Kinetics of Oxidation of *para*-Substituted Phenyl Methyl Sulphides by Pyridinium Chlorochromate in Dipolar Protic and Aprotic Solvents

Kasi Rajasekaran, Thanasekaran Baskaran, and Chinnasamy Gnanasekaran *
Department of Chemistry, VHNSN College, Virudhunagar 626 001, India

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The kinetics of oxidation of phenyl methyl sulphide (PMS) and several *para*-substituted phenyl methyl sulphides by pyridinium chlorochromate have been studied in binary solvent mixtures of 60% (v/v) aqueous acetic acid and 50% (v/v) chlorobenzene–nitrobenzene. Acrylonitrile has no effect on the rates of oxidation. In aqueous acetic acid, there is overall second-order reaction. The Hammett ρ value of -2.12 ± 0.09 (*r* 0.985, *s* 0.104) at 50 °C indicates an electron-deficient transition state. In chlorobenzene–nitrobenzene there is an association equilibrium prior to the rate-limiting step, followed by irreversible decomposition of the complex into products. The complex formation constants (K) and the complex decomposition rate constants (k_1) have been computed from the double reciprocal plots of $1/k_{obs}$ *versus* $1/[PMS]_0$. The decomposition rate constants (k_1) correlate well with Hammett σ values (ρ -1.23 ± 0.054, *r* 0.989, *s* 0.068 at 50 °C). On the basis of the results of the kinetic studies, a suitable mechanism has been proposed.

Much attention has been paid recently to the oxidation of organic sulphur compounds to sulphoxide.[1-10] The mechanism of these oxidations is largely dependent on the nature of the oxidants. The mechanism of these oxidations can be classified broadly into two types. Mechanism (1) involves reversible complex formation between substrate and oxidant in a fast step followed by slow irreversible decomposition of the complex into products.[2,7] In mechanism (2) complex formation is a slow step and the subsequent decomposition of the complex into products is fast.[5,6] Our earlier studies on acid bromate oxidation of several *para*-substituted phenyl methyl sulphides[10] have revealed that substituents at the *para*-position have a pronounced effect on the mechanism. Substrates with $-K$ substituents such as p-$COCH_3$, p-COOH, and p-NO_2 followed mechanism (2) and others mechanism (1).

In spite of numerous observations, the oxidation of organic sulphur compounds by metal oxidants such as Cr^{VI} has received little attention, perhaps because the rates of these oxidations are very fast. The nature of the Cr^{VI} species present in solution is largely dependent on the environmental conditions. The dichromate ion exists only as an acetylchromate ion in aqueous acetic acid[11] and the acetyl group increases the electron-accepting power of Cr^{VI}.[12] Hence oxidations by these species are fast. Even the oxidation of diphenyl sulphides by diacetylchromium is very fast.[13] On the other hand, Cohen *et al.* have shown that chlorochromate ion is a less active oxidising agent[14] than acetylchromate ion. We have noticed that pyridinium chlorochromate oxidation of phenyl methyl sulphides (PMS) proceeds smoothly in the solvent systems dipolar protic [60% (v/v) aqueous acetic acid] and aprotic [50% (v/v) chlorobenzene–nitrobenzene]. This paper presents the results of kinetic studies of the title reaction and shows that the solvent system has a pronounced effect on the mechanism of oxidation of sulphides.

Experimental

Materials.—Pyridinium chlorochromate was prepared by the method of Corey and Suggs.[15] All the phenyl methyl sulphides were prepared by literature methods.[8,16] The purity was ascertained by spectroscopic methods and t.l.c. All the other chemicals used were of AnalaR grade.

Solvents.—Acetic acid was purified by the procedure of Ortan and Bradfield.[17] Doubly distilled water was used for the preparation of the solvent system. Chlorobenzene and nitrobenzene were dried ($CaCl_2$) and distilled in an all-glass apparatus under reduced pressure. The middle fractions were collected after rejecting the head and the tail portions.

Kinetics.—All the kinetic runs were carried out under pseudo-first-order conditions, keeping [PMS] ≫ [oxidant]. The solvent system is either 60% (v/v) aqueous acetic acid or 50% (v/v) chlorobenzene–nitrobenzene unless otherwise mentioned. In the dipolar protic solvent system the course of reaction was followed by monitoring the decrease in absorption of pyridinium chlorochromate (PCC) at 350 nm employing a Hitachi–Perkin-Elmer 200 u.v.–visible spectrophotometer with a variable-temperature accessory. In the aprotic solvent system, the reaction was followed by estimating the unchanged PCC by standard iodometric procedures. The pseudo-first-order rate constants (k_{obs}) for the reactions in both solvent systems were computed by the method of least squares using a Micro 2200 computer (Hindustan Computers). The rate constants are readily reproducible and accurate to within ±2%.

Stoicheiometry.—The stoicheiometry of the reaction was determined by allowing the excess of PCC to react with phenyl methyl sulphide under the reaction conditions. Estimation of untreated PCC after the completion of the reaction revealed that the stoicheiometry was 1 : 1 in both solvent systems.

Product Analysis.—After 80% completion of the reaction, the reaction products were isolated and monitored by t.l.c. [80% (v/v) ethyl acetate–benzene solvent] along with authentic samples of phenyl methyl sulphide, phenyl methyl sulphoxide, and phenyl methyl sulphone. The reaction products gave only two spots corresponding to unchanged phenyl methyl sulphide and phenyl methyl sulphoxide. The oxidation gave sulphoxide exclusively as the product and the reaction proceeded quantitatively according to equation (1). This equation entails a two-electron transfer and is in agreement with the proposal of Brown *et al.*,[18] who recently reported that the exact nature of the reaction product of PCC is not known.

$$C_6H_5SCH_3 + C_5H_5\overset{+}{N}HCrO_3Cl^- \longrightarrow C_6H_5SOCH_3 + CrO_2 + C_5H_5\overset{+}{N}HCl^- \quad (1)$$

Results and Discussion

In both solvent systems, the order of the reaction with respect to PCC was found to be strictly unity as proved by the linearity of log O.D. against time plots and log $(a - x)$ against time plots over 75% of the reaction. Further, varying [PCC] at constant [PMS] does not affect the pseudo-first-order rate constants (k_{obs}). With the condition 10^2 [PMS] = 9.73M, $10^5 k_{obs}$ values were found to be 2.23, 2.18, and 2.24 s^{-1} respectively at 30 °C in the aprotic solvent system for 10^3 [PCC] 4.6, 7.2, and 9.2M. Similarly in the dipolar protic solvent system, with the condition 10^3 [PMS] 5.9M, the $10^4 k_{obs}$ values were 3.22, 3.14, and 3.15 s^{-1} respectively at 30 °C for 10^4 [PCC] varied as 2.4, 4.8, and 7.2M (Table 1).

A plot of log k_{obs} against log [PMS] is linear with a slope of 1.02 ± 0.008 (r 0.999) and a plot of k_{obs} against [PMS] also gives a good straight line (r 0.999) passing through the origin for the dipolar protic solvent systems. These observations lead to the conclusion that the order in [PMS] is unity and the reaction in the dipolar protic solvent systems is strictly second order. However, in aprotic solvent systems k_{obs} increases with increase of $[PMS]_0$ at constant [PCC] but $k_{obs}/[PMS]_0$ decreases with increase of $[PMS]_0$ (Table 1). A plot of $1/k_{obs}$ against $1/[PMS]_0$ is excellently linear and does not pass through the origin (Figure), indicating that the reactions in aprotic solvent systems follow Michaelis–Menten kinetics, *i.e.* a complex is formed prior to the rate-limiting step.

Table 1. Pseudo-first-order and second-order rate constants for the reaction of PMS with PCC at 30 °C

10^3 [PMS]/M	10^4 [PCC]/M	$10^5 k_{obs}/s^{-1}$	$10^3 k_2$/l $mol^{-1} s^{-1}$
5.90[a]	2.4	32.2	54.6
5.90[a]	4.8	31.4	53.2
5.90[a]	7.2	31.5	53.4
2.96[a]	4.8	15.6	52.7
4.44[a]	4.8	23.3	53.0
5.90[a]	4.8	31.4	53.3
7.40[a]	4.8	39.2	53.0
8.80[a]	4.8	47.8	54.3
97.3[b]	46.0	2.23	0.229
97.3[b]	72.0	2.18	0.224
97.3[b]	92.0	2.24	0.230
10.2[b]	52.4	0.46	0.453
20.4[b]	52.4	0.82	0.400
30.8[b]	52.4	1.06	0.344
40.0[b]	52.4	1.27	0.318
51.2[b]	52.4	1.46	0.286
80.0[b]	52.4	1.82	0.228

[a] Dipolar protic solvent. [b] Dipolar aprotic solvent.

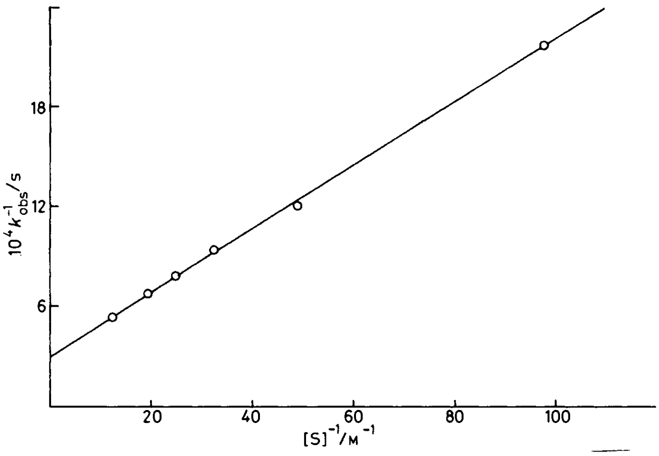


Figure. Plot of $1/k_{obs}$ against $1/[PMS]_0$ for the oxidation reaction in aprotic solvent at 30 °C

Effect of Acrylonitrile.—Experiments conducted in both solvent systems in the presence as well as in the absence of oxygen showed that the vinyl monomer acrylonitrile has no effect on the rates of the oxidation of phenyl methyl sulphide and no visible polymerisation occurs during the reaction

Mechanism and Rate Law.—The results of kinetic studies indicate the formation of a 1:1 complex between PCC and sulphide. The complex subsequently decomposes into products, as in steps (2) and (3). For this scheme, we obtain equations

$$C_6H_5\text{-}S\text{-}CH_3 + PCC \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\text{sulphide-PCC}] \tag{2}$$

$$[\text{sulphide-PCC}] \xrightarrow{k_1} C_6H_5SOCH_3 + Cr^{IV} \tag{3}$$

$$K = \frac{[\text{complex}]}{[PMS][PCC]} = k_2/k_{-2} \tag{4}$$

$$k_1 = -d\,[\text{complex}]/dt \cdot 1/[\text{complex}] \tag{5}$$

(6)—(8) by applying the steady-state approximation.[19] The

$$-\,d[PCC]/dt = \frac{K k_1 [PCC]_0 [PMS]_0}{1 + K[PMS]_0} \tag{6}$$

$$k_{obs} = \frac{K k_1 [PMS]_0}{1 + K[PMS]_0} \tag{7}$$

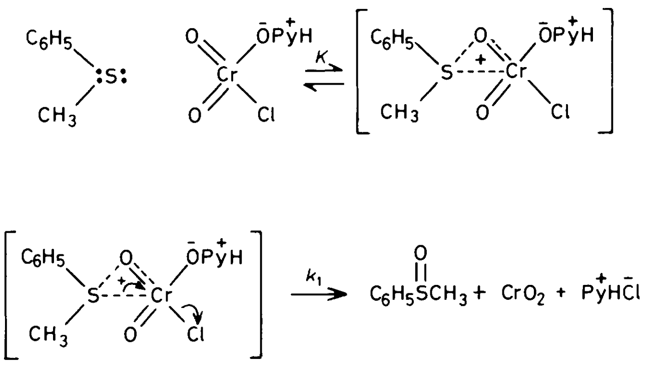
$$^1/k_{obs} = \frac{1}{K k_1 [PMS]_0} + 1/k_1 \tag{8}$$

observed rate constant (k_{obs}) may have the significance $k_{obs} = k_2$ *or* $k_{obs} = K k_1$, depending on the balance between specific rates of formation and breakdown of the intermediate. If $k_{obs} = k^2$, the formation of the intermediate is rate-limiting. However, if $k_{obs} = K k_1$, decomposition of the intermediate into products is rate-limiting.

In aprotic solvents, the decomposition of the complex into products is the rate-limiting step, since the reaction follows Michaelis–Menten-type kinetics. In protic solvent the reaction follows a second-order rate law, *i.e.* $-d[PCC]/dt = k_2[PCC]_0[PMS]_0$. This may be due to either of the following factors: (**1**) complex formation between PCC and sulphide is the rate-limiting step; (**2**) the decomposition of the complex may still be the rate-limiting step, but K might have diminished below the detectable level. Since in both cases the observed rate law is the same, no inference can be drawn regarding the rate-limiting step from the rate law alone.[20] However, other features of the kinetics may throw light upon the mechanism under such circumstances. The use of the protic solvent accelerates the rate by *ca.* 10^2 times (Table 1) and the effect could be primarily on the formation of the complex, resulting in the association equilibrium never being attained. The use of the protic solvent decreases K below the detectable level. This factor may favour the formation of the complex as the rate-limiting step.

The formation of the intermediate complex and its decomposition into products is shown in the Scheme. This Scheme envisages oxygen atom transfer from the oxidant and this is in accord with the earlier observation made for the diacetylchromate oxidation of diphenyl sulphide.[13] In the absence of definite evidence, the Scheme is speculative.

Substituent Effects.—(a) *Aprotic solvent*. To gain more information regarding the nature of the transition state and hence the mechanism, the oxidation of several *para*-substituted phenyl methyl sulphides has been investigated. The experimental rate constants (k_{obs}) for various initial concentrations of several *para*-substituted phenyl methyl sulphides have been determined in aprotic solvent at different temperatures, *viz*. 30, 40 and 50 °C and the data at 50 °C are given in Table 2. From the slopes and intercepts of double reciprocal plots, the complex formation constants (K) and the complex decomposition rate constants (k_1) were evaluated for several *para*-substituted phenyl methyl sulphides and they are presented in Table 3 together with the thermodynamic parameters. Analysis of the data in Table 3 reveals that variation in complex formation constants (K) is not substantial and does not follow any pattern. On the other hand, the variation in complex decomposition rate constants (k_1) is systematic. Electron-releasing substituents increase k_1 while electron-withdrawing ones decrease it. The reactivity pattern is brought out by two different correlations at 50 °C, one of log k_1 with σ values and the other of log k_1 with σ_p^+–σ_p^- values. Since sulphur can act either as an electron donor or acceptor depending upon the nature of the substituent *para* to the methylthio-group,[21] both σ_p^+ and σ_p^- values have been employed simultaneously in several reactions[6,9,21,22] involving a sulphur centre in a single Hammett plot so as to get a better correlation. A satisfactory correlation is obtained with Hammett σ values (ρ −1.23 ± 0.05; *r* 0.989; *s* 0.068), but the correlation with σ_p^+–σ_p^- values[23] is discouraging (ρ −0.697 ± 0.038; *r* 0.980; *s* 0.085). This clearly indicates that the rate constants of substrates having −*K* (NO_2) and +*K* (OCH_3) substituents in the *para*-position correlate better with Hammett σ values. Perhaps the intermediate complex involves some kind of loose association (electrostatic) and this association must be strong enough to prevent the delocalisation of the lone pair of electrons on the sulphur of the sulphide into phenyl rings so that subsequent passage into the transition state for decomposition into products does not give the substituents any opportunity to exhibit substantial resonance effects.



Scheme. Py = pyridine

Table 2. Pseudo-first-order rate constants for the oxidation of *para*-substituted phenyl methyl sulphides by PCC at 50 °C in the aprotic solvent

Substituent	$10^5\ k_{obs}/s^{-1}$			
[Sulphide]/M	0.01	0.02	0.03	0.05
p-OCH_3	9.50	14.30	16.80	24.30
p-CH_3	5.02	7.14	9.91	14.00
p-H	3.15	4.59	5.94	6.74
p-F	2.64	4.17	5.26	6.11
p-Cl	2.06	2.92	3.30	4.60
p-Br	2.04	2.89	3.25	4.62
p-I	2.00	2.80	3.20	4.50
p-NO_2	0.56	0.72	0.90	1.26

(b) *Protic solvent*. The rates of oxidation of several *para*-substituted phenyl methyl sulphides were measured at four different temperatures. The bimolecular rate constants together with the activation parameters are presented in Table 4. Examination of the rate data reveals that electron-releasing substituents increase the rate of the reaction while electron-withdrawing ones decrease it. The rates of oxidation are largely dependent on the electron density of the sulphur of the sulphide. Correlation analyses were carried out on these data with Hammett σ and σ_p^+–σ_p^- values. For the Hammett plot with σ values, a satisfactory correlation was obtained at 50 °C (ρ −2.12 ± 0.09; *r* 0.985; *s* 0.104). A slightly improved correlation exists between log k_2 and σ_p^+–σ_p values (ρ −1.14 ± 0.04; *r* 0.990; *s* 0.086 at 50 °C). The negative ρ values indicate the development of electron-deficient sulphur in the transition state.

The ρ value in the oxidation of alkyl aryl sulphides by bromine[2] is −3.2 and it has been postulated that the formation of intermediate halogenosulphonium ion is the rate-limiting step. In the present study the ρ value in protic solvent is comparable with that of halogen oxidation. This may be considered a further indication that in protic solvent the formation of intermediate complex is the rate-limiting step.

Activation Parameters.—The activation energies were computed from a plot of log *k versus* 1/*T*. The entropies and enthalpies of activation and Arrhenius pre-exponential terms were calculated for the oxidation reactions in protic and aprotic solvents. In protic solvents the entropies of activation are largely negative as expected for a bimolecular reaction[24] and almost constant within the series. In fact, one of the prerequisites for a reaction to obey the Hammett equation is

Table 3. Equilibrium constants (K), decomposition rate constants (k_1), and activation parameters for the oxidation of *para*-substituted phenyl methyl sulphides by PCC in aprotic solvent

	$10^5\ k_1/s^{-1}$							
Substituent	30 °C	40 °C	50 °C	K/l mol^{-1}	E_a/kJ mol^{-1}	$\Delta H^\ddagger$/kJ kJ mol^{-1}	$-\Delta S^\ddagger$/J K^{-1} mol^{-1}	log ρ*z*
p-OCH_3	10.00	15.80	33.20	37	51.0	48.4	161.5	4.8
p-CH_3	5.00	11.00	20.40	33	57.4	55.2	145.2	5.7
p-H	3.30	5.00	9.62	43	62.8	60.3	132.2	6.3
p-F	1.80	4.14	9.60	40	66.9	64.4	123.4	6.8
p-Cl	1.20	2.56	7.48	50	67.8	65.3	123.9	6.8
p-Br	1.20	2.56	6.18	52	67.8	65.3	123.9	6.8
p-I	1.00	2.24	5.48	43	74.5	72.0	103.3	7.8
p-NO_2	0.35	0.67	1.45	60	92.0	89.5	54.0	10.4

Table 4. Bimolecular rate constants (k_2) and activation parameters for the oxidation reactions in dipolar protic solvent

	$10^2\ k_2$/l mol^{-1}s^{-1}							
Substituent	30 °C	35 °C	40 °C	50 °C	E_a/kJ mol^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	log ρz
p-OCH$_3$	287	418	509	583	27.6	25.1	171.5	4.2
p-CH$_3$	113	121	159	223	29.7	27.2	174.0	4.2
p-H	54	63	82	110	30.1	27.6	178.2	3.9
p-F	49	63	77	110	40.0	28.5	176.1	4.0
p-Cl	22	27	33	48	31.8	29.3	179.9	3.8
p-Br	27	33	44	58	32.2	29.7	177.0	4.0
p-I	19	25	31	44	33.9	31.4	174.0	4.1
p-COOH	6	7	9	12	37.7	35.1	174.5	4.3
p-COCH$_3$	5	6	7	10	38.5	36.0	178.7	4.3

that it should be isoentropic.[25,26] The entropies of activation in aprotic solvents are negative but they do not remain constant within the series. In such cases, the variation in $\Delta S^\ddagger$ should be linearly related to changes in $\Delta H^\ddagger$ by equation (9)[27,28] where β

$$\Delta H^\ddagger = \Delta H_0 + \beta\Delta S^\ddagger \qquad (9)$$

is the isokinetic temperature. In aprotic solvents a plot of $\Delta H^\ddagger$ against $\Delta S^\ddagger$ is linear (r 0.986). The existence of a linear relationship between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ indicates that a single mechanism is operating throughout the series.[29]

Comparison of the Kinetic Results in Protic and Aprotic Solvents.—(1) In both the solvent systems studied, the reaction rate is unaffected by the radical trapping agents. (2) In the aprotic solvent, Michaeles–Menten kinetics are exhibited whereas in the protic solvent the oxidation follows the rate law d[PCC]/dt = k_2 [PCC]$_0$[PMS]$_0$. (3) In both solvent systems, the entropies of activation are negative but in the protic solvent they are largely negative and this indicates the formation of intermediate complex is the rate-limiting step. (4) The ρ values in protic and aprotic solvents are −2.12 and −1.23, respectively, at 50 °C. The negative ρ values indicate the development of electron-deficient sulphur in the transition state. The proposed mechanism is consistent with the above observations.

Acknowledgements

We thank Professor P. Ananthakrishna Nadar for his encouragement and the authorities of the Managing Board of VHNSN College, Virudhunagar for providing research facilities. Thanks are also due to the referees for valuable suggestions.

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Received 12*th September* 1983; *Paper* 3/1588