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Mechanistic study on the oxidation of (phenylthio)acetic acids by oxo(salen)manganese(V) complexes and the reactivity–selectivity principle

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Abstract

A systematic study on the kinetics and mechanism of oxidation of several (*para*-substituted phenylthio)acetic acids with various substituted oxo(salen)manganese(V) complexes in acetonitrile at 20 °C is presented. The kinetic data indicate that the reaction is second-order overall, first-order each in (phenylthio)acetic acid and oxo(salen)manganese(V) complex. Rate studies with substituted (phenylthio)acetic acids give an excellent Hammett correlation with σ^+/σ^- constants and the ρ-values are in the range of −0.82 to −1.17 for different oxo(salen)manganese(V) complexes. The $\log k_2$ values observed in the oxidation of each (phenylthio)acetic acid by substituted oxo(salen)manganese(V) complexes correlate with 2σ, giving ρ-values from 0.26 to 0.56. A mechanism involving single electron transfer from the sulfur center of the substrate to the oxo complex in the rate-controlling step is envisaged. Kinetic data were obtained over a temperature range of 15–35 °C and the activation parameters evaluated. Correlation analyses show the presence of an inverse relationship between reactivity and selectivity in the reactions of various (phenylthio)acetic acids with a given oxo(salen)manganese(V) complex and also in various oxo(salen)manganese(V) complexes with a given (phenylthio)acetic acid. Mathematical treatment of the results shows the operation of a valid reactivity–selectivity principle in this redox system.

Keywords: (Phenylthio)acetic acids; Iodosylbenzene; (Salen)Mn^{III} complexes; Catalyzed oxidation; Reaction mechanism

1. Introduction

Selective oxygenation of organic compounds catalyzed by transition metal ions is one of the most productive and elegant techniques for the oxo functionalization of organic substrates [1,2]. Many groups have extensively used the metal–salen complexes (metal = Mn, Cr, Fe, Ru, Co, V and Ti) for the epoxidation reactions [3,4]. But employment of these catalysts for the oxidation of organic substrates containing heteroatoms like S, N and P is limited [4–18]. For the oxygenation reactions of organic substrates the metal-oxo species are generated from transition metal complexes using dioxygen [5] and a wide variety of oxygen transfer agents [8] including iodosylbenzene, percarboxylic acids, hydrogen peroxide, sodium perchlorite and activated N-oxides. High-valent metal-oxo species play important roles in a large number of synthetic and biological transformations [1]. The preparation of Mn-substituted cytochrome P-450 cam by Gelb et al. [19] and the suspected involvement of higher valent oxomanganese species in oxygen evolution in photosynthesis [20] have encouraged studies of oxygen atom transfer reactions catalyzed by manganese complexes. Manganese-oxo complexes of both porphyrin [21] and salen [22] catalysts are implicated in various oxygen atom transfer reactions of considerable synthetic importance and have also served as models for intermediates in heme protein catalyzed oxidations and related reactions. Mn(III) is also present in active sites of enzymes [23] like superoxides dismutase and azide-insensitive catalase which catalyze the redox reactions of oxygen species.

Though a large variety of oxidants have been used in the past five decades for the oxidation of biologically important organic sulfides [24–31], the recent interest is on the oxidation of organic sulfur compounds using transition metal based oxidants [7–18,32–40]. Oxidation of (phenylthio)acetic acids by

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Abbreviation: salen, *N*,*N*′-ethylenebis(salicylideneaminato).

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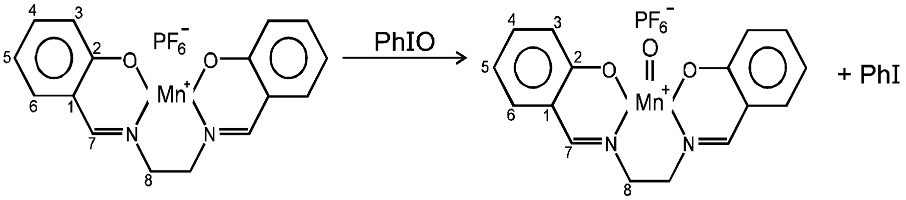
periodic acid with RuO_4 catalyst [41], permanganate [42], potassium peroxydisulfate [43], peroxomonophosphoric acid [44], potassium peroxydiphosphate [45], Chloramine-T [46], Ce(IV) [47], pyridinium fluorochromate [48], *N*-chlorosuccinimide [49], potassium ferrate [50], Bromamine-T [51] and potassium hexacyanoferrate(III) [52] have been reported. We have initiated a systematic study on the oxygenation reactions of organosulfur compounds with oxometal complexes by taking Cr, Mn and Ru as metal ions. Recently we reported the mechanism of oxidation of organic sulfides and sulfoxides with PhIO [8–12], NaOCl [13–15] and H_2O_2 [16] catalyzed by metal–salen complexes. In this paper, we report the kinetics and mechanism of oxidation of (phenylthio)acetic acids with oxo(salen)manganese(V) complexes **2a–f** generated in situ from the corresponding $[Mn^{III}(salen)]^+PF_6^-$ complexes and PhIO as represented in Eq. (1). To our knowledge, this seems to be the first report on the metal-oxo oxygenation of (phenylthio)acetic acids:



1 2

a : unsubstituted
b : 5,5'-$(OCH_3)_2$
c : 5,5'-Cl_2
d : 5,5'-$(NO_2)_2$
e : 7,7'-$(CH_3)_2$
f : 7,7'-$(C_6H_5)_2$

(1)

Reactivity–selectivity principle (RSP) has been tested with hydration, acid–base catalysis, solvolysis, oxidation, reduction and other types of reaction [10,25,53,54]. The study of applicability of RSP to biologically relevant oxygen atom transfer reactions is of current interest. Recently we have reported the applicability of RSP in the oxidation of organic sulfides and sulfoxides with PhIO [9–11] and NaOCl [14,15] catalyzed by $(salen)Mn^{III}$ complexes. Herein we also report the study of applicability of RSP to the present system.

2. Experimental

2.1. Materials

(Phenylthio)acetic acid and (substituted phenylthio)acetic acids were prepared by standard procedure from the corresponding thiophenols and chloroacetic acid in alkaline medium [43]. A different procedure was adopted for obtaining (*p*-nitrophenylthio)acetic acid from *p*-chloronitrobenzene and thioglycollic acid [43]. The physical constants for the (phenylthio)acetic acids were found to agree with literature values [43]. The GC and TLC analyses of each (phenylthio)acetic acid showed the presence of a single entity. Acetonitrile (GR, E. Merck) was first refluxed over P_2O_5 for 5 h and then distilled. Iodosylbenzene was prepared from (diacetoxyiodo)benzene by a standard method [55].

The $[Mn^{III}(salen)]^+PF_6^-$ complexes **1a–f** were synthesized according to a known procedure [3,8–11,13–16]. The IR and UV–vis spectral studies of all of the complexes were found to be identical with literature data [3]. The oxo complexes **2a–f** were generated [8–11] in situ by stirring magnetically 0.15 mmol of finely powdered PhIO in 5 ml of an acetonitrile solution containing 0.015 mmol of the corresponding $(salen)Mn^{III}$ complex for 5 min under nitrogen, followed by filtration at ice temperature to remove the undissolved iodosylbenzene. The conversion of Mn^{III} to Mn^{V} may be considered quantitative in the sense that prolonged stirring causes no change in the initial absorption spectrum of the Mn^{V} solution. Because the oxomanganese(V) complex undergoes auto decomposition, the solutions were prepared freshly for each kinetic run.

2.2. Kinetic measurements

Reaction mixtures for kinetic runs were prepared by quickly mixing the solutions of the oxo complex and the (phenylthio)acetic acid in varying volumes so that in each run the total volume was 5 ml. The progress of the reaction was followed in a PerkinElmer UV–vis spectrophotometer (Lambda 25) fitted with a thermostated cell compartment under pseudo-first-order conditions ([substrate] > [oxo complex]) in acetonitrile at 20 ± 0.1 °C by monitoring the decay of the oxo complex at 680 nm [3,8–11,13–15].

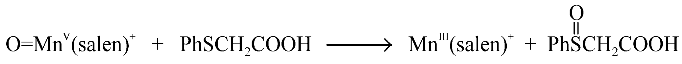
The rate constants were computed from the linear least-squares plots of $\log(A_t - A_\infty)$ versus time, where A_t is the absorbance at time t and A_∞ is the experimentally determined infinity point. The first-order rate constants $k_{1(\mathrm{dec})}$ for the auto decomposition of oxomanganese(V) were determined from the first-order plots up to 50–60% of reaction. The plots for the decay of the oxo complex in the presence of (phenylthio)acetic acid were linear over 50% of the reaction and the pseudo-first-order rate constants $k_{1(\mathrm{obs})}$ were determined from the disappearance of the oxo complex up to this extent. The values of k_1 were obtained [5,8–11,13–15] as $k_1 = k_{1(\mathrm{obs})} - k_{1(\mathrm{dec})}$. The second-order rate constants were obtained by the relation $k_2 = k_1/[\text{substrate}]$.

2.3. *Product analysis*

The reaction mixture from an actual kinetic run (after keeping it for overnight) was extracted with ether and dried over anhydrous Na_2SO_4. The solvent was removed at reduced pressure. TLC analysis (silica gel) of the reaction mixture {solvent system: *n*-butanol–water–acetic acid (4:5:1)-upper layer} gave two spots corresponding to (phenylthio)acetic acid ($R_f = 0.84$) and phenylsulfinylacetic acid ($R_f = 0.45$), respectively, thereby establishing phenylsulfinylacetic acid as the reaction product. The infrared spectrum of the reaction product, separated from the reaction mixture, gave an intense absorption band at $1050\,\mathrm{cm}^{-1}$ characteristic of SO stretching. The product was dissolved in acetonitrile and GC analyses of the samples showed the presence of phenylsulfinylacetic acid and iodobenzene. The yield of phenylsulfinylacetic acid (78–98%) depended on the (phenylthio)acetic acid and oxo complex employed. The lower yield of phenylsulfinylacetic acid may be attributed to the competitive self-decomposition of the oxomanganese(V) complex to the Mn^{III} complex, which is confirmed by the near quantitative recovery of Mn^{III} complex from the reaction mixture.

2.4. *Stoichiometry*

The reaction was carried out under the experimental conditions, [**2**] = 0.0018 M; [$PhSCH_2COOH$] = 0.2 M. The resultant solution after the completion of the reaction gave phenylsulfinylacetic acid in ca.79% yield and (salen)Mn^{III} complex in ca.96% yield. Accordingly, the stoichiometry of the reaction can be represented by the following equation:



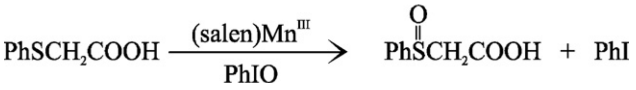
$$\mathrm{O{=}Mn^{V}(salen)^{+} + PhSCH_2COOH \longrightarrow Mn^{III}(salen)^{+} + Ph\overset{\overset{O}{\|}}{S}CH_2COOH}$$

(2)

3. Results and discussion

3.1. *Generation of oxo(salen)manganese(V) complex*

It has been well established that oxo(salen)manganese(V) complexes **2a**–**f** are formed by stirring clear solutions of (salen)Mn^{III} complexes **1a**–**f** in acetonitrile with PhIO [3,8–11]. The formation of oxomanganese(V) species is associated with the following two changes: (i) the light brown color darkens, and (ii) the characteristic peak of (salen)Mn^{III} at $\lambda_{max} \approx 350$ nm disappears and a new absorption band at $\lambda_{max} \approx 530$ nm appears. The dark brown solution, on standing, faded to the original light brown solution within 2–3 h. When the same experiment was carried out in the presence of (phenylthio)acetic acid, fading occurred in less than 15–20 min and phenylsulfinylacetic acid was isolated in 79% yield (Eq. (3)):



$$\mathrm{PhSCH_2COOH \xrightarrow[PhIO]{(salen)Mn^{III}} Ph\overset{\overset{O}{\|}}{S}CH_2COOH + PhI}$$

(3)

The absorption spectrum of the final solution coincided with that of the original (salen)Mn^{III} complex. The active species in the present reaction is considered to be the oxo(salen)manganese(V) complex, as proposed in the earlier reports [3,8–11,13–15] on the (salen)Mn^{III} catalyzed PhIO and NaOCl oxygenation reactions. We could not isolate this oxo(salen)manganese(V) complex and the present spectral data are similar to those in earlier reports [3,8–11,13–15]. Even though there is no report on the structural characterization of the oxo(salen)manganese(V) complex, recent theoretical work [56] suggested a triplet ground state for this species. However, Groves et al. [57] and others [58,59] have characterized oxomanganese(V)–porphyrin complexes. As the isolation of pure oxomanganese(V) complexes is difficult [3,8–11,13–15] they were generated in situ for the studies reported here.

3.2. *Kinetics of oxygen atom transfer from oxo(salen)manganese(V) to (phenylthio)acetic acids*

The oxidation proceeds smoothly and the reaction is first-order in **2a** as evidenced by excellent linear plots ($r > 0.995$) of $\log(A_t - A_\infty)$ against time and also by the constant pseudo-first-order rate constants, k_1, at different initial concentrations of **2a** (Table 1). The data in Table 1 reveals that the k_1 values for the oxidation of (phenylthio)acetic acid [PTAA] by the oxo(salen)manganese(V) increases with increase in substrate concentration. A plot of k_1 versus [PTAA] yielded a straight line

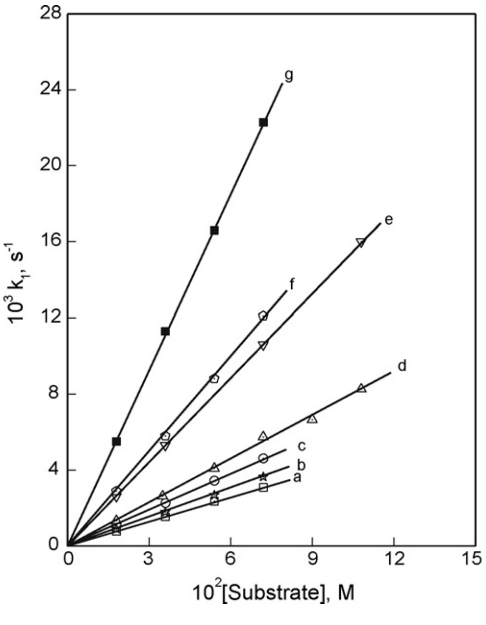


Fig. 1. Plots of k_1 vs. [substrate] for the oxidation of (a) PTAA with **2b**, (b) *p*-BrPTAA with **2a**, (c) PTAA with **2e**, (d) PTAA with **2a**, (e) PTAA with **2c**, (f) *p*-MePTAA with **2a**, and (g) PTAA with **2d**.

Table 1
Rate constants for the oxidation of (phenylthio)acetic acid by oxo(salen)manganese(V) complexes **2a–f** in acetonitrile at 20 °C[a]

$[PTAA]_0 \times 10^2$ (M)	$[\mathbf{2}]_0 \times 10^3$ (M)	$k_{1(obs)}$ [b] $\times 10^3$ (s^{-1})	$k_{1(dec)}$ [c] $\times 10^4$ (s^{-1})	k_1 [d] $\times 10^3$ (s^{-1})	k_2 [e] $\times 10^2$ ($M^{-1}\,s^{-1}$)
2a (0.751)[f]					
3.50	0.83	2.92 ± 0.03	2.43 ± 0.06	2.68 ± 0.02	7.65 ± 0.07
3.50	1.24	2.86 ± 0.04	2.27 ± 0.05	2.63 ± 0.04	7.52 ± 0.10
3.50	1.65	2.83 ± 0.02	2.03 ± 0.05	2.63 ± 0.02	7.51 ± 0.04
3.50	1.80	2.82 ± 0.07	2.04 ± 0.04	2.62 ± 0.07	7.47 ± 0.19
3.50	2.02	2.97 ± 0.05	2.15 ± 0.02	2.76 ± 0.05	7.87 ± 0.14
3.50	3.04	2.87 ± 0.03	2.04 ± 0.02	2.67 ± 0.04	7.62 ± 0.08
1.80	1.80	1.52 ± 0.04	2.04 ± 0.04	1.32 ± 0.04	7.31 ± 0.20
5.40	1.80	4.28 ± 0.04	2.04 ± 0.04	4.08 ± 0.04	7.55 ± 0.07
7.20	1.80	5.94 ± 0.12	2.04 ± 0.04	5.74 ± 0.12	7.97 ± 0.16
9.00	1.80	6.84 ± 0.03	2.04 ± 0.04	6.64 ± 0.03	7.37 ± 0.03
10.8	1.80	8.45 ± 0.04	2.04 ± 0.04	8.25 ± 0.04	7.63 ± 0.03
2b (0.739)[f]					
1.80	1.80	0.93 ± 0.01	1.61 ± 0.01	0.77 ± 0.01	4.27 ± 0.05
3.60	1.80	1.69 ± 0.03	1.61 ± 0.01	1.53 ± 0.03	4.25 ± 0.08
5.40	1.80	2.51 ± 0.05	1.61 ± 0.01	2.35 ± 0.05	4.35 ± 0.09
7.20	1.80	3.25 ± 0.10	1.61 ± 0.01	3.09 ± 0.10	4.29 ± 0.14
2c (0.770)[f]					
1.80	1.80	2.83 ± 0.02	2.11 ± 0.02	2.62 ± 0.02	14.6 ± 0.10
3.60	1.80	5.53 ± 0.01	2.11 ± 0.02	5.32 ± 0.01	14.8 ± 0.02
7.20	1.80	10.8 ± 0.03	2.11 ± 0.02	10.6 ± 0.03	14.7 ± 0.04
10.8	1.80	16.2 ± 0.07	2.11 ± 0.02	16.0 ± 0.07	14.8 ± 0.06
2d (0.798)[f]					
1.80	1.80	5.73 ± 0.01	2.20 ± 0.01	5.51 ± 0.01	30.6 ± 0.05
3.60	1.80	11.5 ± 0.02	2.20 ± 0.01	11.3 ± 0.02	31.4 ± 0.05
5.40	1.80	16.8 ± 0.04	2.20 ± 0.01	16.6 ± 0.04	30.7 ± 0.07
7.20	1.80	22.5 ± 0.03	2.20 ± 0.01	22.3 ± 0.03	31.0 ± 0.04
2e (0.747)[f]					
1.80	1.80	1.34 ± 0.03	2.01 ± 0.05	1.14 ± 0.03	6.33 ± 0.14
3.60	1.80	2.46 ± 0.05	2.01 ± 0.05	2.26 ± 0.05	6.28 ± 0.13
5.40	1.80	3.64 ± 0.11	2.01 ± 0.05	3.44 ± 0.11	6.37 ± 0.19
7.20	1.80	4.81 ± 0.12	2.01 ± 0.05	4.61 ± 0.12	6.40 ± 0.16
2f (0.744)[f]					
1.80	1.80	1.26 ± 0.01	1.74 ± 0.01	1.01 ± 0.01	6.03 ± 0.05
3.60	1.80	2.39 ± 0.01	1.74 ± 0.01	2.22 ± 0.01	6.16 ± 0.03
5.40	1.80	3.50 ± 0.03	1.74 ± 0.01	3.33 ± 0.03	6.16 ± 0.05
7.20	1.80	4.52 ± 0.08	1.74 ± 0.01	4.35 ± 0.08	6.04 ± 0.10

[a] As determined by a spectrophotometric technique following the disappearance of the oxo complex at 680 nm; the error quoted in k values is the 95% confidence limit of the Student's *t*-test.

[b] Estimated from pseudo-first-order plots over 50% reaction.

[c] Estimated from first-order plots over 50–60% reaction in the absence of (phenylthio)acetic acid.

[d] Obtained as $k_1 = k_{1(obs)} - k_{1(dec)}$.

[e] Individual k_2 values estimated as $k_1/[PTAA]_0$.

[f] Reduction potential values of oxo(salen)Mn^V complexes taken from Ref. [8].

passing through the origin (Fig. 1) indicating that the reaction is overall second-order, first-order in each reactant. Similar results were obtained for the oxidation of substituted (phenylthio)acetic acids with oxo(salen)manganese(V) complexes **2a–f** (Table 1, Fig. 1). Hence, the rate law can be depicted as in the following equation:

$$-\frac{d[\mathbf{2}]}{dt} = k_2[\mathbf{2}][PTAA]_0 \qquad (4)$$

Addition of pyridine N-oxide (PyO), a donor ligand, to the dark brown solution of **2a** caused no change in the absorption spectrum of oxo(salen)manganese(V). The effect of donor ligand on the reaction rate was determined by measuring k_1 for the oxidation of (phenylthio)acetic acid with oxo(salen)manganese(V) species **2a** at various concentrations of added PyO. The rate constant values listed in Table 2 indicate that PyO has no appreciable effect on the reaction rate. The constancy of k_2 values at different [PyO] points out that PyO is not binding with oxomanganese(V) species. If binding of PyO were occurred as in the case of oxochromium(V) complexes [60], then changes in absorption spectrum and reaction rates would have been observed.

The data provided in Table 3 point out that the redox reaction between oxo(salen)manganese(V) complexes and (phenylthio)acetic acids is highly sensitive to the introduction of the substituents in the aryl moiety of (phenylthio)acetic acids and in the 5,5′-positions of the salen ligand. The intro-

Table 2
Effect of pyridine N-oxide on the rate of oxidation of (phenylthio)acetic acid by **2a** in acetonitrile at 20 °C[a]

$[PTAA]_0 \times 10^2$ (M)	$[\mathbf{2a}]_0 \times 10^3$ (M)	$[PyO]_0 \times 10^2$ (M)	$k_{1(obs)}$ [b] $\times 10^3$ (s^{-1})	$k_{1(dec)}$ [c] $\times 10^4$ (s^{-1})	k_1 [d] $\times 10^3$ (s^{-1})	k_2 [e] $\times 10^2$ ($M^{-1} s^{-1}$)
1.80	1.80	0.02	1.62 ± 0.03	2.25 ± 0.04	1.40 ± 0.03	7.75 ± 0.14
1.80	1.80	0.05	1.63 ± 0.03	2.21 ± 0.07	1.41 ± 0.02	7.83 ± 0.13
1.80	1.80	0.10	1.65 ± 0.04	2.26 ± 0.10	1.42 ± 0.03	7.91 ± 0.17
1.80	1.80	0.15	1.65 ± 0.04	2.26 ± 0.05	1.42 ± 0.04	7.91 ± 0.19
1.80	1.80	0.20	1.67 ± 0.02	2.18 ± 0.04	1.45 ± 0.02	8.07 ± 0.09

[a] As determined by a spectrophotometric technique following the disappearance of the oxo complex at 680 nm; the error quoted in k values is the 95% confidence limit of the Student's *t*-test.

[b] Estimated from pseudo-first-order plots over 50% reaction.

[c] Estimated from first-order plots over 50–60% reaction in the absence of (phenylthio)acetic acid.

[d] Obtained as $k_1 = k_{1(obs)} - k_{1(dec)}$.

[e] Individual k_2 values estimated as $k_1/[PTAA]_0$.

Table 3
Second-order rate constants and ρ-values for the reactions of p-$XC_6H_5SCH_2COOH$ with **2a–d** in acetonitrile at 20 °C[a]

No.	X	E_{ox} (V)[b]	Oxo(salen)manganese(V) complex, $k_2 \times 10^2$ ($M^{-1} s^{-1}$)				ρ[c]	r
			2b	**2a**	**2c**	**2d**		
1.	OMe	1.408	38.8 ± 0.79	56.1 ± 0.54	86.7 ± 0.65	134 ± 0.36	0.256 ± 0.035	(0.982)
2.	Me	1.445	10.9 ± 0.25	16.0 ± 0.95	27.9 ± 0.22	55.4 ± 0.05	0.341 ± 0.031	(0.992)
3.	*i*-Pr	1.447	8.67 ± 0.11	15.4 ± 0.10	25.7 ± 0.19	48.3 ± 0.34	0.351 ± 0.044	(0.985)
4.	F	1.465	5.16 ± 0.09	7.63 ± 0.09	16.2 ± 0.11	32.7 ± 0.28	0.392 ± 0.052	(0.983)
5.	H	1.466	4.28 ± 0.06	7.34 ± 0.21	14.6 ± 0.08	30.6 ± 0.06	0.411 ± 0.048	(0.986)
6.	Cl	1.474	2.83 ± 0.04	5.61 ± 0.04	13.2 ± 0.03	25.0 ± 0.02	0.450 ± 0.082	(0.969)
7.	Br	1.477	2.44 ± 0.01	4.92 ± 0.01	12.2 ± 0.03	24.4 ± 0.04	0.477 ± 0.084	(0.970)
8.	NO_2	1.535	0.33 ± 0.01	0.56 ± 0.01	1.88 ± 0.01	4.61 ± 0.04	0.563 ± 0.090	(0.976)
ρ[d]			−1.17 ± 0.04	−1.12 ± 0.02	−0.920 ± 0.03	−0.815 ± 0.01		
r			(0.997)	(0.999)	(0.997)	(0.999)		

[a] General conditions: $[\mathbf{2}]_0 = 0.0018$ M; $[substrate]_0 = 0.018$ M.

[b] Oxidation potential values of substituted (phenylthio)acetic acids estimated using Marcus equation [8].

[c] The values were obtained by correlating $\log k_2$ with $2\sigma_p$ for the reaction of various oxo(salen)manganese(V) complexes with a given (phenylthio)acetic acid.

[d] The values were obtained by correlating $\log k_2$ with σ^+/σ^- for the reaction of various (phenylthio)acetic acids with a given oxo(salen)manganese(V) complex.

duction of substituents in the *para*-position of the phenyl ring of (phenylthio)acetic acid alters the rate appreciably; i.e., the electron-donating substituents accelerate the rate and electron-withdrawing groups decelerate the rate. It is of interest to find out if any Hammett type of correlation exists for the oxidation of (phenylthio)acetic acids by oxo(salen)manganese(V). The reactivity pattern is brought out by two different correlations, one a $\log k_2$ versus σ plot and the other with $\log k_2$ and σ^+/σ^-. Since sulfur atom can exhibit the dual character of both electron-releasing and electron-accepting type, we have used both $\sigma^+$and σ^- simultaneously in the second correlation. There are several reactions involving a sulfur center where both σ^+ and σ^- were simultaneously employed [25,26,43]. Though a satisfactory correlation is observed with σ values [43] ($r = 0.970$, $\rho = -1.66 \pm 0.17$, $s = 0.150$), an excellent correlation exists when σ^+/σ^- values [43] are plotted against $\log k_2$ (Fig. 2, $r = 0.999$, $\rho = -1.12 \pm 0.02$, $s = 0.027$). The negative ρ-value indicates that the sulfur center of the substrate is more positively charged in the transition state than it is in the reactant. The ρ-values for the substituent variation in (phenylthio)acetic acids for each oxo complex fall in the range of −0.815 to −1.17 (Table 3). Further, the plot of $\log k_2$ against the oxidation potential, E_{ox}, of (phenylthio)acetic acids calculated from the analysis of the kinetic data in terms of Marcus equation

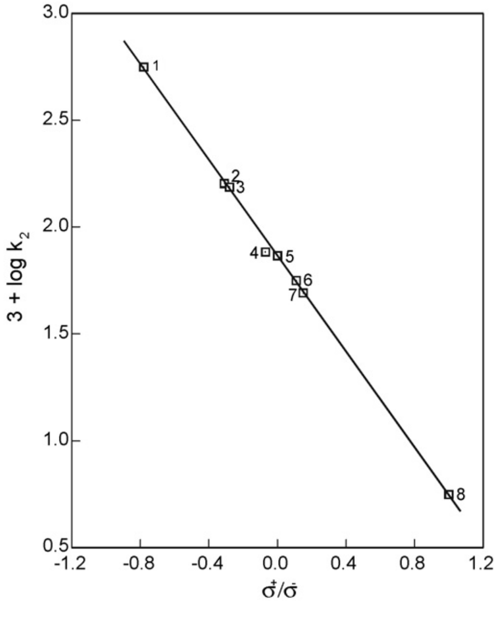


Fig. 2. Hammett plot for the oxidation of (phenylthio)acetic acids by **2a**. The points are referred to by the same numbers as in Table 3.

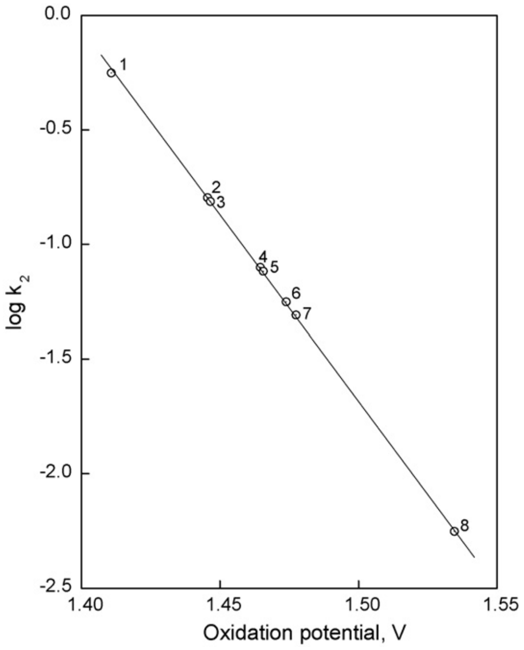


Fig. 3. Plot of $\log k_2$ vs. oxidation potential for the oxidation of (substituted phenylthio)acetic acids by **2a**. The points are referred to by the same numbers as in Table 3.

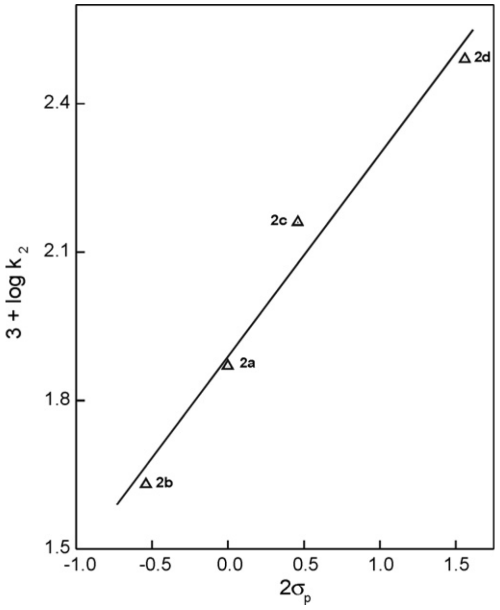


Fig. 4. Hammett plot for the oxidation of PTAA by substituted oxo(salen)manganese(V) complexes.

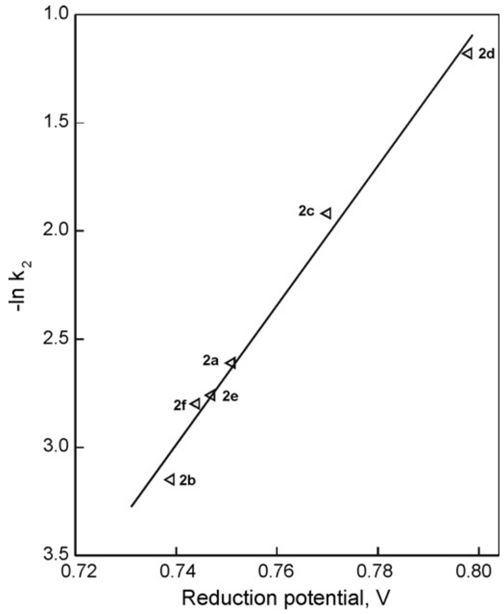


Fig. 5. Plot of $\ln k_2$ vs. reduction potential of oxo(salen)manganese(V) complexes **2a**–**f**.

[8] is linear (Table 3, Fig. 3, $r = 0.999$) with a slope of -16.2. The introduction of a substituent in the salen ligand also alters the rate of the reaction substantially. It is seen that the electron-withdrawing substituents at the 5,5′-positions of the salen ligand enhance the rate, whereas electron-releasing substituents retard it (Tables 1 and 3). Hammett correlation of $\log k_2$ with $2\sigma_p$ shows a satisfactory linear relationship with a positive slope of 0.411 ± 0.048 (Fig. 4, $r = 0.986$, $s = 0.071$). The ρ-values range from 0.256 to 0.563 for the substituent variation in the oxo complexes for each (phenylthio)acetic acid (Table 3). A plot of $\ln k_2$ versus the reduction potential values, E^0, of Mn^V/Mn^{IV} couple [8] is perfectly linear (Table 1, Fig. 5, $r = 0.999$). To realize the role of steric effect in this reaction, oxo(salen)manganese(V) complexes with methyl or phenyl groups in 7 and 7′ positions of the salen ligand (complexes **2e** and **2f**) are used to study the kinetics of the oxygenation reaction. Comparison of the kinetic data for complexes **2a**, **2e** and **2f** in the oxidation of (phenylthio)acetic acid (Table 1) reveals that the presence of methyl or phenyl group at the 7,7′-positions of salen ligand slightly reduces the rate, as in the sulfide [8,13] and sulfoxide [11,15] oxidations. Thus, the steric effect observed with Mn^V complexes is small, which is contrary to the substantial steric effect noted in the oxo(salen)Cr^V complexes oxidation of alkynes [61] and organic sulfides [17].

3.3. *Mechanism of (phenylthio)acetic acid oxidation with oxo(salen)manganese(V) complex*

In the oxygenation reactions, single oxygen atom donors like iodosylbenzene, sodium oxychloride, etc., first transfer the oxygen to metal complex and then to the substrate. The catalytic efficiency of a metal complex depends on factors like nature of the metal center and the geometry of the complex molecule. The selection of the metal is important because the complex derived from it should form an oxo-cation. Oxygen transfer by hypervalent oxometal species has been proposed to proceed by electron transfer [6,7], radical addition [62], carbocation formation [63], metallaoxetane formation [64], or a combination of these mechanisms [65]. In the present investigation, since we identified oxo(salen)manganese(V) species as the crucial intermediate for the catalytic oxidation, let us now consider how the oxygen atom is actually transferred from the oxo species to the (phenylthio)acetic acid in the rate-limiting step.

Of the two possible mechanisms for the oxidation of organosulfur compounds, one involves nucleophilic attack of sulfur on the metal center (S_N2) and the second mechanism involves single electron transfer (SET) from sulfur to the oxidant. The oxidants such as peroxybenzoate [28], hydroperoxidase [30], Cr(VI) [27], Ce(IV) [36] and oxoruthenium(IV) complexes [7] oxidize sulfides by a SET mechanism. The oxidation of sulfides by peroxoanions [25], molybdenum peroxypolyoxoanions [37], sulfamyloxaridines [31], phenyliodoso diacetate [26], pyridinium chlorochromate [29], permanganate [35] and oxo(salen)manganese(V) [11,13] follow a S_N2 mechanism. The oxidation of sulfoxides by oxo(salen)manganese(V) [11,15] follow a S_N2 mechanism. In the present study, (phenylthio)acetic acids are taken as a simple model system to comprehend the reactivity and mechanism of the oxometal complexes towards organic compounds containing heteroatoms. The formation of phenylsulfinylacetic acid in the absence of other oxygen sources (i.e., at inert atmosphere and in non-aqueous solvent) clearly indicates that the oxygen atom incorporated in the substrate is derived from the oxomanganese(V) ions. The k_1 values obtained for different initial concentrations of (phenylthio)acetic acid (Table 1) and the linear plots in Fig. 1 show that the kinetics saturation is not observed even at high concentration of (phenylthio)acetic acid. This suggests that the oxidation via preliminary coordination of (phenylthio)acetic acid to oxomanganese(V) can be ruled out. The results obtained from the influence of electronic effects on substrate and oxidant throw more light on the mechanism of oxygen atom transfer. The observed ρ-value of -1.12 in the present study is comparable to the ρ-values found for the oxidation of substituted thioanisoles by *tert*-butyl *p*-chloroperoxybenzoate [28] ($\rho = -1.68$), by singlet oxygen [24] ($\rho = -1.63$), by carboxylato-bound chromium(V) [39] ($\rho = -1.19$) and by oxo(phosphine)–ruthenium(IV) complexes [7] ($\rho = -1.56$). For all these cases, SET mechanism has been proposed. Also SET mechanism has been postulated in the cytochrome P-450 ($\rho = -0.20$) and $Fe(NN)_3^{3+}$ (NN = 2,2′-bipyridyl or 1,10-phenanthroline) ($\rho = -3.21$) oxidation of ArSMe [32,38]. Partial polar and polar mechanisms have been proposed for the oxidation of (phenylthio)acetic acids with potassium peroxydisulfate [43] ($\rho = -0.62$) and potassium peroxydiphosphate [45] ($\rho = -0.45$), respectively. A mechanism involving reversible proton abstraction followed by reversible electron transfer step has been postulated in the rate studies on substituted phenylsulfanylacetates [52] with potassium hexacyanoferrate(III) ($\rho = 1.31$). In the Ce(IV) oxidation of (phenylthio)acetic acids [47], a ρ-value of -1.86 has been obtained and a free radical mechanism is proposed. In the Bromamine-T [51] oxidation of phenylsulfanylacetate ions, a ρ-value of -2.42 is obtained. Electrophilic attack of the BrO^- on the phenylsulfanylacetate ions in the rate-determining step is proposed. Hence, the low or high magnitude of the ρ-value cannot be taken as evidence for the operation of a SET or S_N2 mechanism in a particular reaction. According to Miller et al. [30], a decision on reaction mechanism simply based on the magnitude of the ρ-value cannot be reliable.

Reactions [33,34,38,39] that involve rate-limiting SET from sulfur to yield radical cation intermediates are known to give better Hammett correlations when σ^+ substituent constants are used. For the oxidation of thioanisoles by oxo(phosphine) ruthenium(IV) complexes, Takeuchi and co-workers [7] have suggested a SET mechanism based on the excellent correlation between $\log k_x/k_H$ and σ^- values. In the potassium peroxydisulfate oxidation of (phenylthio)acetic acids [43] a better correlation of $\log k_2$ with σ^+/σ^- than σ exists and a partial polar mechanism is proposed. Hence, the observed better correlation of $\log k_2$ with σ^+/σ^- than σ may be taken as a clue for the operation of a SET mechanism in the present investigation. This is in accordance with the Hammond postulate [66] that for a single electron transfer mechanism the transition state resembles a radical cation and a better correlation is observed with σ^+ values. It is pertinent to mention here that in the oxidation of organic sulfides with NaOCl catalyzed by (salen)Mn^{III} complexes [13], a S_N2 mechanism is proposed based on the better correlation of $\log k_2$ with σ than σ^+/σ^-. Further, from the linear $\log k_2$ versus E_{ox} plot (Fig. 3) we can obtain useful information on the mechanism of the reaction by comparing the present results with the recent observations made by Goto et al. [40] on sulfoxidation catalyzed by high-valent intermediates of heme enzymes. Goto et al. [40] observed a slope of -10.5 when the reaction proceeds through an electron transfer mechanism and -2.2 in the case of the reaction proceeding via direct oxygen transfer. Hence, the observed slope of -16.2 in the present study is in favour of a mechanism proceeding through single electron transfer. Based on similar arguments, a direct oxygen transfer mechanism has been proposed for the oxo(salen)iron [18] (slope = -1.70) and oxo(salen)manganese [13] (slope = -3.5) oxygenation of organic sulfides.

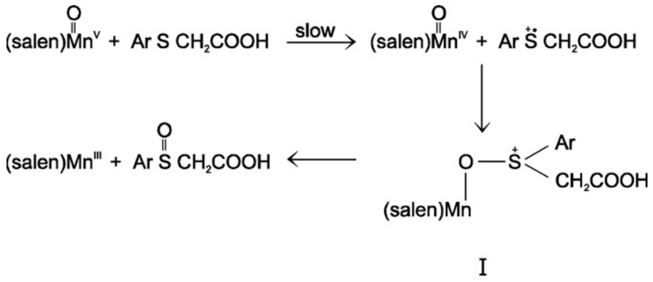
The effects of electron-donating and electron-withdrawing substituents at the 5,5′-positions of salen ligand on the reaction rate shown in Table 1 can be interpreted as a reflection of a changing electron density in the oxomanganese(V) functionality. The observed positive ρ-value (0.411) indicates the build-up of a negative charge on the metal center in the transition state of the rate-determining step, as would be expected in the reduction of manganese(V) to manganese(III) [67]. The observed linear plot of $\ln k_2$ versus the reduction potentials E^0 of $Mn^V{=}O$ complexes (Fig. 5) also supports single electron transfer in the rate-determining step.

Based on the arguments presented and the kinetic data obtained, a SET mechanism shown in Scheme 1 is proposed for the oxidation of (phenylthio)acetic acids by oxo(salen) manganese(V) complexes. The mechanism envisages the formation of a radical cation in the slow step. The formation of cation radicals during the oxidation of organic substrates has been firmly established [36]. The formation of oxametallacyclic intermediate has been excluded, because the reaction involves little steric effect when bulky methyl and phenyl groups are introduced in the 7,7′-positions (Table 1) [59]. Then the intermediate I decomposes to give Mn(III) and phenylsulfinylacetic acid as the products. The rate acceleration by electron-withdrawing nitro-substituents on the 5 and 5′ positions of salen and by the

Table 4
Second-order rate constants and activation parameters for the oxidation of p-$XC_6H_5SCH_2COOH$ by **2a** in acetonitrile at five temperatures[a]

X	$k_2 \times 10^2$ ($M^{-1}\ s^{-1}$)					$\Delta H\neq$ (kJ mol^{-1})	$\Delta S\neq$ (J K^{-1} mol^{-1})
	288 K	293 K	298 K	303 K	308 K		
OMe	31.3 ± 0.20	56.1 ± 0.54	96.1 ± 0.95	164 ± 2.69	311 ± 3.10	81.1	26.9
Me	9.00 ± 0.07	16.0 ± 0.95	26.6 ± 0.21	50.4 ± 0.28	103 ± 0.30	86.3	34.3
i-Pr	8.44 ± 0.04	15.4 ± 0.10	24.2 ± 0.19	42.3 ± 0.25	85.6 ± 0.66	80.7	14.7
H	4.22 ± 0.03	7.34 ± 0.21	11.7 ± 0.04	24.4 ± 0.03	49.8 ± 0.12	87.9	33.5
F	5.06 ± 0.05	7.63 ± 0.09	13.7 ± 0.09	30.3 ± 0.08	62.8 ± 0.26	92.0	48.5
Cl	3.11 ± 0.01	5.61 ± 0.04	8.61 ± 0.10	18.9 ± 0.14	39.3 ± 0.34	90.1	38.6
Br	2.89 ± 0.01	4.92 ± 0.01	7.72 ± 0.03	17.5 ± 0.14	35.8 ± 0.20	90.3	38.5
NO_2	0.39 ± 0.01	0.56 ± 0.01	0.67 ± 0.02	0.94 ± 0.03	1.36 ± 0.06	42.0	−145

[a] General conditions: $[\mathbf{2a}]_0 = 0.0018$ M; $[\text{substrate}]_0 = 0.018$ M.



Scheme 1. Mechanism of $[(\text{salen})\text{Mn}^{\text{V}}{=}\text{O}]^+$ oxidation of (phenylthio)acetic acids.

electron-donating p-methoxy group on (phenylthio)acetic acid support this formulation.

The oxo(salen)manganese(V) oxidation of (*para*-substituted phenylthio)acetic acids was carried out at five different temperatures, and the thermodynamic parameters evaluated using the Eyring equation are collected along with k_2 values in Table 4. The $\Delta H\neq$ (42–92 kJ mol^{-1}) and $\Delta S\neq$ (−145 to 48.5 J K^{-1} mol^{-1}) values are in favor of SET mechanism. Even though the correlation between $\Delta H\neq$ and $\Delta S\neq$ is not satisfactory, a plot of log k_2 at 15 °C and 35 °C gives an excellent correlation ($r = 0.994$, $s = 0.072$) implying that all the (substituted phenylthio)acetic acids follow the same mechanism.

3.4. Reactivity–selectivity principle

The reactivity–selectivity principle (RSP) says that there is an inverse relationship between the reactivity of a reagent and its selectivity among a set of similar substrates. The last row of Table 3 contains reaction constant values for substituent variation in (phenylthio)acetic acid for each oxo complex while the last column shows ρ-values for the substituent variation in oxo complex for each (phenylthio)acetic acid. The reaction constant data show that there is a significant variation of reaction constants (selectivity) on varying the nature of the substituent in either the oxo complex or the (phenylthio)acetic acid. Also, it is apparent that as the reactivity of either the (phenylthio)acetic acid or oxo complex decreases the reaction constant value increases, i.e., there is an inverse relationship between reactivity and selectivity in both cases.

The applicability of RSP is verified by Exner [54] method. Accordingly, the rate data reported in Table 3 were subjected to mathematical treatment using Eqs. (5) and (6):

$$\log k_{\text{F}i} = a + b \log\ k_{\text{S}i} + \varepsilon_i \tag{5}$$

$$\Delta = \frac{\sum_i \log k_{\text{F}_i} - \sum_i \log k_{\text{S}_i}}{N} \tag{6}$$

where $k_{\text{F}i}$ and $k_{\text{S}i}$ are the second-order rate constants for the reactions of fast and slow reagents (oxo complexes), respectively, with each (phenylthio)acetic acid, ε_i is the error of the $\log k_{\text{F}i}$ versus $\log k_{\text{S}i}$ correlation, and Δ is the mean difference. The values of b and Δ were calculated for all of the six possible combinations of one fast and one slow reagent (among the four oxo complexes) with a series of similar substrates (eight (phenylthio)acetic acids). The results summarized in Table 5 show a valid RSP in all cases as the value of b is less than unity and Δ is not too small.

In a system involving more than one reagent and the same set of substrates, the existence of a “magic point” [54] in the $\log k_{\text{F}i}$ versus $\log k_{\text{S}i}$ plots is an indication for a strong RSP. The magic point represents some limiting value of reactivity in which, for a particular substrate, the reaction rate is independent of the reagent and vice versa. In this aspect, the present

Table 5
Results of correlation between $\log k_{\text{F}i}$ and $\log k_{\text{S}i}$ according to Eq. (5) for (phenylthio)acetic acids[a]

Results	Oxo(salen)manganese(V) complexes (F and S)					
	2a and **2b**	**2c** and **2b**	**2c** and **2a**	**2d** and **2b**	**2d** and **2a**	**2d** and **2c**
r	0.996	0.993	0.998	0.996	0.999	0.999
b	0.952 ± 0.034	0.780 ± 0.039	0.821 ± 0.021	0.691 ± 0.027	0.726 ± 0.014	0.883 ± 0.017
Δ	0.226	0.546	0.320	0.842	0.616	0.296

[a] $[\mathbf{2}]_0 = 0.0018$ M.

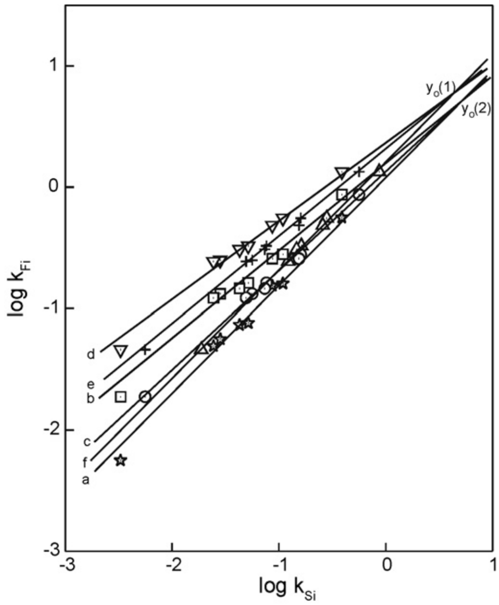


Fig. 6. log k_{Fi} vs. log k_{Si} plots for the reactions of (phenylthio)acetic acids with (a) **2a** and **2b**; (b) **2c** and **2b**; (c) **2c** and **2a**; (d) **2d** and **2b**; (e) **2d** and **2a**; and (f) **2d** and **2c**.

system reveals interesting results (Fig. 6). The correlations involving nitro-substituted oxo complex **2d** (lines d–f) produce one magic point, $y_0(1)$, and the correlations involving other oxo complexes (lines a–c) produce another magic point, $y_0(2)$. Both magic points are situated on the side of high reactivity, as expected for a valid RSP as observed in the (salen)Mn^{III}-catalyzed oxidation of sulfides [9,10,14], and sulfoxides [11,15] with PhIO–NaOCl, in the oxidation of aliphatic alcohols [68] and substituted benzyl alcohols [69] with PhIO catalyzed by (salen)Mn^{III} complexes and in the oxidation of sulfides with oxo(salen)chromium(V) complexes [12], and oxo(salen)iron complexes [18]. The successful application of RSP to the present system indicates that the same mechanism is operating in all reactions.

4. Conclusions

The oxygenation of several (phenylthio)acetic acids with oxo(salen)manganese(V) complexes has been studied in acetonitrile at 20 °C. The (phenylthio)acetic acids are converted to phenylsulfinylacetic acids. Electronic-substrate and electronic-oxidant effects on the reaction have been analyzed. A mechanism involving single electron transfer in the rate-determining step has been proposed for the oxygen transfer from oxo(salen) manganese(V) complex to (phenylthio)acetic acid. The operation of a valid reactivity–selectivity principle is established in this redox system.

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