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STERIC EFFECTS IN THE REACTION OF ALKYL-PHENYL AND DIALKYL-SULPHIDES WITH CHLORAMINE-T

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Abstract—The rate of the reaction of dialkyl- and alkyl-phenyl-sulphides with TsNHCl increases with the increasing +I effect of the S-substituents, while the steric effect is only of minor importance. Rate constants of the reaction of dialkyl sulphides can be correlated with the Taft equation ($\rho^* = -1.96$, $\delta = 0.285$). The effect of ring size of cyclic sulphides on the reaction is discussed. The change of the rate constants with varying S-alkyl substituents is in agreement with a sterically unhindered electrophilic addition of Cl^+ on bivalent sulphur, leading to chlorosulphonium ion. Sulphimides and sulphoxides are formed from the chlorosulphonium intermediates in the subsequent S_N-type reactions with different steric control.

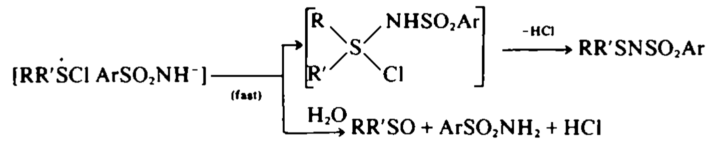
Previous investigations[1] have shown that the mechanism of the Mann-Pope reaction, i.e. the conversion of sulphides to sulphimides and sulphoxides, by treatment with sodium salts of N-chloro-arene sulphonamides (e.g. by chloramine-T, $TsNCl^-Na^+$), can be described by eqns (1–8).

Chlorosulphonium salts are formed as intermediates in the rate-determining addition of Cl^+ on bivalent sulphur, while fast S_N displacements on the three-coordinated sulphonium centre lead to sulphimides and sulphoxides.

In order to clarify the steric requirements of the rate-determining and product-controlling steps for further understanding of the mechanism of the Mann–Pope reaction, the kinetics and the product distribution of the reactions of chloramine-T (TsNClNa) with sulphides (RSR') bearing different alkyl groups were investigated. As far as the reactions of organic sulphur compounds is concerned, it is well known that the steric effect is usually

$$ArSO_2NCl^- + H^+ \underset{K_a}{\overset{(fast)}{\rightleftharpoons}} ArSO_2NHCl \qquad (1)$$

$$RR'S + ArSO_2NHCl \xrightarrow[(slow)]{k_1'} \underset{\text{intermediate}}{[RR'SCl^+ ArSO_2NH^-]} \qquad (2)$$

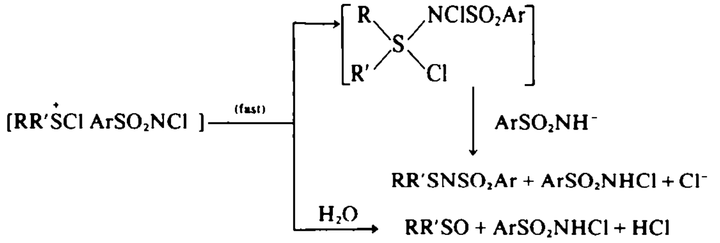


(3)

(4)

$$ArSO_2NHCl + ArSO_2NCl^- \underset{k_{-d}'\,(fast)}{\overset{k_d'\,(slow)}{\rightleftharpoons}} ArSO_2NCl_2 + ArSO_2NH^- \qquad (5)$$

$$RR'S + ArSO_2NCl_2 \xrightarrow[(fast)]{k_2} \underset{\text{intermediate}}{[RR'\overset{+}{S}Cl\ ArSO_2NCl^-]} \qquad (6)$$



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not very significant if there are only slight differences between the geometry of the reactants and that of the transition state.[2-6] On the other hand, S_N2 type reactions on sulphur have the same steric requirements, as in the case of carbon compounds.[6-12]

The kinetic studies and product-analysis were based on the general method published earlier.[1] Measurements were carried out in buffered 1:1 (v/v) water–ethanol solutions at constant pH values. Using these solvents the reactions were successfully conducted with both the reactants and the buffer in a homogeneous phase.

RESULTS AND DISCUSSION

(1) *Kinetic studies*

(a) *Reaction of alkylphenylsulphides with chloramine-T.* The reaction of methyl phenyl sulphide with chloramine-T in buffered 1:1 (v/v) water–ethanol solution was studied extensively earlier by kinetic method and product-analysis.[1] Rate eqn (9) was found to be valid for the reaction in a wide pH and concentration ranges; in eqn (9), $[C] = [TsNCl^-] + [TsNHCl]$, $[S] = [RSR']$. From k_i and k_d values measured experimentally the rate constants k_i' and k_d' independent of pH were calculated by eqns (10) and (11), respectively, where the pre-equilibrium (eqn (1); $pK_a = 5.76$) was taken into account.

$$-\frac{d[C]}{dt} = k_i[S][C] + k_d[C]^2 \qquad (9)$$

$$k_i = \frac{[H^+]}{K_a + [H^+]} \cdot k_i' \qquad (10)$$

$$k_d = \frac{K_a[H^+]}{(K_a + [H^+])^2} \cdot k_d' \qquad (11)$$

The reactivities of other alkyl phenyl sulphides towards chloramine-T were also studied by the same method, and the results are summarized in Table 1. As expected, k_d' relating to the disproportionation of chloramine-T (eqn 5) is independent of sulphide species. On the other hand, k_i' values (see/eqn 2) show a moderate increase with the increasing +I effect and bulkiness of the R substituent, indicating the minor influence of the steric effect. (Nevertheless, the exceptional order S-propyl < S-ethyl in the relative rates may be attributed to the steric factor.) This is in agreement with the rate-determining addition of Cl^+ on bivalent sulphur atom and, at the same time, excludes a rate-determining step involving a typical S_N2 displacement on three-coordinated sulphur atom. In the latter case the reactivity of S-isopropyl and S-tert-butyl derivatives would be 10^2–10^6 times lower than that of S-methyl derivative (see Refs. 7–11).

Applying the Taft equation[13] (eqn 12) for k_i' data, we tried to estimate separately the influence of the inductive and steric affects of R groups on the chlorination of RPhS sulphides by TsNHCl.

$$\log(k/k_0) = \rho^*\sigma^* + \delta E_s. \qquad (12)$$

By using the least-square method $\rho^* = -0.79$ and $\delta = -0.085$ values ($r = 0.775$) were computed. The correlation coefficient being very poor, experimental data seem not to fit eqn (12).

Apparently, the reactivity of the nucleophilic sulphur atom is controlled not only by the inductive and steric effects of the S-alkyl group but by the resonance effect of the S-phenyl group, as well. Unfortunately this third effect cannot be taken into account quantitatively, because the resonance of the phenyl moiety in RSPh is not independent of R group. From the UV spectra of RSPh sulphides, it was concluded[14] earlier that S-phenyl resonance shows a decrease with increasing steric requirements of S-alkyl groups.

(b) *Reaction of dialkyl sulphides with chloramine-T.* Dialkyl sulphides are more effective nucleophiles than alkyl phenyl sulphides. Consequently, relatively high k_i' and k_i values are presumed to imply the rate-determining chlorination; k_i being much higher than k_d, rate eqn (9) can be simplified to eqn (13).

$$-\frac{d[C]}{dt} = k_i[S][C]. \qquad (13)$$

In order to determine the rate constant k_i kinetic measurements must be carried out in strongly alkaline media, where k_i should be of small value (see eqn 10), and hence the rate of reaction can be followed by the usual method.

With dibutyl sulphide chosen as a typical model, the simple second-order kinetics of the chlorination step was established (Table 2). The comparison of 0.525 and $2.5 \times 10^{-4}\,l\,mol^{-1}\,sec^{-1}$ values, found and calculated at pH 10.7

Table 2. Rate constants (k_i) for the reaction of Bu_2S with $TsNCl^-Na^+$ (20°; pH: 10.7; solvent: 1:1 (v/v) water–ethanol, 0.05 M Britton–Robinson buffer)

$[S]_0 \times 10^3$ (mol/l)	$[C]_0 \times 10^3$ (mol/l)	$k_i \times 10^3$ (l/mol. sec)
1.05	3.04	550
1.05	2.12	510
1.01	1.25	522
1.01	1.01	529
1.01	0.82	523
1.05	0.51	514
average value		525

Table 1. Rate constants for the reaction of alkyl phenyl sulphides with chloramine-T (20°; pH: 8.05; solvent: 1:1 (v/v) water–ethanol, 0.05 M KH_2PO_4–K_2HPO_4 buffer)

Sulphide	$k_i \times 10^3$	k_i'		$k_d \times 10^3$	k_d'
	(l/mol. sec)	(l/mol. sec)	relative rates	(l/mol. sec)	(l/mol. sec)
MeSPh	106 ± 2	20.8	1	99 ± 5	19.5
EtSPh	133 ± 6	26.1	1.23	95 ± 4	18.7
PrSPh	93 ± 3	18.3	0.86	102 ± 4	20.3
^{i}PrSPh	193 ± 6	37.9	1.79	102 ± 7	20.3
^{t}BuSPh	260 ± 9	51.0	2.41	98 ± 5	19.3

for k_1 and k_d constants,[†] respectively, indicates that Bu_2S is chlorinated only by TsNHCl and the other possible competing reaction between Bu_2S and $TsNCl_2$, controlled by the slow formation of $TsNCl_2$ intermediate, may be disregarded. As expected, in the region of pH 9–12,[‡] k_1 was found to depend linearly on $[H^+]$. Experimental data fitted equation $\log k_1 = -0.981(pH) + 10.23$, ($r = 0.999$). (As $[H^+] \ll K_a$, $k_1 = [H^+]k_1'/K_a$; see eqn 10.)

The k_1 rate constants found for different symmetrical dialkyl sulphides and alkyl methyl sulphides (Table 3) are in a rather narrow range showing that the reactivity of all these compounds is similar. The pH-independent rate constants k_1' clearly indicate the high reactivity of dialkyl sulphides as compared to that of alkyl aryl sulphides.

The polar and steric effects of S-alkyl groups in the rate-determining chlorination step can be discussed by comparing of relative rates found for sulphides with different alkyl groups (Table 3). These data show that the reactivity of dialkyl sulphides is also not controlled markedly by the bulkiness of the alkyl groups, whereas the reaction rate increases with the increasing +I effect of the alkyl group. Applying the Taft-equation[13] (eqn 12), $\rho^* = -1.96$ and $\delta^* = 0.285$ ($r = 0.983$) were calculated. The negative ρ^* value, similar to $\rho = -4.25$ found earlier[1] for XC_6H_4SMe sulphides, indicates that the nucleophilic sulphur atom of sulphides is positively polarized in the transition state of the chlorination step. The relatively small δ value implies that the addition of Cl^+ on bivalent sulphur atom is not controlled markedly by the steric effect of the alkyl group.

Other experimental data known in the literature are also in agreement with the moderate steric control in addition reactions involving bivalent sulphur atom. For example, alkyl sulphides with large alkyl groups (e.g. $^tBu_2S$) were shown to react more readily with iodine to form complexes than dimethyl sulphide ($K_{tBu}/K_{Me} = 2.24$).[15] We found that equilibrium constants fit the Taft-equation with $\rho^* = -2.14$ and $\delta = -0.30$ ($r = 0.985$). The similarity of small δ values for the rate-controlling chlorination step in the Mann–Pope reaction and for the equilibrium iodo-complex formation from sulphides is obviously due to the same steric requirements and to the minor influence of the steric effect for both reactions (cf. the pyramidal structure of the sulphide-iodine complex[16]).

(c) *Reaction of cyclic sulphides with chloramine-T.* The reactions of $(CH_2)_nS$ ($n = 3$–6) cyclic sulphides with chloramine-T were investigated by the method used for dialkyl sulphides. The kinetic equation (13) was found to be valid showing that cyclic sulphides react in the same way as the open-chain compounds.

The rate constants for cyclic sulphides are within one order of magnitude (Table 4) and the compounds with 5–7

Table 3. Rate constants for the reaction of dialkyl sulphides with chloramine-T (20°; pH: 10.7; solvent: 1 : 1 (v/v) water–ethanol, 0.05 M Britton–Robinson buffer)

Sulphide	$k_1 \times 10^3$ (l/mol. sec)	$k_1' \times 10^{-4}$ (l/mol. sec)	relative rate	$\Sigma\sigma^*$[†]	ΣE_s[†]
Me_2S	310 ± 10	2.70	1	0	0
Et_2S	761 ± 18	6.62	2.46	−0.20	−0.14
Pr_2S	525 ± 15	4.57	1.69	−0.23	−0.72
$^iPr_2S$	834 ± 20	7.26	2.69	−0.38	−0.94
Bu_2S	525 ± 15	4.57	1.69	−0.26	−0.78
$^iBu_2S$	239 ± 9	2.08	0.77	−0.25	−1.86
$^sBu_2S$	429 ± 12	3.73	1.39	−0.42	−2.26
$^tBu_2S$	681 ± 18	5.92	2.20	−0.60	−3.08
EtSMe	499 ± 17	4.34	1.61	−0.10	−0.07
PrSMe	470 ± 22	4.09	1.52	−0.115	−0.36
^{i}PrSMe	501 ± 31	4.36	1.62	−0.19	−0.47
BuSMe	377 ± 17	3.28	1.22	−0.13	−0.39
^{i}BuSMe	276 ± 10	2.40	0.89	−0.125	−0.93
^{s}BuSMe	378 ± 12	3.29	1.22	−0.21	−1.13
^{t}BuSMe	589 ± 25	5.12	1.90	−0.30	−1.54

[†] Lit.[13]

Table 4. Rate constants for the reaction of cyclic sulphides with chloramine-T (20°; pH: 10.7; solvent: 1 : 1 (v/v) water–ethanol, 0.05 M Britton–Robinson buffer)

				Relative rates for the reaction with		
Sulphide	σ^*[†]	$k_1 \times 10^3$ (l/mol. sec)	$k_1' \times 10^{-4}$ (l/mol. sec)	TsNHCl	I_2[‡]	H_2O_2[§]
$(CH_2)_3S$	−0.24	287 ± 11	2.50	0.185	0.442	0.483
$(CH_2)_4S$	−0.26	1550 ± 60	13.5	1	1	1
$(CH_2)_5S$	−0.18	1310 ± 50	11.4	0.844	0.633	0.571
$(CH_2)_6S$	—	918 ± 34	7.99	0.593	—	0.548

[†] Lit.[17]
[‡] Lit.[15]
[§] Lit.[3]

[†] k_d was evaluated from eqn (11) with $k_d' = 20.3$ l/mol. sec and $pK_a = 5.76$.[1]

[‡] Since Bu_2S is much more reactive than MePhS, the pH-dependence of k_1 cannot be investigated in such a wide range as in the case of MePhS.[1]

membered rings proved to be more reactive than their open-chain analogs, indicating that steric factors are less effective in the rate-determining addition of Cl^+ on cyclic sulphides than in the same reaction of acyclic analogs. Obviously, the front-side attack of the chlorinating agent on bivalent sulphur is favoured by the rigidity of the cyclic system. Nevertheless, there is no definite correlation between σ^{*17} and k'_1 values of the compounds listed in Table 4. This means that the reaction is not controlled exclusively by the +I effect of the S-substituent, and the steric factors may not be neglected. Although the maximum reactivity of $(CH_2)_4S$ corresponds to the highly negative σ^* value of the $(CH_2)_4$ group, the reactivity of $(CH_2)_3S$ with 4-membered ring is surprisingly low. However, in the latter case, the addition of Cl^+ on bivalent sulphur is somewhat hindered because the CSC bond angle of about 90° in the transition state seems to be unfavourable since the addition would create more steric strain in the resulting intermediate than the original sulphide, in which the sulphide group is made less nucleophilic due to the internal strain. (On the other hand, in C_4–C_6 cyclic sulphides the CSC bond angles of bigger than 90° are favourable for a strain-less transition state.)

The relative rates of the reaction of cyclic sulphides with TsNHCl are similar to those found for two other addition reactions of the same substrates. Similarly to the chlorination brought about by TsNHCl, the relative rates of the reaction of sulphides with iodine[15] and hydrogen peroxide[3] do not change dramatically with closing the S-substituents into a ring or with changing the ring size (Table 4). All these observations indicate the minor steric requirements of addition reactions involving bivalent sulphur.

(2) *Product-analysis*

Polarographic product-analysis showed that alkyl phenyl sulphides are converted quantitatively to sulphimides and sulphoxides† (see Ref. 1). Product-distribution depends on the bulkiness of the R group in RSPh; with branched-chain R substituent (^{i}Pr, ^{t}Bu) more sulphimide is formed (Table 5). A similar trend was observed for sulphimide formation in the case of dialkyl sulphides, as well. Since the yield of dialkyl sulphoxides cannot be determined by polarographic method, only the yields of sulphimide products are listed in Table 6.

Table 6. Yields of sulphimides in the reaction of dialkyl-sulphides with chloramine-T ($[S]_0 = [C]_0 = 10^{-3}$ mol/l; 20°; solvent: unbuffered 1:1 (v/v) water–ethanol)

Sulphide	Yield of sulphimide (%)
Me_2S	48
EtSMe	52
^{s}BuSMe	66
^{t}BuSMe	75
Et_2S	48
^{i}Pr$_2$S	63
Bu_2S	49
^{t}Bu$_2$S	0
$(CH_2)_3S$	40
$(CH_2)_4S$	34
$(CH_2)_5S$	88
$(CH_2)_6S$	62

No sulphimide is formed from ^{t}Bu$_2$S, although this compound is converted by TsNHCl in a reaction following the usual second order kinetics at a relatively high rate due to the efficient +I effect of tert-butyl groups (cf. the reaction of ^{t}Bu$_2$S with ^{t}BuOCl and amide ions[18]). It seems very likely that ^{t}Bu$_2$SCl$^+$ ion is regularly formed but this intermediate is transformed in a particular way by loss of tert-butyl cation. The split of the same carbonium ion has been observed in other reactions involving tert-butyl sulphonium ions, e.g. in the racemization of tert-butyl phenyl sulphoxide[19] and in the acid-catalyzed hydrolysis of S-tert-butyl sulphimide.[20]

Table 5. Sulphimide-sulphoxide product-distribution for the reactions of alkyl-phenyl-sulphides with chloramine-T ($[S]_0 = [C]_0 = 10^{-3}$ mol/l; 20°; solvent: unbuffered 1:1 (v/v) water–ethanol)

Sulphide	Product-distribution sulphimide mol%	Product-distribution sulphoxide mol%
MeSPh	34	66
EtSPh	30	70
PrSPh	30	70
^{i}PrSPh	60	40
^{t}BuSPh	89	11

Comparing the yield of sulphimides in the reactions of cyclic sulphides and acyclic sulphides having no bulky substituents, we found the following order: 6-membered ring > 7-membered ring > acyclic > 4-membered ring > 5-membered ring (Table 6); obviously the reverse order is valid for the formation of sulphoxides.

Product analysis gives further support for an earlier suggestion[1] that sulphimides and sulphoxides are formed from chlorosulphonium salts in S_N type reactions of different steric requirements.

Since the yield of the sulphoxide decreases with the increasing bulkiness of the R substituents, this compound seems to be produced in an S_N2 type hydrolysis reaction of the chlorosulphonium ions, controlled significantly by steric factor.

A similar order of reactivity (6 < 7 < acyclic < 4 < 5) was observed[6,9] for the S_N2 type reduction of sulphoxides with iodide ions, where the

$\mathrm{Hal}\cdots\cdots\mathrm{S}\cdots\cdots\mathrm{OH}$

transition state is similar to that for the hydrolysis of chlorosulphonium ions leading to sulphoxides.

The formation of sulphimides from chlorosulphonium ions seems to depend much less on steric factors. As discussed earlier (see Ref. 1), this is probably due to the "front-side" addition of the N-nucleophile on the sulphonium centre taking place before the separation of the $[RR'SCl^{+}\,{}^{-}N(Q)SO_2Ar]$ ion-pair. (Sulphimide is then produced by departing of Cl^- from the sulphurane intermediate.) Small steric effect was also observed in other reactions going through a sulphurane intermediate without inversion of the central sulphur atom.[5,6]

All these observations seem to indicate that in reactions

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†Product analyses were carried out with the same initial concentration of the reactants as kinetic measurements. In dilute solutions there are bigger differences in the yield of sulphimides from different sulphides (see Ref. 1).

leading to a relatively great amount of sulphimides the formation of these compounds is not much faster than in other cases, however the sterically hindered hydrolysis of chlorosulphonium cations giving sulphoxides is relatively slow.

EXPERIMENTAL

Materials. Chloramine-T was commercial product of reagent grade. Me_2S, Et_2S, Bu_2S, $^{t}Bu_2S$, $(CH_2)_3S$, $(CH_2)_4S$ sulphides were commercial products, other sulphides were prepared using general methods. Alkyl phenyl sulphides were oxidized to the corresponding sulphoxides by the procedure of Leonard *et al.*[21] Sulphimides were prepared from sulphides with chloramine-T.[22] Compounds were purified by distillation or crystallization; their purity was checked by m.p. or b.p. determination, analysis, spectroscopic methods and GLC.

S,S-*Trimethylene*-N-*p*-*tolylsulphonylsulphimide*

Trimethylene sulphide (0.37 g 0.005 mol) was dissolved in MeOH (10 ml) chloramine-T (1.4 g 0.005 mol) in methanol (10 ml) was added. The reaction mixture was allowed to stand at room temp. for 1 h, then filtered and the solvent evaporated in vacuum. The oily residue was shaken with 50 ml ether. The crystalline sulphimide was filtered and recrystallized from dioxan–ether. Yield: 0.61 g (50%); m.p. 98°; characteristic bands of IR spectrum (in KBr pellet): ν_{SO_2}: 1282, 1141 cm^{-1}, ν_{SNS}: 948, 759 cm^{-1} (Found: C, 49.2; H, 5.5; N, 5.7; S, 26.2. Calc. for $C_{10}H_{13}NO_2S_2$ (243.4): C, 49.4; H, 5.4; N, 5.8; S, 26.4%).

Kinetics. The kinetic measurements were carried out in 1:1 (v/v) water–ethanol solution (see Ref. 1) at constant pH and $20.00 \pm 0.05^{\circ}$. 0.05 M KH_2PO_4–K_2HPO_4 and 0.05 M Britton–Robinson buffer was used in the reaction of alkyl phenyl sulphides and dialkyl sulphides, respectively. As described previously[1] in detail, the samples taken from the reaction mixture were poured into acidic KI solutions and the iodine produced in the reaction of I^- ions with chloramine-T not consumed by sulphide was determined spectrophotometrically at 353 nm.

Product analysis

The concentration of sulphimides and alkyl phenyl sulphoxides in the reaction mixtures was determined by polarographic method published earlier.[1]

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