

Kinetics and mechanism of oxidation of aromatic sulfides and arylmercaptoacetic acids by *N*-chlorosuccinimide

2 PERKIN

Duraisamy Thenraja, Perumal Subramaniam and Chockalingam Srinivasan*

Department of Materials Science, Madurai Kamaraj University, Madurai 625 021, India.
E-mail: ceesri@yahoo.com

Received (in Cambridge, UK) 5th July 2002, Accepted 10th September 2002

First published as an Advance Article on the web 15th October 2002

Kinetic measurements of the oxidation of divalent organic sulfur compounds by *N*-chlorosuccinimide in acetonitrile–water mixture at constant $[H^+]$ show that the reaction is first order in both the oxidant and the organic sulfur compound. While the rate of oxidation of methyl phenyl sulfide or diphenyl sulfide increases with $[H^+]$, that of phenylmercaptoacetic acid decreases. Therefore it has been concluded that protonated *N*-chlorosuccinimide and *N*-chlorosuccinimide are the active oxidising species in the oxidation of aromatic sulfides and *N*-chlorosuccinimide is the active species in the case of phenylmercaptoacetic acids. Structure–reactivity correlations for the oxidation of aryl methyl sulfides, diaryl sulfides and arylmercaptoacetic acids result in a high negative reaction constant, providing evidence for the formation of a chlorosulfonium ion intermediate.

Introduction

The sulfoxidation of sulfides is an area of attraction for many groups.^{1–4} Although there are many reactions in which sulfides or sulfoxides are oxidized, systematic studies are few.⁵ We have been interested in the elucidation of the mechanism of oxidation of organic sulfides by several oxidants for more than two decades.^{4,6–11} Though the oxidation of dialkyl, diaryl and benzyl phenyl sulfides by *N*-chlorosuccinimide (NCS) to give the corresponding sulfoxides has been reported by Harville and Reed,¹² the kinetics of oxidation of divalent organic sulfur compounds by NCS have not been reported. NCS is mainly used as a chlorinating agent in the chlorination of organic sulfides and sulfoxides in organic preparations. In aqueous solution containing chloride ions the reactive species is molecular chlorine which results in chlorination followed by hydrolysis to give the oxidised products. In this paper we report the results of our extensive studies on the kinetics and mechanism of reaction of aryl methyl sulfides, diaryl sulfides and arylmercaptoacetic acids by NCS and this investigation includes the influence of substituents in the organic divalent sulfur compounds on the rate.

Experimental

Materials

All the aryl methyl sulfides,¹³ diaryl sulfides⁹ and arylmercaptoacetic acids¹⁴ were prepared by known methods. The sulfides and aryl mercaptoacetic acids were purified by distillation or recrystallisation before the kinetic studies. The purity of the compounds was established from their sharp melting behaviour with solids, single spots on TLC and spectral studies. AR grade NCS was used. Doubly distilled water was used throughout, the second distillation being from permanganate. A commercial sample of acetonitrile was purified by refluxing with phosphorous pentoxide in all glass apparatus and then distilled.¹⁵ All other chemicals used were of AR grade.

Kinetic measurement

The kinetic runs for the oxidation of aryl methyl sulfides by NCS were carried out in 95% acetonitrile–5% water (v/v) as

solvent. In the oxidation of diaryl sulfides the solvent was 60% acetonitrile–40% water (v/v) and with phenylmercaptoacetic acids the solvent was 75% acetonitrile–25% water (v/v). All these kinetic runs were carried out in acid medium, the acid strength being maintained by the addition of perchloric acid and the ionic strength by sodium perchlorate. The kinetics were followed by estimating the unconsumed NCS. Aliquots (5 mL) of the reaction mixture at regular intervals of time were added to an iodine flask containing potassium iodide (10 mL, 5%) and then added 2M hydrochloric acid (5 mL). Unconsumed NCS liberated a proportionate amount of iodine and the latter was estimated by standard sodium thiosulfate solution to a starch end point. In all these oxidation the rates were followed for not less than 70–80% completion. Reproducible results giving good first-order plots ($r > 0.997$) were obtained for reactions run in duplicate and the mean values were quoted in the discussions.

Product analysis

The reaction mixture from an actual kinetic run was evaporated under reduced pressure to remove the solvent and extracted with chloroform and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the solution was analysed by TLC in a solvent system of benzene–ethyl acetate (80%–20%). Methyl phenyl sulfoxide and diphenyl sulfoxide were identified as final products in the oxidation of methyl phenyl sulfide (MPS) and diphenyl sulfide (DPS) respectively. GC analysis also indicated that only sulfoxides were formed.

Results and discussion

Kinetic studies with aryl methyl and diaryl sulfides

MPS and DPS were selected as representatives respectively for aryl methyl sulfides and diaryl sulfides. The kinetics were carried out in 95% acetonitrile–5% water (v/v) for MPS and 60% acetonitrile–40% water (v/v) for DPS under pseudo-first-order conditions keeping the substrate always in excess. The acid strength was maintained at 0.001 M using perchloric acid. The rate of the reaction was followed by estimating the unconsumed NCS by iodometric method at different time intervals.

Table 1 Pseudo-first-order and second-order rate constants for the oxidation of MPS and DPS by NCS; $[\text{HClO}_4] = 0.001 \text{ M}$

$10^2[\text{Sulfide}]/\text{M}$	$10^3[\text{NCS}]/\text{M}$	$10^4 k_1/\text{s}^{-1}{}^a$	$10^2 k_2{}^a$
MPS^b			
1.0	1.0	4.13 ± 0.03	4.13 ± 0.03
2.0	1.0	8.01 ± 0.21	4.00 ± 0.10
3.0	1.0	12.6 ± 0.14	4.20 ± 0.05
4.0	1.0	17.6 ± 0.34	4.40 ± 0.08
5.0	1.0	20.8 ± 0.46	4.15 ± 0.09
2.0	0.50	8.11 ± 0.08	4.06 ± 0.04
2.0	1.5	8.74 ± 0.15	4.37 ± 0.08
2.0	2.0	8.55 ± 0.09	4.27 ± 0.04
DPS^c			
1.0	1.0	1.78 ± 0.01	1.78 ± 0.01
2.0	1.0	3.65 ± 0.02	1.83 ± 0.01
3.0	1.0	5.55 ± 0.05	1.85 ± 0.02
4.0	1.0	7.62 ± 0.07	1.90 ± 0.02
5.0	1.0	9.71 ± 0.07	1.94 ± 0.01
2.0	0.50	3.68 ± 0.02	1.84 ± 0.01
2.0	1.5	3.68 ± 0.02	1.84 ± 0.01
2.0	2.0	3.64 ± 0.01	1.82 ± 0.01

^a The error quoted in k_1 and k_2 values in all tables is 95 % CL of Student's t (see ref. 30) ^b Solvent: 95% acetonitrile–5% water (v/v); temperature = 20 °C ^c Solvent: 60% acetonitrile–40% water (v/v); temperature = 45 °C

For both substrates, the plots of $\log(a - x)$ against time are linear (not shown) indicating the first-order dependence on $[\text{NCS}]$. This is also confirmed by the constant values of k_1 (Table 1) at different initial concentrations of NCS. The first-order dependence on $[\text{sulfide}]$ has been revealed by (i) the constant second-order rate constants ($k_2 = k_1/[\text{sulfide}]$) at varying initial concentrations of sulfide and (ii) the unit slope of $\log k_1$ vs. $\log[\text{sulfide}]$ (MPS: slope = 1.03 ± 0.03 , $r = 0.999$, $s = 0.02$; DPS: slope = 1.05 ± 0.01 , $r = 0.999$, $s = 0.01$). The plots of $1/k_1$ vs. $1/[\text{MPS}]$ or $1/[\text{DPS}]$ yield excellent straight lines passing through origin. Consequently a reaction pathway involving the formation of an intermediate complex in a fast pre-equilibrium and its slow decomposition can be excluded.

That the reaction proceeds through two paths, *viz.* acid-dependent and acid-independent paths, is revealed by the fact that k_2 varies linearly with $[\text{H}^+]$ with a positive intercept (Fig. 1. MPS: $r = 0.998$; DPS: $r = 0.979$).

The rate is unaffected by the change in ionic strength of the medium brought about by the addition of sodium perchlorate.

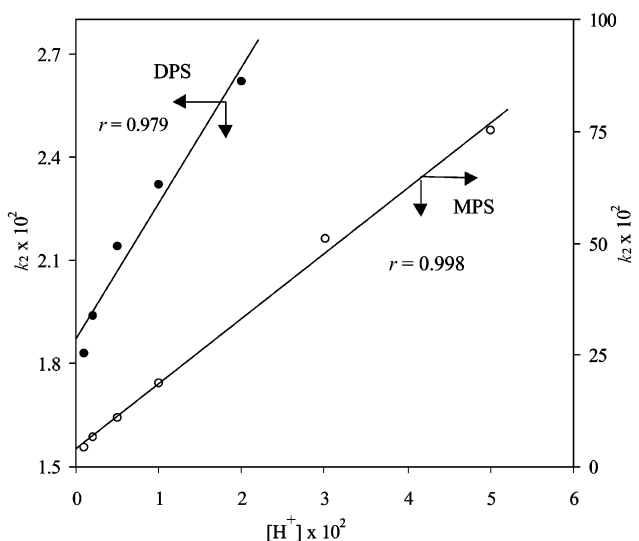
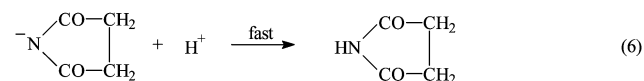
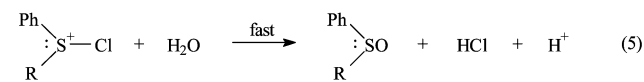
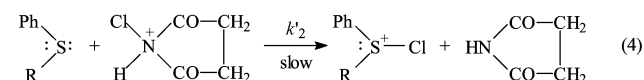
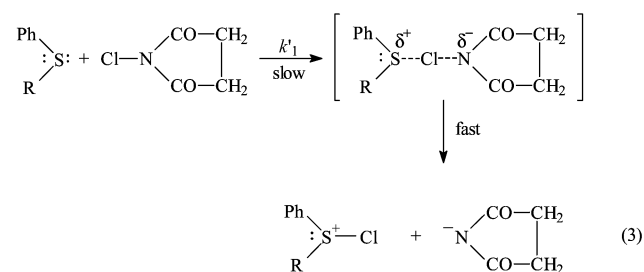
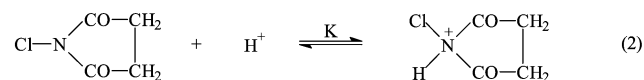
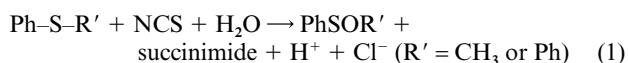


Fig. 1 Effect of $[\text{H}^+]$ in NCS oxidation of MPS and DPS. $[\text{MPS}] = 0.01 \text{ M}$; $[\text{NCS}] = 0.001 \text{ M}$; $[\text{I}] = 0.06 \text{ M}$; $T = 20 \text{ }^\circ\text{C}$; solvent 95% acetonitrile–5% water (v/v). $[\text{DPS}] = 0.02 \text{ M}$; $[\text{NCS}] = 0.001 \text{ M}$; $[\text{I}] = 0.10 \text{ M}$; $T = 45 \text{ }^\circ\text{C}$; solvent 60% acetonitrile–40% water (v/v).

It is found that added succinimide has no influence on the rate of oxidation and this excludes the reversible nature of the rate-determining step (Scheme 1) which involves succinimide as one of the products. The operation of a one-electron oxidation giving rise to free radicals is excluded as the rate of oxidation is unaffected in the presence of acrylonitrile, a radical scavenger. When the reaction has been studied in binary mixtures of acetonitrile and water as solvent, the rate increases with increase in polarity of the medium (Table 2). The solvent effect supports the formation of a polar intermediate.

The activation parameters for both oxidations have been evaluated from the slope and intercept of Eyring's plot of $\log(k_2/T)$ against $1/T$, which is linear. The activation parameters (Tables 3 and 4) are of the order expected for a bimolecular nucleophilic reaction. The high negative entropy of activation in both cases suggests a definite orientation in the transition state and this may be in part due to the solvation of the activated complex.

Methyl phenyl sulfoxide and diphenyl sulfoxide were isolated as the products in the oxidation of MPS and DPS respectively. The stoichiometry of the reaction was found to be 1 : 1 and the oxidation of sulfides may be represented by



(R = CH₃ or Ph)

Scheme 1

Mechanism and rate law

The foregoing kinetic data show that the oxidation is found to be first order with respect to NCS and MPS or DPS. *N*-Halogeno-amides are known to undergo hydrolysis and/or disproportionation in aqueous solution to give hypohalous acids which have been proposed as the reactive species in many reactions.^{16–18} However, the lack of any effect of succinimide on the reaction rate rules out the involvement of any pre-equilibria

Table 2 Effect of solvent composition on the rate of oxidation of MPS and DPS by NCS. [NCS] = 0.001 M. [HClO₄] = 0.001 M. [I] = 0.02 M

H ₂ O–CH ₃ CN (%) (v/v)	10 ² k ₂ /M ⁻¹ s ⁻¹
MPS^a	
25–75	155 ± 2.8
15–85	35.9 ± 0.23
10–90	11.4 ± 0.13
5–95	4.13 ± 0.03
DPS^b	
60–40	8.15 ± 0.17
50–50	5.98 ± 0.05
40–60	1.83 ± 0.01
30–70	0.542 ± 0.01
20–80	0.146 ± 0.001
10–90	0.059 ± 0.001

^a [MPS] = 0.01 M; T = 20 °C. ^b [DPS] = 0.02 M; T = 45 °C.

in the present investigation. As the plot of k_2 vs. $[H^+]$ is linear with a positive intercept (Fig. 1), it appears that NCS and its protonated species are the oxidising species in the oxidation of sulfides. The mechanism shown in Scheme 1 is proposed.

From Scheme 1, the rate law may be obtained

$$-d[\text{NCS}]/dt = k_1'[\text{PhSR}][\text{NCS}] + k_2'[\text{PhSR}][\text{NCSH}^+] = \frac{k_1'[\text{PhSR}][\text{NCS}] + Kk_2'[\text{PhSR}][H^+][\text{NCS}]}{k_1'[\text{PhSR}][\text{NCS}] + Kk_2'[\text{PhSR}][H^+][\text{NCS}]}$$

$$\text{as } [\text{NCSH}^+] = K[H^+][\text{NCS}].$$

Therefore,

$$-d[\text{NCS}]/dt = \{k_1' + Kk_2'[H^+]\}[\text{PhSR}][\text{NCS}] \quad (7)$$

Therefore the observed second-order rate constant is expressed as

$$k_2 = k_1' + Kk_2'[H^+] \quad (8)$$

Eqn. (8) predicts that k_2 should vary linearly with $[H^+]$ with a definite intercept. This has indeed been observed (Fig. 1).

Structure–reactivity correlation

(i) Substituent effect

As the study of influence of substituents on the rate of oxidation often provides an insight into the nature of the transition state, the rates of oxidation of a number of *meta*- and *para*-substituted phenyl methyl sulfides and 4-substituted and 4-nitro-4'-substituted diphenyl sulfides were determined in the presence of perchloric acid at constant ionic strength (in most cases at three temperatures) and the activation parameters were evaluated (Tables 3 and 4). In both series of sulfides, electron-releasing groups accelerate the rate of oxidation. The rates of oxidation of aryl methyl sulfides correlate well with Hammett substituent constants giving a negative reaction constant at 20 °C ($\rho = -3.33 \pm 0.10$, $r = 0.995$, $s = 0.11$, $n = 13$). The negative reaction constant points to an electrophilic attack on the sulfur atom by the oxidant and the high ρ value provides support for the chlorosulfonium ion intermediate in the reaction. This conclusion is supported by the fact that the ρ values in the oxidation of alkyl aryl sulfides by Br^+ and Cl^+ proceeding through RArSBr^+ and RArSCI^+ are -3.20^{16} and -4.25^{19} respectively.

As the reaction of NCS with 4-nitrodiphenyl sulfide, 4-nitro-4'-chlorodiphenyl sulfide and 4,4'-dinitrodiphenyl sulfide are too small to follow even at high substrate concentration and at high temperature, their rates were not studied. The correlation between $\log k_2$ values of diaryl sulfides and Hammett

substituent constants is excellent giving a ρ value of -3.26 ± 0.10 at 60 °C ($r = 0.997$, $s = 0.08$, $n = 7$) which is analogous to the reaction constant observed for aryl methyl sulfides. The plot of $\log k_2$ values at 35 °C of substituted phenyl methyl sulfides and diphenyl sulfides is linear with a slope of unity (slope = 0.984 ± 0.09 , $r = 0.988$). This confirms that diaryl sulfides and aryl methyl sulfides follow the same mechanism in the NCS oxidation.

Isokinetic relationship

Generally the Hammett correlation appears to apply to a reaction series in which either ΔS^\ddagger is constant or in which the variation in ΔS^\ddagger is linearly related to changes in ΔH^\ddagger .^{20–23} In the latter case these two variables are correlated^{23–26} by eqn. (9).

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

Though in both series of sulfides the Petersen error criterion is satisfied, i.e., $\Delta \Delta H^\ddagger > 2\delta$, the relation between ΔH^\ddagger and ΔS^\ddagger can be assumed to be valid²⁷ in the present study. However, the correlation between ΔH^\ddagger and ΔS^\ddagger is not very good. According to Exner²⁸ a good linear log–log plot of the rate constants at two different temperatures is an indication of the existence of an isokinetic relationship. The good correlation obtained in Exner's excellent plots (Fig. 2, $r > 0.995$) leads to the conclusion

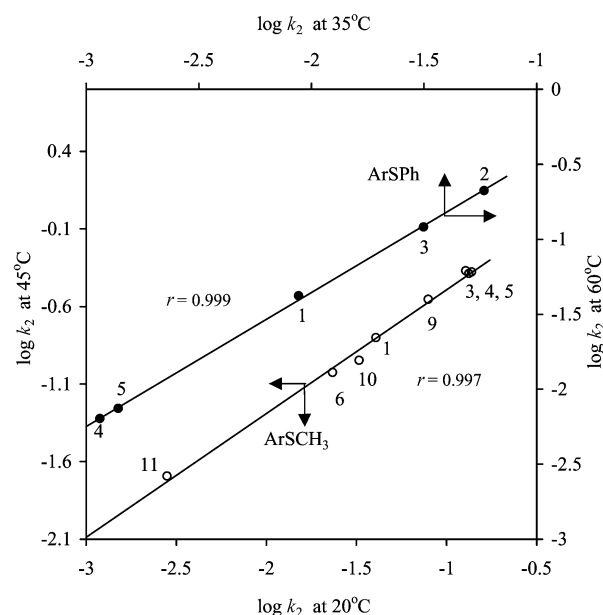


Fig. 2 Isokinetic plots in NCS oxidation (Exner plots, numbers as in Table 3 for ArSCH₃ and Table 4 for ArSPh).

that the mechanism of the reaction NCS and all the aryl methyl sulfides and also that of NCS and diaryl sulfides is one and the same.

Kinetic studies with phenylmercaptoacetic acids

The rates of oxidation of phenylmercaptoacetic acid (PMAA) and several substituted phenylmercaptoacetic acids (divalent organic sulfur compounds) have been studied in 75% acetonitrile–25% water (v/v) in the presence of 0.001 M perchloric acid and at an ionic strength of 0.02 M. Detailed kinetic investigations were made with PMAA as the representative of the series under pseudo-first-order conditions of $[\text{PMAA}] \gg [\text{NCS}]$. The oxidation has been found to be first order both in $[\text{PMAA}]$ and in $[\text{NCS}]$ from the following facts:

(i) The plots of $\log[\text{NCS}]$ vs. time are linear (not shown) and the pseudo-first-order rate constant k_1 values are independent of initial $[\text{NCS}]$ (see Table 5).

Table 3 Second-order rate constants, enthalpies and entropies of activation for the oxidation of X-C₆H₄-SCH₃ by NCS. [Ar-S-CH₃] = 0.01 M. [HClO₄] = 0.001 M. [NCS] = 0.001 M. [I] = 0.02 M

Solvent: 95% acetonitrile–5% water (v/v)						
X	10 ² k ₂ /M ⁻¹ s ⁻¹			ΔH [‡] /kJ M ⁻¹	–ΔS [‡] /J K ⁻¹ M ⁻¹	
	20 °C ^a	35 °C	45 °C			
1	H	4.06 ± 0.06	8.45 ± 0.05	15.8 ± 0.05	38.5 ± 0.34	140 ± 1.2
2	<i>p</i> -OMe	46 ± 0.44	93.1 ± 1.9	29.6 ± 0.47 ^b	30.9 ± 0.89	146 ± 3.5
3	<i>p</i> -Me	12.8 ± 0.14	23.9 ± 0.32	42.7 ± 0.79	34.2 ± 0.89	145 ± 3.1
4	<i>p</i> -Et	13.8 ± 0.16	27.9 ± 0.22	41.8 ± 1.0	31.9 ± 0.90	152 ± 3.2
5	<i>p</i> -Pr ⁱ	13.3 ± 0.15	26.4 ± 0.42	40.9 ± 0.37	32.2 ± 0.75	152 ± 3.2
6	<i>p</i> -F	2.33 ± 0.02	5.33 ± 0.04	9.44 ± 0.13	40.6 ± 0.62	138 ± 2.2
7	<i>p</i> -Cl	0.661 ± 0.01	1.38 ± 0.01	—	34.3 ± 0.81	169 ± 2.9
8	<i>p</i> -Br	0.564 ± 0.01	1.67 ± 0.02	—	51.8 ± 0.95	111 ± 3.3
9	<i>m</i> -Me	7.91 ± 0.08	16.9 ± 0.19	27.9 ± 0.40	36.4 ± 0.73	142 ± 2.6
10	<i>m</i> -OMe	3.28 ± 0.02	7.47 ± 0.07	11.3 ± 0.08	36.1 ± 0.47	150 ± 1.7
11	<i>m</i> -Cl	0.281 ± 0.01	0.948 ± 0.02	2.02 ± 0.01	58.6 ± 0.69	93.8 ± 2.5
12	<i>p</i> -Ac	0.105 ± 0.001 ^c	—	—	—	—
13	<i>p</i> -NO ₂	0.011 ± 0.001 ^d	—	—	—	—

^a Average k₂ for two substrate concentrations; ^b temp. = 10 °C; ^c [ArSCH₃] = 0.02 M; ^d [ArSCH₃] = 0.05. The precisions of ΔH[‡] and ΔS[‡] values were calculated using the method of Petersen *et al.*²⁷

Table 4 Second-order rate constants, enthalpies and entropies of activation for the oxidation of X-C₆H₄-S-C₆H₄-Y by NCS [Ar-S-Ar] = 0.02 M. [HClO₄] = 0.001 M. [NCS] = 0.001 M. [I] = 0.02 M

Solvent: 60% acetonitrile–40% water (v/v)							
X	Y	10 ² k ₂ /M ⁻¹ s ⁻¹			ΔH [‡] kJ M ⁻¹	–ΔS [‡] J K ⁻¹ M ⁻¹	
		35 °C ^a	45 °C	60 °C			
1	H	H	0.880 ± 0.01	1.80 ± 0.01	4.20 ± 0.01	50.4 ± 0.31	121 ± 1.0
2	4-OMe	H	5.85 ± 0.04	10.3 ± 0.10	21.1 ± 0.13 ^b	41.0 ± 0.52	136 ± 1.7
3	4-Me	H	3.15 ± 0.02	5.57 ± 0.02	12.1 ± 0.11 ^b	43.2 ± 0.43	134 ± 1.5
4	4-Cl	H	0.115 ± 0.001	0.212 ± 0.002	0.636 ± 0.004	57.1 ± 0.55	117 ± 1.9
5	4-Br	H	0.39 ± 0.001	0.262 ± 0.002	0.743 ± 0.01	54.8 ± 0.55	122 ± 1.9
6	4-NO ₂	4'-OMe	—	—	0.082 ± 0.001 ^b	—	—
7	4-NO ₂	4'-Me	—	—	0.028 ± 0.001	—	—

^a Average k₂ for two substrate concentrations ^b [ArSAr] = 0.01 M.

Table 5 Pseudo-first-order and second-order rate constants for the oxidation of PMAA by NCS at 35 °C. [HClO₄] = 0.001 M. [I] = 0.02 M

Solvent: 75% acetonitrile–25% water (v/v)			
10 ² [PMAA]/M	10 ³ [NCS]/M	10 ⁴ k ₁ /s ⁻¹	10 ² k ₂ /M ⁻¹ s ⁻¹
1.0	1.0	6.02 ± 0.13	6.02 ± 0.13
2.0	1.0	12.2 ± 0.20	6.10 ± 0.10
3.0	1.0	18.0 ± 0.23	6.05 ± 0.08
4.0	1.0	24.0 ± 0.46	6.01 ± 0.11
5.0	1.0	30.6 ± 0.62	6.11 ± 0.12
7.0	1.0	43.1 ± 0.61	6.15 ± 0.09
10	1.0	60.9 ± 0.73	6.09 ± 0.07
2.0	0.50	12.3 ± 0.11	6.14 ± 0.05
2.0	1.5	11.9 ± 0.26	5.95 ± 0.13
2.0	2.0	11.9 ± 0.21	5.97 ± 0.10

(ii) The plot of k₁ vs. [PMPAA] is linear and passes through the origin (not shown).

(iii) The plot of log k₁ vs. log[PMAA] is linear with a slope of unity (not shown), and the second-order rate constants, k₂, are constant at various [PMAA] (Table 5).

However, the rate of oxidation decreases with increase in [H⁺]. The second-order rate constants at 35 °C in 75 % acetonitrile–25 % water at [HClO₄] = 0.001, 0.002, 0.005, and 0.01 M are 7.33 × 10⁻², 6.01 × 10⁻², 4.13 × 10⁻², and 3.74 × 10⁻² M⁻¹ s⁻¹ respectively ([PMAA] = 0.01 M; [NCS] = 0.001 M; [I] = 0.05 M). In this respect the oxidation differs from those of aryl methyl and diaryl sulfides. The rate is neither affected by the addition of a vinyl monomer, acrylonitrile nor by succinimide.

Table 6 Effect of temperature on the rate of oxidation of PMAA by NCS and activation parameters. [PMAA] = 0.01 M. [HClO₄] = 0.001 M. [NCS] = 0.001 M. [I] = 0.02 M

Solvent: 75% acetonitrile–25% water (v/v)			
Temperature/°C	10 ² k ₂ /M ⁻¹ s ⁻¹	ΔH [‡] /kJ M ⁻¹	–ΔS [‡] /J K ⁻¹ M ⁻¹
20	3.18 ± 0.05	—	—
30	4.90 ± 0.08	29.2 ± 1.1	174 ± 4.0
35	6.02 ± 0.13	—	—
45	8.84 ± 0.17	—	—

The increase in the ionic strength of the medium results in a slight increase in the rate. The rate is also enhanced when the water content is increased in the medium of the binary mixture. From the measured rates at four temperatures (Table 6) and from the slope and intercept of the plot of log(k₂/T) against 1/T, ΔH[‡] and ΔS[‡] have been evaluated.

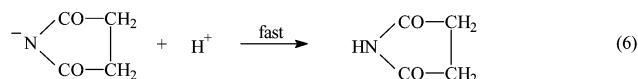
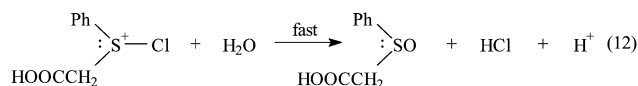
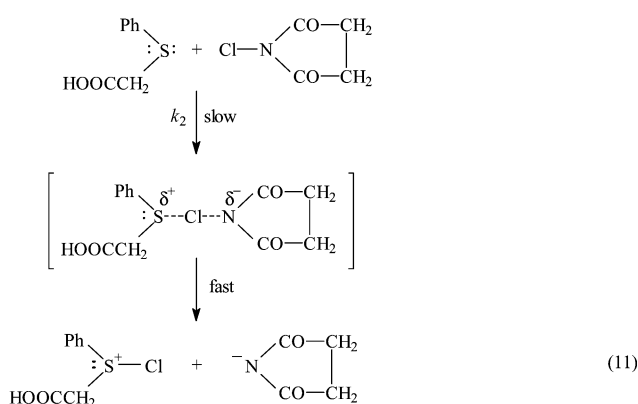
Mechanism and rate law

Since added succinimide has not influenced the rate, an equilibrium involving hypohalous acid is ruled out. The kinetic results obtained in the present study can be rationalized if NCS itself is considered to be the active species. The mechanism shown in Scheme 2 is proposed for the NCS oxidation of PMAA.

The mechanism accounts for the decrease in rate of oxidation with increasing [HClO₄]. Equilibrium (10) shifts to the right with increasing [HClO₄], decreasing the concentration of the

Table 7 Second-order rate constants for the oxidation of X-C₆H₄-S-CH₂COOH by NCS at 35 °C. [Ar-S-CH₂COOH] = 0.02 M. [HClO₄] = 0.001 M. [NCS] = 0.001 M. [I] = 0.02 M

Solvent: 75% acetonitrile–25% water (v/v)		
	X	10 ² k ₂ /M ⁻¹ s ⁻¹
1	H	6.10 ± 0.10
2	<i>p</i> -OMe	65.1 ± 0.77
3	<i>p</i> -Me	18.0 ± 0.23
4	<i>p</i> -Et	18.1 ± 0.28
5	<i>p</i> -Pr ⁱ	18.5 ± 0.25
6	<i>p</i> -F	3.86 ± 0.05
7	<i>p</i> -Cl	1.29 ± 0.03
8	<i>p</i> -Br	1.14 ± 0.03
9	<i>p</i> -NO ₂	0.085 ± 0.01
10	<i>m</i> -Me	9.78 ± 0.18
11	<i>m</i> -OMe	4.27 ± 0.10
12	<i>m</i> -Cl	0.441 ± 0.07



Scheme 2

active species of NCS. In the bromination of anisole by *N*-bromosuccinimide (NBS),²⁹ it has been concluded that NBS is the oxidising species, since the rate decreases with increasing [H⁺].

The influence of substituents on the rate of oxidation has been investigated by employing, several substituted phenyl-mercaptoacetic acids. It is observed that the electron-releasing groups in the phenyl ring favour the reaction (Table 7) and electron-withdrawing substituents retard the rate. A satisfactory linear free-energy relationship is found between log *k*₂ and σ values ($r = 0.986$, $s = 0.14$, $n = 12$) with the reaction constant (ρ) value of -2.73 ± 0.14 at 35 °C. The negative ρ value indicates an electron-deficient transition state and this value is analogous to the one observed for the oxidation of aryl methyl and diaryl sulfides (*vide supra*).

Difference in reactivity of MPS, DPS and PMAA

Since the kinetics of aryl methyl sulfides, diaryl sulfides and arylmercaptoacetic acids have been measured in different solvent mixtures, a complete discussion for the difference in behaviour involving all the substrates is not possible. However, it is observed that the second-order rate constants for the NCS oxidation of MPS and DPS are $15.8 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$ (in 95% acetonitrile–5% water (v/v) and $5.9 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$ (in 90% acetonitrile–10% water (v/v) respectively at 45 °C and at [HClO₄] = 0.001 M and [I] = 0.02 M. The considerable lower reactivity of DPS may be attributed to a possible steric effect offered by the additional phenyl group during the attack of the oxidising species. The observed rate constants for the oxidation of MPS and PMAA at 35 °C and [HClO₄] = 0.001 M and [I] = 0.02 M in 95% acetonitrile–5% water (v/v) are $8.45 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$ and $1.67 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ respectively. The lower rate of PMAA is not unexpected as the carboxyl group is electron-attracting, the availability of electron density on the sulfur atom in this substrate is somewhat reduced compared to MPS.

References

- C. A. Bunton and N. D. Gillitt, *J. Phys. Org. Chem.*, 2002, **15**, 29.
- V. K. Sivasubramanian, M. Ganesan, S. Rajagopal and R. Ramaraj, *J. Org. Chem.*, 2002, **67**, 1506.
- M. Taki, S. Itoh and S. Fukuzumi, *J. Am. Chem. Soc.*, 2002, **124**, 998.
- D. Thenraja, P. Subramaniam and C. Srinivasan, *Tetrahedron*, 2002, **58**, 4283.
- S. Oae, *Organic Sulfur Chemistry: Structure and Mechanism*, CRC Press, Boca Raton, FL, 1991.
- R. Sevel, S. Rajagopal, C. Srinivasan, N. I. Alhaji and A. Chellamani, *J. Org. Chem.*, 2000, **65**, 3334.
- (a) C. Srinivasan, P. Kuthalingam and N. Arumugam, *J. Chem. Soc., Perkin Trans. 2*, 1980, 170; (b) C. Srinivasan, P. Kuthalingam and N. Arumugam, *Int. J. Chem. Kinet.*, 1982, **14**, 1139; (c) C. Srinivasan, P. Kuthalingam and N. Arumugam, *Can. J. Chem.*, 1978, **56**, 3043.
- C. Srinivasan, A. Chellamani and P. Kuthalingam, *J. Org. Chem.*, 1982, **47**, 428.
- C. Srinivasan, A. Chellamani and S. Rajagopal, *J. Org. Chem.*, 1985, **50**, 1201.
- C. Srinivasan, S. Rajagopal and A. Chellamani, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1839.
- C. Srinivasan and P. Subramaniam, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1061.
- R. Harville and S. F. Reed Jr., *J. Org. Chem.*, 1968, **33**, 3976.
- V. Baliah and M. Uma, *Tetrahedron*, 1963, **19**, 455.
- C. Srinivasan and K. Pitchumani, *Indian J. Chem., Sect. A*, 1985, **17**, 162.
- D. D. Perrin, A. L. F. Armargo and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, New York, 1980.
- U. Miotti, G. Modena and L. Seda, *J. Chem. Soc., B*, 1970, 802.
- V. Thiagarajan and N. Venkatasubramanian, *Can. J. Chem.*, 1967, **49**, 694.
- (a) J. Mukherjee and K. K. Banerji, *J. Org. Chem.*, 1981, **46**, 2323; (b) V. Sharma and K. K. Banerji, *J. Chem. Res.*, 1985, (S) 340, (M) 3551).
- F. Ruff and A. Kucsmann, *J. Chem. Soc., Perkin Trans. 2*, 1975, 509.
- P. R. Wells, *Chem. Rev.*, 1963, **63**, 171.
- R. W. Taft, Jr., in *Steric Effects in Organic Chemistry*, ed. M. S. Newman, Wiley, New York, 1956, p. 660.
- L. L. Schaleger and F. A. Long, *Adv. Phys. Org. Chem.*, 1963, **1**, 1.
- J. E. Leffler, *J. Org. Chem.*, 1955, **20**, 1202.
- J. E. Leffler, *J. Chem. Phys.*, 1955, **23**, 2199.
- R. C. Petersen, *J. Org. Chem.*, 1964, **29**, 3133.
- C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, 1964, **2**, 323.
- R. C. Petersen, J. H. Markgraf and S. D. Ross, *J. Am. Chem. Soc.*, 1961, **83**, 3819.
- (a) O. Exner, *Nature*, 1964, **201**, 488; (b), *Coll. Czech. Chem. Commun.*, 1964, **20**, 1004.
- C. Srinivasan and A. Chellamani, *React. Kinet. Catal. Lett.*, 1981, **18**, 187.
- D. G. Peters, J. M. Hayes and G. M. Hieftje, *Chemical Separations and Measurements—Theory and Practice of Analytical Chemistry*, Saunders Golden Series: London, 1974, p. 32.