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Kinetics and Mechanism of the Oxidation of Organic Sulfides by Bis(2,2′-bipyridyl)copper(II) Permanganate

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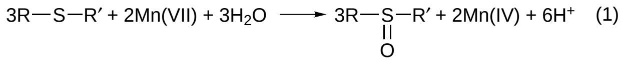
The oxidation of 34 sulfides by bis(2,2′-bipyridyl)copper(II) permanganate (BBCP) resulted in the formation of the corresponding sulfoxide. The reaction is first order with respect to BBCP. Michaelis−Menten type kinetics were observed with respect to the sulfides. The reaction is catalyzed by H^+. The rate of the reaction increases with an increase in the amount of acetic acid in the solvent. The rates of oxidation of meta- and para-substituted phenyl methyl sulfides showed excellent correlation with Charton's LDR equation. The rates of the ortho-compounds showed excellent correlation with the LDRS equation. The oxidation of the ortho- and para-compounds is more susceptible to the delocalization effect. The oxidation of the meta-compounds exhibited a greater dependence on the field effects. The reaction is subject to steric inhibition when an ortho-substituent is present. The oxidation of alkyl phenyl sulfides is subject to both polar and steric effects of the alkyl groups. The polar reaction constants are negative, indicating an electron-deficient sulfur center in the rate-determining step. Probable mechanisms are discussed.

Bis(2,2′-bipyridyl)copper(II) permanganate (BBCP) is a mild and selective oxidant and has been used in the oxidation of a number of organic compounds.[1,2] We have been interested in the mechanistic aspects of oxidation reactions promoted by BBCP. There seems to be no report on the kinetics of oxidation of organic sulfides by BBCP. In continuation of our earlier work related to oxidations by BBCP,[3−6] we report here the kinetics of oxdiation of 34 organic sulfides by BBCP in aqueous acetic acid. Attempts have been made to correlate the rate and structure in this reaction. Mechanistic aspects are discussed.

Results

Oxidation of organic sulfides resulted in the formation of the corresponding sulfoxides. Analysis of products and stoichiometric determination indicate the following overall reaction (1).



$$3R{-}S{-}R' + 2Mn(VII) + 3H_2O \longrightarrow 3R{-}\underset{\underset{O}{\|}}{S}{-}R' + 2Mn(IV) + 6H^+ \quad (1)$$

BBCP is reduced to Mn(IV). To confirm that Mn(IV) is indeed formed as a result of reduction of BBCP by sulfides, rates were determined by monitoring the increase in [Mn(IV)] at 418 nm also.[7,8] The rates of decay at 529 nm and of increase at 418 nm agreed to within ±12%. It was also observed that BBCP has virtually no absorption at 418 nm. This agrees with the observations of earlier workers.[7,8]

Table 1. Rate Constants for the Oxidation of Methyl Phenyl Sulfide by BBCP at 293 K

10^4[BBCP] (mol dm^{-3})	[MeSPh] (mol dm^{-3})	[H^+] (mol dm^{-3})	10^4k_{obs} (s^{-1})
2.0	0.1	1.0	5.47
2.0	0.2	1.0	8.08
2.0	0.4	1.0	10.6
2.0	0.6	1.0	11.9
2.0	0.8	1.0	12.6
2.0	1.2	1.0	13.4
2.0	1.5	1.0	13.8
2.0	3.0	1.0	14.6
2.0	0.8	1.0	12.3[a]
3.0	0.8	1.0	12.8
5.0	0.8	1.0	12.5
8.0	0.8	1.0	13.0
10.0	0.8	1.0	12.2

[a] Contained 0.005 mol dm^{-3} acrylonitrile.

The reactions are first order with respect to BBCP. Further, the values of k_{obs} are independent of the initial concentration of BBCP. The reaction rate increases with an increase in the concentration of sulfides, but the order is less than one (Table 1). A plot between 1/sulfide against $1/k_{obs}$ was linear ($r^2 = 0.9998$) with an intercept on the rate ordinate. Thus the reaction exhibits Michaelis−Menten-type kinetics with respect to sulfides. This leads to the postulation of the following overall mechanism (reactions 2 and 3) and rate law (4).

$$R{-}S{-}R' + BBCP \overset{K}{\rightleftharpoons} [\text{complex}] \qquad (2)$$

$$[\text{complex}] \xrightarrow{k_2} \text{products} \qquad (3)$$

$$\text{rate} = k_2K[R{-}S{-}R'][BBC]/(1 + K[R{-}S{-}R']) \qquad (4)$$

The dependence on the concentration of the sulfide was studied at different temperatures, and the values of K and k_2 were evaluated from double reciprocal plots. The thermodynamic parameters for complex formation and activation parameters of the decomposition of the complexes were calculated from the values of K and k_2, respectively, at different temperatures (Tables 2 and 3).

The oxidation of methyl phenyl sulfide, in an atmosphere of nitrogen, failed to induce polymerization of

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(1) Firouzabadi, H.; Naderi, M.; Sardarian, A.; Vessel, B. *Synth. Commun.* **1983**, *13*, 611.

(2) Walker, F. A.; Sigel, H.; McCormick, *Inorg. Chem.* **1972**, *11*, 2756.

(3) Kothari, S. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1991**, *103*, 747.

(4) Kothari, S.; Sharma, V.; Sharma, P. K.; Banerji, K. K. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1992**, *104*, 583.

(5) Satsangi, B. K.; Kothari, S.; Banerji, K. K. *J. Chem. Res. (S)* **1994**, 208. *Idem. J. Chem. Res.* (M) 1134. *Idem. Transition Met. Chem.* **1995**, *20*, 288.

(6) Mohnot, K.; Sharma, P. K.; Banerji, K. K. *J. Org. Chem.* **1996**, *71*, 1310.

(7) Freeman, F.; Kappos, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6628.

(8) Lee, D. G.; Perez-Benito, J. F. *J. Org. Chem.* **1988**, *53*, 5728.

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Table 2. Formation Constants and Thermodynamic Parameters for the Sulfide−BBCP Complexes

	K, $dm^3\ mol^{-1}$				ΔH, $kJ\ mol^{-1}$	ΔS, $J\ mol^{-1}\ K^{-1}$	ΔG, $kJ\ mol^{-1}$
subst	283 K	293 K	303 K	313 K			
(i) Aryl Methyl Sulfides							
H	6.22	5.45	4.58	3.65	−15.5 ± 0.9	−31 ± 3	−6.4 ± 0.7
p-Me	5.89	5.08	4.35	3.55	−14.8 ± 0.6	−29 ± 2	−6.3 ± 0.5
p-OMe	5.44	4.69	3.92	3.05	−16.5 ± 1.0	−36 ± 3	−6.0 ± 0.8
p-F	6.15	5.33	4.52	3.72	−14.8 ± 0.6	−29 ± 2	−6.4 ± 0.5
p-Cl	5.56	4.71	3.98	3.18	−16.0 ± 0.7	−34 ± 2	−6.1 ± 0.5
p-Br	5.81	5.01	4.21	3.35	−15.9 ± 0.8	−33 ± 3	−6.2 ± 0.7
p-NO_2	5.90	5.13	4.40	3.56	−14.7 ± 0.7	−29 ± 3	−6.3 ± 0.6
p-COMe	5.32	4.55	3.72	3.01	−16.5 ± 0.6	−36 ± 2	−5.9 ± 0.5
p-COOMe	5.46	4.62	3.84	3.07	−16.5 ± 0.6	−36 ± 2	−6.0 ± 0.5
p-NHAc	5.85	5.03	4.25	3.49	−15.1 ± 0.5	−30 ± 2	−6.2 ± 0.4
p-NH_2	6.02	5.24	4.46	3.71	−14.3 ± 0.5	−27 ± 2	−6.4 ± 0.4
m-Me	6.13	5.35	4.62	3.64	−15.0 ± 1.0	−29 ± 3	−6.4 ± 0.8
m-OMe	5.99	5.18	4.42	3.70	−14.3 ± 0.4	−27 ± 1	−6.3 ± 0.3
m-Cl	5.45	4.78	4.01	3.26	−15.1 ± 0.8	−31 ± 3	−6.1 ± 0.6
m-Br	5.73	4.95	4.15	3.33	−15.7 ± 0.8	−33 ± 3	−6.2 ± 0.6
m-I	5.66	4.87	4.06	3.24	−16.1 ± 0.7	−34 ± 3	−6.1 ± 0.6
m-NO_2	6.20	5.22	4.35	3.50	−16.4 ± 0.6	−34 ± 2	−6.3 ± 0.4
m-COOMe	5.27	4.45	3.80	3.02	−15.9 ± 0.7	−34 ± 2	−5.9 ± 0.6
o-Me	5.56	4.75	4.02	3.29	−15.3 ± 0.5	−31 ± 2	−6.1 ± 0.4
o-OMe	5.30	4.52	3.91	3.11	−15.3 ± 0.8	−32 ± 3	−6.0 ± 0.6
o-NO_2	6.02	5.25	4.52	3.71	−14.3 ± 0.6	−27 ± 2	−6.4 ± 0.5
o-COOMe	5.96	5.18	4.36	3.56	−15.1 ± 0.7	−30 ± 2	−6.3 ± 0.5
o-NH_2	5.48	4.70	3.91	3.08	−16.5 ± 0.9	−36 ± 3	−6.0 ± 0.7
o-Cl	6.05	5.30	4.58	3.80	−15.3 ± 0.6	−30 ± 2	−6.3 ± 0.5
o-Br	5.98	5.18	4.35	3.62	−14.8 ± 0.5	−29 ± 2	−6.3 ± 0.4
o-I	5.90	5.15	4.38	3.50	−15.1 ± 0.9	−30 ± 3	−6.3 ± 0.7
o-CN	6.11	5.33	4.58	3.72	−14.5 ± 0.7	−28 ± 2	−6.4 ± 0.6
(ii) Alkyl Phenyl Sulfides							
Et	6.18	5.34	4.52	3.68	−15.1 ± 0.6	−30 ± 2	−6.4 ± 0.5
Pr	5.92	5.05	4.22	3.45	−15.7 ± 0.5	−32 ± 2	−6.2 ± 0.4
i-Pr	5.45	4.72	4.01	3.31	−14.7 ± 0.5	−29 ± 2	−6.1 ± 0.4
t-Bu	5.86	5.11	4.41	3.62	−14.4 ± 0.7	−28 ± 2	−6.2 ± 0.6
(iii) Other Sulfides							
Me_2S	5.61	4.85	4.16	3.38	−14.8 ± 0.7	−29 ± 2	−6.1 ± 0.5
Pr_2S	5.35	4.61	3.92	3.21	−14.9 ± 0.6	−30 ± 2	−6.0 ± 0.5
Ph_2S	5.79	5.00	4.26	3.55	−14.5 ± 0.4	−28 ± 2	−6.3 ± 0.4

acrylonitrile. Further, the addition of acrylonitrile had no effect on the reaction rate (Table 1).

Effect of 2′,2′-Bipyridine. The rates of oxidation were not affected by an addition of 2,2′-bipyridine (Table 4).

Effect of Acidity. The reaction rate increases with an increase in the concentration of hydrogen ions (Table 5). A plot of rate versus $[H^+]$ is concave to the rate axis and makes an intercept on the rate axis. The dependence of the reaction rate on the concentration of MeSPh was studied at $[H^+] = 0.20$, 1.00, and 1.80 mol dm^{-3}. It was observed that formation constant K does not vary appreciably with the hydrogen-ion concentration, while the rate constant for the decomposition of complex, k_2, is affected by the changes in the hydrogen-ion concentration.

Effect of Solvent Composition. The rate of oxidation was determined in solvents containing different amounts of acetic acid and water. It was observed that the rate increased with an increase in the amount of acetic acid in the solvent.

To ascertain whether the change in the solvent composition is affecting the formation constant for the complex and/or the rate of its decomposition, the dependence of the reaction rate on the concentration of methyl phenyl sulfide was studied in the solvents of different compositions. The results recorded in Table 6 showed that the rate constant of the decomposition of the complex increases with an increase in the amount of acetic acid in the solvent. The formation constant K remains practically constant.

Discussion

Not much is known about the structure of BBCP. In particular, the nature of the bonding of the permanganate anions with the $[bpy_2Cu(II)]$ cation is not certain. However, in the corresponding halide complexes, it has been shown that one halide ion is joined to the central atom by a covalent bond and another by an electrovalent bond.[9] Based on that analogy, BBCP may also be represented as $[bpy_2Cu(MnO_4)]MnO_4$, although we do not have any direct evidence to support our contention that permanganate acts as a ligand to copper(II).

A plot of log k_2 at 283 K is linearly related to log k_2 at 313 K ($r = 0.9964$, slope $= 0.8397 \pm 0.0127$). The value of the isokinetic temperature is 714 ± 86 K. A linear isokinetic relationship is a necessary condition for the validity of linear free energy relationships.[10] It also implies that all the sulfides are oxidized by the same mechanism.[10]

An analysis of the hydrogen-ion dependence of the reaction rate showed that at $[H^+] \le 1.0$ mol dm^{-3}, the dependence has the form $k_{obs} = a + b[H+]$ ($a = 1.15 \pm 0.07 \times 10^{-4}\ s^{-1}$, $b = 9.33 \pm 0.11 \times 10^{-4}\ dm^3\ mol^{-1}\ s^{-1}$, $r = 0.9996$]. At $[H^+] > 1.0$ mol dm^{-3}, the dependence has the form $k_{obs} = c[H^+]^2$ ($c = 8.86 \pm 0.01 \times 10^{-4}\ dm^6\ mol^{-2}\ s^{-1}$, $r = 0.9996$). This is reminiscent of the effect observed in the oxidation of aromatic aldehydes.[6] Therefore, it is suggested that the oxidation of sulfides by BBCP also

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[9] Baclay, G. A.; Hoskins, B. F.; Kennard, C. H. L. *J. Chem. Soc.* **1963**, 5691.

[10] Exner, O. *Prog. Phys. Org. Chem.* **1973**, *10*, 411.

Table 3. Rate Constants for the Decomposition of Sulfide−BBCP Complexes and the Corresponding Activation Parameters

subst	10^4k_2 (dm^3 mol^{-1} s^{-1}) 283 K	293 K	303 K	313 K	$\Delta H^‡$ kJ mol^{-1}	$\Delta S^‡$ J mol^{-1} K^{-1}	$\Delta G^‡$ kJ mol^{-1}
H	5.83	15.5	40.6	105	68.4 ± 0.8	−66 ± 3	87.8 ± 0.6
p-Me	11.6	30.3	75.0	187	65.5 ± 0.6	−70 ± 2	86.2 ± 0.5
p-OMe	21.1	52.1	124	289	61.7 ± 0.4	−79 ± 1	84.9 ± 0.3
p-F	5.13	13.8	35.5	88.8	67.4 ± 0.4	−70 ± 1	88.1 ± 0.3
p-Cl	3.65	9.85	26.6	67.7	69.3 ± 0.6	−66 ± 2	88.9 ± 0.5
p-Br	3.60	9.73	26.3	66.8	69.3 ± 0.5	−66 ± 2	88.9 ± 0.4
p-NO_2	0.44	1.30	3.76	11.1	76.5 ± 1.1	−58 ± 4	93.7 ± 0.9
p-COMe	1.01	3.05	8.51	25.4	76.2 ± 1.1	−52 ± 4	91.7 ± 0.9
p-COOMe	1.38	4.06	11.8	32.3	74.9 ± 0.6	−54 ± 2	90.9 ± 0.5
p-NHAc	11.9	30.2	75.4	181	64.3 ± 0.5	−74 ± 2	86.2 ± 0.4
p-NH_2	67.6	154	354	769	57.3 ± 0.5	−84 ± 2	82.3 ± 0.4
m-Me	11.2	27.3	68.5	176	65.0 ± 1.4	−72 ± 5	86.4 ± 1.1
m-OMe	13.5	30.1	74.1	183	61.6 ± 1.7	−83 ± 6	86.1 ± 1.4
m-Cl	2.24	5.70	16.2	43.8	70.8 ± 1.6	−65 ± 5	90.1 ± 1.3
m-Br	2.22	5.62	15.8	43.0	70.5 ± 1.7	−66 ± 6	90.1 ± 1.3
m-I	2.55	6.55	18.4	51.0	71.2 ± 1.7	−63 ± 6	89.8 ± 1.3
m-NO_2	0.25	0.73	2.21	6.55	77.7 ± 0.7	−59 ± 4	95.1 ± 1.0
m-COOMe	1.01	3.08	8.56	24.4	75.3 ± 0.7	−55 ± 2	91.7 ± 0.5
o-Me	2.71	7.65	21.0	58.5	72.7 ± 0.9	−57 ± 3	89.5 ± 0.7
o-OMe	7.24	19.9	52.4	137	69.5 ± 0.6	−60 ± 2	87.2 ± 0.5
o-I	0.46	1.38	4.23	13.4	80.1 ± 0.6	−45 ± 5	93.5 ± 1.3
o-Cl	0.77	2.25	6.75	20.8	78.3 ± 1.7	−48 ± 5	92.3 ± 1.2
o-Br	0.55	1.69	5.25	16.7	81.1 ± 1.4	−40 ± 5	92.9 ± 1.2
o-NO_2	0.18	0.49	1.57	5.02	79.4 ± 2.5	−56 ± 8	95.9 ± 1.9
o-CN	0.24	0.70	2.23	7.15	80.9 ± 1.9	−48 ± 6	95.1 ± 1.5
o-COOMe	0.37	1.09	3.25	10.1	78.5 ± 1.5	−53 ± 5	94.1 ± 1.2
o-NH_2	24.1	59.5	152	367	64.5 ± 0.8	−68 ± 3	84.5 ± 0.7
(ii) Alkyl Phenyl Sulfides							
Et	9.22	24.3	62.0	157	66.9 ± 0.7	−67 ± 2	86.7 ± 0.5
Pr	6.05	16.7	42.2	113	68.9 ± 0.9	−63 ± 3	87.6 ± 0.7
i-Pr	7.50	20.8	52.7	138	68.6 ± 0.7	−62 ± 2	87.1 ± 0.6
t-Bu	2.16	6.03	17.4	50.9	75.0 ± 1.5	−51 ± 5	89.9 ± 1.2
(iii) Other Sulfides							
Me_2S	18.5	47.5	116	276	63.7 ± 0.3	−72 ± 1	85.1 ± 0.2
Pr_2S	27.1	67.2	170	415	64.5 ± 0.8	−66 ± 3	84.2 ± 0.7
Ph_2S	3.46	9.66	27.5	76.9	73.6 ± 1.1	−51 ± 4	88.4 ± 0.9

Table 4. Effect of 2,2′-Bipyridine on the Oxidation of Methyl Phenyl Sulfide by BBCP[a]

[bpy], mol dm^{-3}	0.00	0.01	0.02	0.03	0.05	0.10
10^4k_{obs}, s^{-1}	10.5	11.0	10.6	10.2	11.2	10.4

[a] [BBCP] = 0.0002 mol dm^{-3}, [MeSPh] = 0.40 mol dm^{-3}, [H$^+$] = 1.0 mol dm^{-3}, T = 293 K.

Table 5. Dependence of the Rate of Oxidation of Methyl Phenyl Sulfide by BBCP on the Hydrogen-Ion Concentration[a]

[H$^+$], mol dm^{-3}	0.10	0.20	0.30	0.50	0.75	1.00
10^4k_{obs}, s^{-1}	1.96	3.12	4.02	5.81	8.10	10.5
[H$^+$], mol dm^{-3}	1.2	1.50	1.80	2.50	3.75	5.00
10^4k_{obs}, s^{-1}	12.8	19.6	28.4	53.7	127	220

[a] [BBCP] = 0.0002 mol dm^{-3}, [MeSPh] = 0.40 mol dm^{-3}, T = 293 K.

Table 6. Dependence of k_{obs} for the Oxidation of Methyl Phenyl Sulfide by BBCP on Substrate Concentration in solvents of Different Compositions[a]

10^2 [MeSPh], mol dm^{-3}	at % AcOH (v/v) 20	40	50	60	70	80
	10^4k_{obs}, s^{-1}					
0.1	1.93	3.30	5.47	9.16	36.9	146
0.2	2.84	4.90	8.10	13.6	54.2	215
0.4	3.72	6.47	10.6	18.1	71.0	282
0.8	4.39	7.70	12.6	21.5	83.6	333
1.2	4.68	8.22	13.4	23.0	88.9	355
1.5	4.81	8.45	13.8	23.7	91.3	364
3.0	5.07	8.95	14.6	25.1	96.3	385
	K, dm^3 mol^{-1}					
	5.61	5.32	5.45	5.22	5.68	5.58
	k_2, 10^{-4} s^{-1}					
	5.38	9.51	15.5	26.7	102	408

[a] [BBCP] = 0.0002 mol dm^{-3}, [H$^+$] = 1.0 mol dm^{-3}, T = 293 K.

follows an acid-independent path and two acid-dependent paths, involving singly protonated and doubly protonated forms of a reactant as reactive species, at moderate and higher concentrations of hydrogen-ion, respectively.

The Hammett acidity function, H_0, for low concentrations of perchloric acid in a series of acetic acid−water mixtures has been determined.[11] The acidity increases as the water concentration decreases. Since the reation under investigation is an acid-catalyzed one, an increase in the proportion of acetic acid in the solvent results in an increase in the rate of oxidation.

Correlation Analysis of Reactivity. A perusal of data of Tables 2 and 3 revealed that the formation constant K of the sulfide−BBCP complex did not vary with the nature of substituent on the sulfide molecule. The rate constant of the decomposition of the complex, k_2, however, showed considerable variation. Similar observations have earlier been recorded in the oxidation of benzyl alcohols[12] and mandelic acids[13] by ceric ammonium nitrate, of aliphatic primary alcohols by pyridinium fluorochromate,[14] and pyridinium hydrobromide

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[11] Wiberg, K. B.; Evans, R. *J. Am. Chem. Soc.* **1958**, *80*, 3019.

[12] Young, Y. B.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1969**, *91*, 5060.

[13] Banerji, K. K. *J. Indian Chem. Soc.* **1975**, *52*, 573.

[14] Banerji, K. K. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1547.

Table 7. Temperature Dependence for the Reaction Constants for the Oxidation of Substituted Benzaldehydes by BBCP

T, K	L	D	R	S	η	R^2	sd	ψ	P_D	P_s
				Para-Substituted						
283	−1.43 ±0.01	−1.63 ±0.01	−1.54 ±0.07	–	0.94	0.9998	0.01	0.01	53.3	–
293	−1.37 ±0.01	−1.53 ±0.01	−1.41 ±0.05	–	0.92	0.9997	0.01	0.01	52.8	–
303	−1.31 ±0.01	−1.45 ±0.01	−1.33 ±0.06	–	0.92	0.9998	0.01	0.01	52.5	–
313	−1.25 ±0.01	−1.33 ±0.01	−1.25 ±0.05	–	0.94	0.9997	0.01	0.01	51.6	–
				Meta-Substituted						
283	−1.82 ±0.02	−1.40 ±0.02	−1.20 ±0.19	–	0.86	0.9996	0.01	0.02	43.5	–
293	−1.76 ±0.01	−1.35 ±0.01	−1.12 ±0.06	–	0.83	0.9999	0.01	0.01	43.4	–
303	−1.63 ±0.02	−1.28 ±0.02	−0.79 ±0.10	–	0.62	0.9999	0.01	0.01	43.9	–
313	−1.57 ±0.02	−1.20 ±0.02	−0.82 ±0.19	–	0.68	0.9995	0.01	0.01	43.3	–
				Ortho-Substituted						
283	−1.43 ±0.02	−1.54 ±0.02	−1.81 ±0.12	−1.21 ±0.02	1.07	0.9998	0.01	0.01	51.9	28.9
293	−1.41 ±0.01	−1.51 ±0.01	−1.45 ±0.06	−1.12 ±0.01	0.96	0.9999	0.01	0.01	51.7	27.7
303	−1.32 ±0.01	−1.46 ±0.01	−1.34 ±0.07	−1.06 ±0.01	0.92	0.9999	0.01	0.01	52.5	27.6
313	−1.30 ±0.02	−1.36 ±0.01	−1.29 ±0.09	−0.96 ±0.02	0.95	0.9998	0.02	0.01	51.1	26.5

perbromide,[15] and of aliphatic primary alcohols and benzaldehydes by BBCP.[5,6] The rate constants k_2 were therefore subjected to correlation analysis.

(i) Aryl Methyl Sulfides. In the late 1980s, Charton[16] introduced a triparametric LDR equation for the quantitative description of structural effects on chemical reactivities. We have applied the LDR equation [eq 5] to the rate constants k_2 for the oxidation of aryl methyl sulfides.

$$\log k_2 = L\sigma_1 + D\sigma_d + R\sigma_e + h \tag{5}$$

Here, σ_1 is a localized effect parameter. σ_d is the intrinsic delocalized electrical effect parameter when active site electronic demand is minimal, and σ_e represents the sensitivity of the substituent to changes in electronic demand by the active site. The latter two substituent parameters are related by eq 6

$$\sigma_D = \eta\sigma_e + \sigma_d \tag{6}$$

where η represents the electronic demand of the reaction site which is given by $\eta = R/D$, and σ_D represents the delocalized electrical parameter of the diparametric LD equation.

For ortho-substituted compounds, it is necessary to account for the possibility of steric effects, and the LDR equation has, therefore, been modified to LDRS eq 7.[16]

$$\log k_2 = L\sigma_1 + D\sigma_d + R\sigma_e + SV + h \tag{7}$$

where V is the well known Charton's steric parameter based on Van der Waals radii.[17]

The rates of oxidation of the ortho-, meta-, and para-substituted sulfides show excellent correlations with structure in terms of the LDR/LDRS equations (Table 7). All three series of aryl methyl sulfides meet the requirement of minimum number of substituents for analysis by the LDR and LDRS equations.[16] We have used the standard deviation (sd), the coefficient of multiple determination (R^2), and Exner's[18] parameter ψ, as measures of goodness of fit.

The comparison of the L and D values for the substituted phenyl methyl sulfides showed that the oxidation of para- and ortho-substituted aryl methyl sulfides is more susceptible to the delocalization effect than to the localized effect. However, the oxidation of meta-substituted compounds exhibited a greater dependence on the field effect. In all the cases, the magnitude of the reaction constants decreases with an increase in the temperature, pointing to a decrease in selectivity with an increase in temperature.

All the three regression coefficients, L, D, and R, are negative, indicating an electron-deficient sulfur center in the transition state of the rate-determining step. The positive value of η adds a negative increment to σ_d (eq 6), thereby increasing electron-donating power of the substituent and its capacity to stabilize a cationic species.

The negative value of S indicates that the reaction is subjected to steric hindrance by the ortho-substituent. This may be due to steric hindrance of the ortho-substituent to the approach of the oxidizing species.

The percent contribution[16] of the delocalized effect, P_D is given by following eq 8.

$$P_D = \frac{(D \times 100)}{(L + D)} \tag{8}$$

Similarly, the percent contribution of the steric parameter[16] to the total effect of the substituent, P_S, was determined by using eq 9.

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(15) Mathur, D.; Sharma, P. K.; Banerji, K. K. *J. Chem. Soc., Perkin Trans. 2* **1993**, 205.

(16) Charton, M.; Charton, B. *Bull. Soc. Chim. Fr.* **1988**, 199 and references cited therein.

(17) Charton, M. *J. Org. Chem.* **1975**, *40*, 407.

(18) Exner, O. *Collect. Czech. Chem. Commun.* **1966**, *31*, 3222.

$$P_{\mathrm{s}} = \frac{(S \times 100)}{(L + D + S)} \tag{9}$$

The values of P_D and P_S are also recorded in Table 7. The value of P_D for the oxidation of ortho- and para-substituted aryl methyl sulfides is ca. 52%, whereas its value for the meta-substituted sulfides is ca. 43%. The value of P_s shows that the steric effect is considerable in this reaction.

In earlier studies of oxidation of sulfides involving a direct oxygen transfer via an electrophilic attack on the sulfide-sulfur, the reaction constants were negative but of relatively small magnitude, e.g. by hydrogen peroxide (−1.13),[19] periodate (−1.40),[20] permanganate (−1.52),[21] and peroxydisulfate (−0.56).[22] Large negative reaction constants were exhibited by oxidations involving formation of halogeno-sulfonium cations, e.g. by chloramine-T (−4.25),[23] bromine (−3.2),[24] and *N*-bromoacetamide (−3.75).[25] In the oxidation by *N*-chloroacetamide (NCA),[26] the values of field (ρ_I) and resonance (ρ^+_R) at 298 K are −1.3 and −1.7, respectively.

(ii) Alkyl Phenyl Sulfides. The rates of oxidation of alkyl phenyl sulfides did not yield any significant correlation separately with Taft's σ^* or E_s values. The rates were therefore analyzed in terms of Pavelich−Taft's[27] dual substituent-parameter (DSP) eq 10.

$$\log k_2 = \rho^*\sigma^* + \delta E_s + \log l_0 \tag{10}$$

The correlations are excellent (Table 8). Though the number of compounds is small (five) for any analysis by the DSP equation, the results can be used qualitatively. The negative polar reaction constant confirms that the electron-donating power of the alkyl group enhances the reaction rate. The steric effect plays a minor inhibitory role.

Table 8. Correlation of Rate of Oxidation of Alkyl Phenyl Sulfides with the Pavelich−Taft Equation[a]

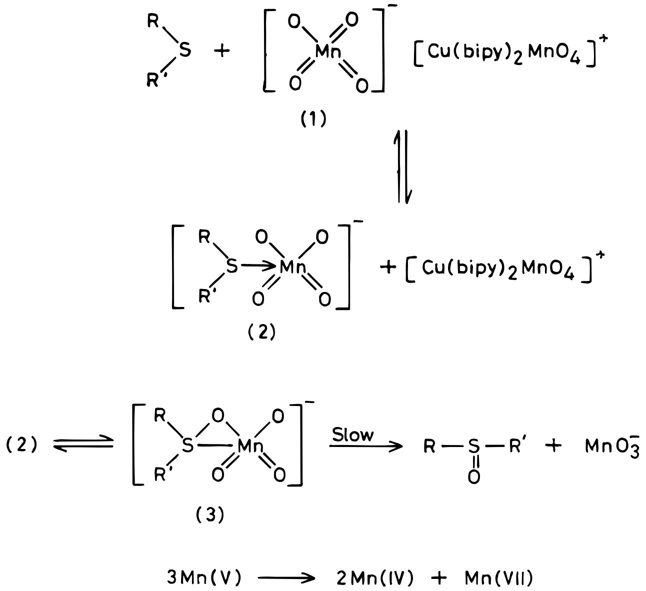
temp, K	ρ^*	δ	R^2	sd
283	−2.47 ± 0.06	0.76 ± 0.01	0.9998	0.01
293	−2.53 ± 0.12	0.76 ± 0.02	0.9991	0.01
303	−2.30 ± 0.02	0.69 ± 0.01	0.9999	0.01
313	−2.18 ± 0.05	0.63 ± 0.01	0.9997	0.01

[a] Number of data points = 5.

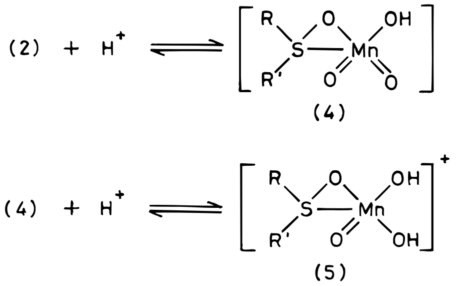
Mechanism

In view of the absence of any effect of radical scavenger, acrylonitrile, on the reaction rate, it is unlikely that a one-electron reaction, giving rise to free radicals, is operative in this oxidation. The observed Michaelis−Menten kinetics with respect to sulfides led us to suggest the formation of a 1:1 complex of BBCP and sulfides in a rapid preequilibrium. With the present data it is not possible to definitely state the nature of the intermediate complex. Theoretical calculations[28] have shown that there is a substantial amount of charge transfer from the metal to the oxygens in permanganate, and the manganese is essentially dipositive as in reaction **1**. The most logical mode of interaction between sulfides and BBCP would, therefore, be nucleophilic attack at the metal. Donation of an unshared pair of electrons to an empty d-orbital on the metal would result in the formation of a coordinate covalent bond as in reaction **2**. The initially formed intermediate is likely to undergo a further rapid reaction in which the incipient oxide and sulfonium ions bond to form a highly structured intermediate (**3**) that would rearrange to give a sulfoxide and manganese(V) (Scheme 1). The observed acid-catalysis may well be due to the successive protonation of the intermediate **2** prior to the further reactions (Scheme 2).

Scheme 1



Scheme 2



Experimental Section

Materials. The sulfides were either commercial products or prepared by known methods,[29−35] and were purified by distillation under reduced pressure or crystallization. Their purity was checked by comparing their boiling or melting points with the literature values. BBCP was prepared by the

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(19) Modena, G.; Maioli, L. *Gazz. Chim. Ital.* **1957**, *87*, 1306.

(20) Ruff, F.; Kucsman, A. *J. Chem. Soc., Perkin Trans. 2* **1985**, 683.

(21) Banerji, K. K. *Tetrahedron* **1988**, *44*, 2969.

(22) Srinivasan, C.; Kuthalingam, P.; Arumugam, N. *Can. J. Chem.* **1978**, *56*, 3043.

(23) Ruff, F.; Kucsman, A. *J. Chem. Soc., Perkin Trans. 2* **1975**, 509.

(24) Miotti, U.; Modena, G.; Sadea, L. *J. Chem. Soc., B* **1975**, 802.

(25) Perumal, S.; Alagumalai, S.; Selvaraj, S.; Arumugam, N. *Tetrahedron* **1986**, *42*, 4867.

(26) Agarwal, A.; Bhatt, P.; Banerji, K. K. *J. Phys. Org. Chem.* **1990**, *3*, 174.

(27) Pavelich, W. H.; Taft, R. W. *J. Am. Chem. Soc.* **1956**, *79*, 4935.

(28) Ziegler, T.; Rauk, A.; Baerends, E. J. *Chem. Phys.* **1976**, *16*, 209.

(29) Ruff, F.; Kucsman, A. *J. Chem. Soc., Perkin Trans. 2* **1985**, 683.

(30) Srinivasan, C.; Kuthalingam, P.; Chelamani, A.; Rajagopal, S.; Arumugam, N. *Proc. Indian Acad. Sci., Chem. Sci.* **1984**, *95*, 157.

(31) Zuncke, T.; Swartz, H. *Chem. Ber.* **1913**, *46*, 775. *Ibid.* **1915**, *48*, 1242.

(32) Hofmann, A. W. *Chem. Ber.* **1887**, *20*, 2260.

(33) Gilman, H.; Gainer, G. C. *J. Am. Chem. Soc.* **1949**, *71*, 1747.

(34) Saggiomo, A. J.; Craig, P. N.; Gordon, M. J. *J. Org. Chem.* **1958**, *23*, 1906.

(35) Nodiff, E. A.; Lipschutz, S.; Craig, P. N.; Gordon, M. J. *J. Org. Chem.* **1960**, *25*, 60.

reported method.[1] Acetic acid was refluxed with chromic oxide and acetic anhydride for 3 h and then fractionated. The perchloric acid (Merck) was used as the source of hydrogen ions.

Product Analysis. Methyl phenyl sulfide (0.01 mol) and BBCP (0.01 mol) were dissolved in 50 mL of 1:1 (v/v) acetic acid−water, and the mixture was allowed to stand for ca. 20 h. Most of the solvent was removed under reduced pressure. The residue was diluted with water and extracted with chloroform (3 × 50 mL). The chloroform layer was dried over anhydrous magnesium sulfate, the solvent was removed by evaporation, and the residue was analyzed by IR and ^{1}H NMR spectroscopy. The spectra were identical with those of MeSOPh. Peaks characteristic of MeSPh and $MeSO_2Ph$ could not be detected.

Stoichiometry. To determine the stoichiometry, BBCP (3.07 g, 0.005 mol) and methyl phenyl sulfide (0.12 g, 0.001 mol) were made up to 100 mL in 1:1 (v/v) acetic acid−water, in the presence of 0.1 mol dm^{-3} perchloric acid. The reaction was allowed to stand for ca. 10 h to ensure the completion of the reaction. The residual BBCP was determined spectrophotometrically at 529 nm. Several determinations with different sulfides showed that 2 mol of BBCP is consumed for every 3 mol of the sulfide oxidized.

Kinetic Measurements. The reactions were carried out under pseudo-first-order conditions by maintaining a large excess of the sulfides (×15 or more) over BBCP. The solvent was a 1:1 (v/v) acetic acid−water mixture (pH = 2.04), unless otherwise mentioned. The reactions were carried out at a constant temperature (±0.1 K) and followed up to 80% reaction by monitoring the decrease in absorption due to [BBCP] at 529 nm. The pseudo-first-order rate constants, k_{obs}, were computed from the linear ($r > 0.990$) least-squares plots of log[BBCP] versus time. Duplicate kinetic runs showed that the rate constants were reproducible within ±4%. The average error in the values of K and k_2 are ±5% and ±6%, respectively. Preliminary experiments showed that the oxidation is not sensitive to ionic strength; therefore, no attempt was made to keep it constant. All kinetic measurements, except those to study acid-catalysis, were performed in the absence of any added mineral acid.

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