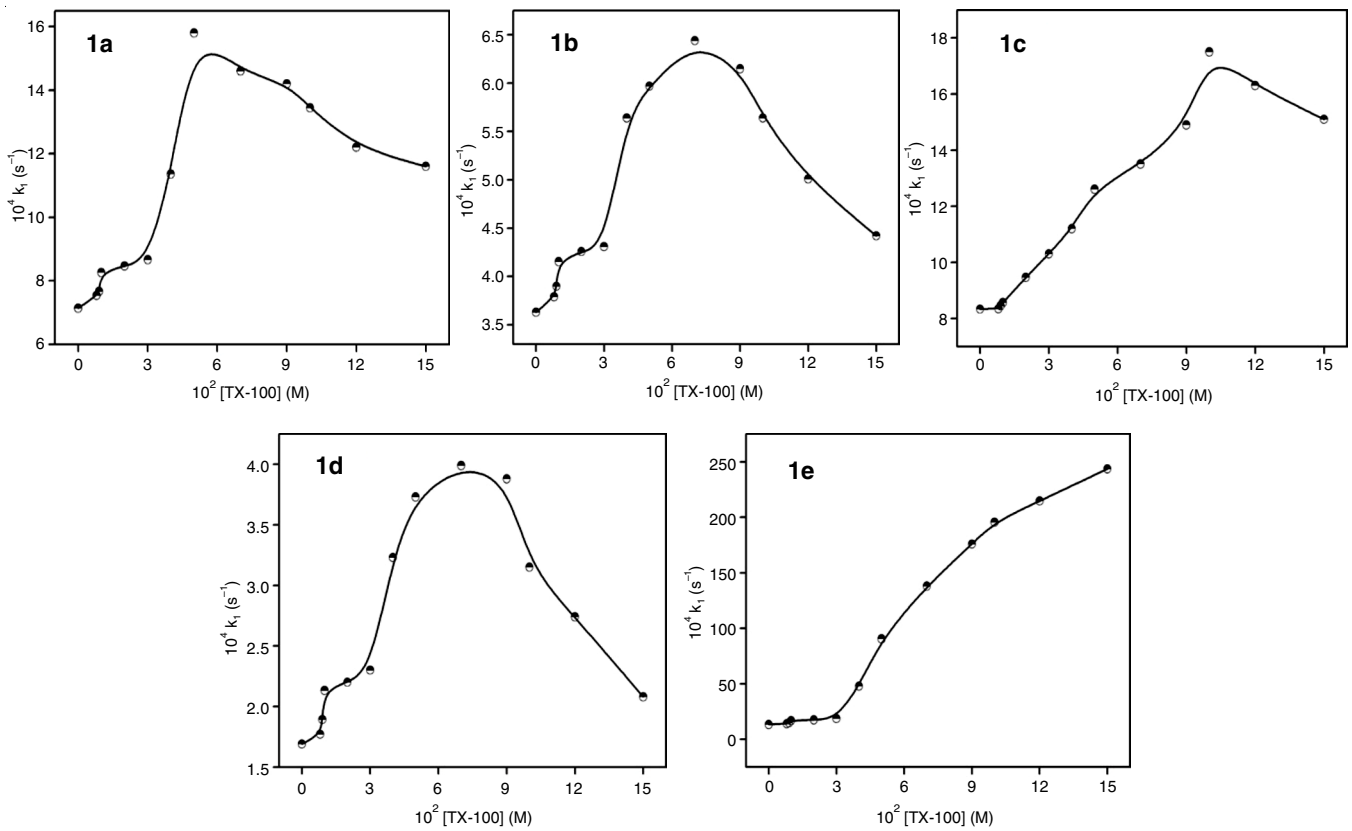


Fig. 12. Variation of rate constants with [TX-100]

reaction takes place in micellar medium and both the reactants are associated or incorporated into micellar phase. The neutral PSAA molecule can concentrate in the micellar phase by hydrophobic interaction or hydrogen bonding or both together. PSAA has a carboxyl hydrogen which can form hydrogen bond with TX-100 through its oxyethylene oxygen atom. Thus, PSAA has a free hydrogen bonding site and due to this hydrogen bond, the stoichiometric concentration of the reactant molecule, PSAA increases at the Stern layer of TX-100. Enhancement of rate observed in the oxidation of methionine by colloidal MnO_2, oxidation of dextrose by N-bromophthalimide, in TX-100 medium was explained by hydrogen bond formation between the polar ethylene oxide of TX-100 and the substrate.

The oxidant, $[Fe(NN)_3]^{3+}$ cation also bind to the neutral head groups of TX-100 of course less strongly by a weak electrostatic attraction between the π-electrons of benzene ring in the head group of TX-100 and the positive charge on the oxidizing species, $[Fe(NN)_3]^{3+}$. Thus, the reactants PSAA and $[Fe(NN)_3]^{3+}$ are lying closer together in the stern layer of micelle by hydrogen bonding and electrostatic force of attraction, respectively. Because of their closer proximity in micellar medium, the reactants react faster than in aqueous media. At low concentrations of TX-100, the extent of positioning of the reactants and their stoichiometric concentration in micellar phase increase which result in an increase in the rate constant.

Conclusion

The kinetics of the electron transfer reactions between phenylsulfinylacetic acids (PSAAs) and $[Fe(NN)_3]^{3+}$ where NN = 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 studied in the presence of non-ionic surfactant, (TX-100) in order to gain a better understanding of their oxidizing properties. The calculated low values of Michaelis-Menten constant (K_m) ensures strong binding of PSAA to iron(III) polypyridyl complexes during intermediate formation in TX-100 medium. Smaller the binding constant value, greater will be the interaction between the reactants. On applying the Hammett substituent constants to the overall rate constants obtained in TX-100 medium, it gave non-linear concave upward Hammett plots. The rate enhancement observed in the electron transfer reaction between PSAAs and $[Fe(NN)_3]^{3+}$ in TX-100 was attributed to the hydrogen bonding and hydrophobic interaction occurring between the surfactant and reactants.

ACKNOWLEDGEMENTS

One of the authors, RJER, thanks The UGC-South Eastern Regional Office (SERO), Hyderabad, the Management of Nazareth Margoschis College and Manonmaniam Sundaranar University for the award of a fellowship under faculty development program (FDP). The authors also gratefully thank the Management, Aditanar College of Arts and Science, Tiruchendur, India for providing essential research facilities.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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