Mechanism of the Reaction of Sulphides with *N*-Chloroarenesulphonamides

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The kinetics of the reaction of R^1R^2S ($R^1 = R^2$ = alkyl or aryl) and $ArSO_2NCl^-Na^+$ were investigated in buffered water–ethanol solution. Analytical methods have been elaborated to follow the reaction which affords $R^1R^2SNSO_2Ar$ and R^1R^2SO. From the reaction scheme proposed, kinetic equations are deduced and supported experimentally. In fast and slow (k_d') equilibrium reactions, respectively, $ArSO_2NCl^-Na^+$ in water is transformed into $ArSO_2NHCl$ and $ArSO_2NCl_2$ which are reactive electrophiles and which, in their turn, react with R^1R^2S, the first in a slow (k_1') and the second in a relatively fast (k_2) step to form reactive intermediates. The rate constants k_d', k_1', and k_2 have been determined for different reactants and the observed substituent effects are correlated with the formation of an ($R^1R^2SCl^+ArSO_2NQ^-$) ion-pair intermediate (Q = H or Cl). Me_2S is converted by TsNHCl ($k_1' \gg k_d'$), Ph_2S by $TsNCl_2$ ($k_1' \ll k_d'$), and MeSPh by both chlorinating agents ($k_1' \sim k_d'$). For the reactions of MeSPh with $TsNCl_2$ and TsNHCl k_2/k_1' is $3{\cdot}5 \times 10^6$. MeSPh is chlorinated by $TsNCl_2$ 1500 times faster than Ph_2S. For XC_6H_4SMe, electron-donating X groups increase the rate of reaction with both TsNHCl and $TsNCl_2$ (ρ $-4{\cdot}25$ and $-3{\cdot}56$, respectively). For $YC_6H_4SO_2NHCl$, electron-withdrawing Y groups produce an increase in reactivity toward MeSPh (ρ $+1{\cdot}76$). From the ion-pair intermediate $R^1R^2SNSO_2Ar$ and R^1R^2SO are formed, probably *via* a sulphurane intermediate, in fast, competitive S_N reactions under different steric control. The formation of sulphoxides is more hindered by bulky R groups than that of sulphimides. Other product-controlling factors are also discussed.

MANN AND POPE [1] found that sulphides react with salts of *N*-chlorosulphonamides (*e.g.* with chloramine T) to yield sulphimides [equation (1)]. In media containing water, sulphoxides are also produced [equation (2)].

$$R^1R^2S + ArSO_2NCl^-Na^+ \longrightarrow R^1R^2SNSO_2Ar + Na^+Cl^- \qquad (1)$$

$$R^1R^2S + ArSO_2NCl^-Na^+ \xrightarrow{H_2O} R^1R^2SO + ArSO_2NH_2 + Na^+Cl^- \qquad (2)$$

The product distribution is influenced by the water content of the solvent and by the structure of the reactants.[2-6] The reaction proceeds similarly when *N*-chlorocarboxamides are used as reactants.[7-9]

As the ' Mann–Pope reaction ' [equations (1) and (2)] is widely used in preparative work, investigation of the mechanism seemed profitable. The characteristics of the reaction are reflected in several experimental data and can be summarized as follows. (a) The reaction proceeds quantitatively according to equations (1) and (2), and can be followed kinetically by measuring the concentration of the reactants,[2,5,10,11] or that of the products.[2] The products are formed in competing reactions, sulphoxides not being produced by hydrolysis of sulphimides.[4] (b) In the reaction sulphides behave as nucleophiles.[5,11,12] The electrophilic partners can be formed from $ArSO_2NCl^-Na^+$ by equilibrium reactions,[13-15] and their reactivities should follow the order $ArSO_2NCl_2 > ArSO_2NHCl > HOCl > ArSO_2NCl^-$.[16]

Since the concentration of HOCl in the reaction mixture is very low,[14] and reaction does not occur in strongly alkaline medium, HOCl, $ArSO_2NCl^-$ as reactants may be neglected. Several authors have considered $ArSO_2NHCl$ as the effective electrophile.[5,10] Nevertheless, this species cannot be the only electrophile reacting with sulphides. We have found [2] that the rate equation [5] $v = k[MeSPh][TsNCl^-Na^+]$ which can be derived for buffered solutions from $v = k'[MeSPh][TsNHCl]$ is valid only if the initial concentration of the reactants are equal. $ArSO_2NCl_2$ may also take part in converting sulphides. We observed earlier [2] that in buffered 1 : 1 (v/v) water–ethanol $TsNCl_2$ reacts very fast with MeSPh to give a mixture of MePhSO and MePhSNTs. The same product is formed when MeSPh is converted by $TsNCl^-Na^+$ in a measurably slow reaction.

(c) Chloronium ion transfers between *N*-chloro-compounds and sulphides may give $R^1R^2SCl^+$ [5,8,10] and $ArSO_2NH^-$ ions, and fast competing S_N reactions involving chlorosulphonium ion substrates may lead irreversibly to the products. If $R^1R^2SCl^+$ ions react with *N*-nucleophiles, sulphimides are produced, while hydrolysis of the same ions will give sulphoxides.[10]

It is obvious that the Mann–Pope reaction is much more complicated than would appear from equations (1)

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and (2). We have studied the kinetics of the reaction more intensively to clear up the real sequence of simple steps. Kinetic measurements were carried out in homogeneous, buffered 1 : 1 (v/v) water–ethanol solutions at constant pH.

RESULTS AND DISCUSSION

Mechanism.—On the basis of experimental data discussed later we suggest Scheme 1 for the reaction between $\mathrm{R^1R^2S}$ and $\mathrm{ArSO_2NCl^-Na^+}$.

The fast conversion of reactive intermediates formed in steps (4) and (6) may be formulated in more detail as shown in Scheme 2.

$$\mathrm{ArSO_2NHCl} \underset{\text{fast}}{\overset{K_a}{\rightleftharpoons}} \mathrm{ArSO_2NCl^-} + \mathrm{H^+} \tag{3}$$

$$\mathrm{ArSO_2NHCl} + \mathrm{R^1R^2S} \xrightarrow[\text{slow}]{k_1'} \underset{\text{Intermediate}}{\{\mathrm{ArSO_2NH^-R^1R^2SCl^+}\}} \xrightarrow{\text{fast}} \text{Products} \tag{4}$$

$$\mathrm{ArSO_2NHCl} + \mathrm{ArSO_2NCl^-} \underset{k_{-d}',\ \text{fast}}{\overset{k_d',\ \text{slow}}{\rightleftharpoons}} \mathrm{ArSO_2NCl_2} + \mathrm{ArSO_2NH^-} \tag{5}$$

$$\mathrm{ArSO_2NCl_2} + \mathrm{R^1R^2S} \xrightarrow[\text{fast}]{k_2} \underset{\text{Intermediate}}{\{\mathrm{ArSO_2NCl^-R^1R^2SCl^+}\}} \xrightarrow{\text{fast}} \text{Products} \tag{6}$$

$$\mathrm{ArSO_2NH_2} \xrightarrow[\text{fast}]{K_a^{SA}} \mathrm{ArSO_2NH^-} + \mathrm{H^+} \tag{7}$$

SCHEME 1

$$\{\mathrm{R^1R^2SCl^+ArSO_2NH^-}\} \xrightarrow{-\mathrm{Cl^-}} \mathrm{R^1R^2}\overset{+}{\mathrm{S}}\mathrm{NHSO_2Ar} \xrightarrow{-\mathrm{H^+}} \mathrm{R^1R^2SNSO_2Ar} \tag{8}$$

$$\Updownarrow$$

$$\mathrm{R^1R^2SCl^+} + \mathrm{ArSO_2NH^-} \xrightarrow{\mathrm{H_2O}} \mathrm{R^1R^2SO} + \mathrm{ArSO_2NH_2} + \mathrm{HCl} \tag{9}$$

$$\{\mathrm{R^1R^2SCl^+ArSO_2NCl^-}\} \xrightarrow{-\mathrm{Cl^-}} \mathrm{R^1R^2}\overset{+}{\mathrm{S}}\mathrm{NClSO_2Ar} \tag{10}$$

$$\Updownarrow$$

$$\mathrm{R^1R^2SCl^+} + \mathrm{ArSO_2NCl^-} \xrightarrow{\mathrm{H_2O}} \mathrm{R^1R^2SO} + \mathrm{ArSO_2NHCl} + \mathrm{HCl} \tag{11}$$

$$\mathrm{R^1R^2}\overset{+}{\mathrm{S}}\mathrm{NClSO_2Ar} \xrightarrow[-\mathrm{H^+}]{\mathrm{H_2O}} \mathrm{R^1R^2SNSO_2Ar} + \mathrm{HOCl} \tag{12}$$

$$\mathrm{ArSO_2NH_2} + \mathrm{HOCl} \rightleftharpoons \mathrm{ArSO_2NHCl} + \mathrm{H_2O} \tag{13}$$

SCHEME 2

In order to gain support for this mechanism, the kinetics of the reaction of MePhS with $\mathrm{TsNCl^-Na^+}$ were investigated extensively. Scheme 1 was established by determining the rate constants k_1', k_d', and k_2. This scheme proved to be valid for the reactions of other sulphides, $\mathrm{R^1R^2S}$, RArS, and $\mathrm{Ar_2S}$, and $\mathrm{ArSO_2NCl^-Na^+}$ salts. Also, Scheme 2 proved to be in agreement both with the substituent effects observed and with the data obtained from product analysis.

Kinetic Equations.[*]—Starting from Scheme 1, equations (14) and (15) may be written for the change in the concentration of $\mathrm{ArSO_2NCl^-Na^+}$ and for that of the reactive intermediate $\mathrm{ArSO_2NCl_2}$. Taking into account equilibria (3) and (7) as well as the relations $[\mathrm{C}] = [\mathrm{ArSO_2NHCl}] + [\mathrm{ArSO_2NCl^-}]$ and $[\mathrm{SA}] = [\mathrm{ArSO_2NH_2}] + [\mathrm{ArSO_2NH^-}]$, equations (16) and (17) are obtained, where the rate constants k_1, k_d, and k_{-d} are dependent on pH. The correlations with the rate constants k_1', k_d', and k_{-d}' which are independent of pH are given in equations (18)—(20)

$$-\mathrm{d}[\mathrm{C}]/\mathrm{d}t = k_1'[\mathrm{ArSO_2NHCl}][\mathrm{S}] + 2k_d'[\mathrm{ArSO_2NHCl}][\mathrm{ArSO_2NCl^-}] - 2k_{-d}'[\mathrm{D}][\mathrm{ArSO_2NH^-}] - k_2[\mathrm{D}][\mathrm{S}] \tag{14}$$

$$\mathrm{d}[\mathrm{D}]/\mathrm{d}t = k_d'[\mathrm{ArSO_2NHCl}][\mathrm{ArSO_2NCl^-}] - k_{-d}'[\mathrm{D}][\mathrm{ArSO_2NH^-}] - k_2[\mathrm{D}][\mathrm{S}] \tag{15}$$

From earlier observations [2,15] it follows that $\mathrm{ArSO_2NCl_2}$ is formed in a slow reaction but it is converted very fast ($k_d' \ll k_{-d}'$ or k_2). Thus, the concentration of $\mathrm{ArSO_2NCl_2}$ in the reaction mixture is always low, *i.e.* $[\mathrm{C}] \gg [\mathrm{D}]$. Consequently, in the course of the reaction the amount of active chlorine measured in the reaction

$$-\mathrm{d}[\mathrm{C}]/\mathrm{d}t = k_1[\mathrm{C}][\mathrm{S}] + 2k_d[\mathrm{C}]^2 - 2k_{-d}[\mathrm{D}][\mathrm{SA}] - k_2[\mathrm{D}][\mathrm{S}] \tag{16}$$

$$\mathrm{d}[\mathrm{D}]/\mathrm{d}t = k_d[\mathrm{C}]^2 - k_{-d}[\mathrm{D}][\mathrm{SA}] - k_2[\mathrm{D}][\mathrm{S}] \tag{17}$$

$$k_1 = \frac{[\mathrm{H^+}]}{[\mathrm{H^+}] + K_a}\, k_1' \tag{18}$$

$$k_d = \frac{K_a[\mathrm{H^+}]}{(K_a + [\mathrm{H^+}])^2}\, k_d' \tag{19}$$

$$k_{-d} = \frac{K_a^{SA}}{K_a^{SA} + [\mathrm{H^+}]}\, k_{-d}' \tag{20}$$

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[*] Hereinafter [C] and [SA] represent stoicheiometric concentrations of $\mathrm{ArSO_2NCl^-Na^+}$ and $\mathrm{ArSO_2NH_2}$; [D], [S], [SI], and [SO] represent concentrations of $\mathrm{ArSO_2NCl_2}$, $\mathrm{R^1R^2S}$, $\mathrm{R^1R^2SNSO_2Ar}$, and $\mathrm{R^1R^2SO}$, respectively.

mixture should correspond (within the limits of experimental errors) to that of unchanged $ArSO_2NCl^-Na^+$. Applying the steady-state approximation to the reactive intermediate $ArSO_2NCl_2$ ($d[D]/dt = 0$), equation (21) is obtained and can be used to follow the kinetics of the Mann–Pope reaction in a buffered solution.

$$-d[C]/dt = k_1[C][S] + \frac{k_d[C]^2k_2[S]}{k_{-d}[SA] + k_2[S]} \quad (21)$$

Determination of rate constants k$_1$ *and* k$_d$. Since a very high value must be attributed to k_2, the inequality $k_{-d}[SA] \ll k_2[S]$ is undoubtedly valid in the initial stage of the Mann–Pope reaction, when the concentration of $ArSO_2NH_2$ formed is relatively low. Thus equation (21) reduces to the rate equation (22). This is divided by $[C]^2$ to give the linear equation (23) which may be used for the estimation of k_1 and k_d by a graphical method ($v = -d[C]/dt$).

$$-d[C]/dt = k_1[C][S] + k_d[C]^2 \quad (22)$$

$$v/[C]^2 = k_1[S]/[C] + k_d \quad (23)$$

Using the rate data evaluated from [C] against t plots by graphical differentiation, $v/[C]^2$ values are plotted against [S] : [C] ratios. If the reaction follows equation (22), a straight line will be obtained. The slope and the intercept correspond to the approximate values of k_1 and k_d, respectively. From these data the refined values fitting best to the experimental [C] against t plots may be computed by iteration (least-squares method) on the basis of the definite integral of equation (22).

Determination of rate constant k$_2$. $ArSO_2NCl_2$ and R^1R^2S undergo a fast reaction as shown in equation (6). An indirect determination of k_2 independent of pH is based on equation (21). It is assumed that in alkaline solution containing $ArSO_2NH_2$ in great excess ($[SA] \gg [S]$) $ArSO_2NH^-$ competes significantly with R^1R^2S in consuming $ArSO_2NCl_2$ [equations (5) and (6)]. Since $ArSO_2NHCl$ and $ArSO_2NCl^-$ are regenerated in the former reaction, the rate of the Mann–Pope reaction will decrease.

By transforming equation (21), the linear equation (24) which can be used for estimating k_2 by a graphical method is obtained. Using the known k_1 and k_d values as well

$$k_d[C]^2/(v - k_1[C][S]) = k_{-d}[SA]/k_2[S] + 1 \quad (24)$$

as the rate data (v) evaluated from [C] against t plots by graphical differentiation the left hand term of equation (24) is plotted against [SA] : [S] ratios.* If the reaction follows equation (21), a straight line will be obtained. The slope gives the ratio $k_{-d} : k_2$ from which the approximate value of k_2 can be simply calculated from the k_{-d} value determined for buffered water–ethanol solutions by a known method.[15] Knowing the approximate values of k_2, in addition to k_1, k_d, and k_{-d}, k_2 values best fitting the experimental [C] against t plots can be computed by iteration (least-squares method) on the basis of the integrated form of equation (21).

Determination of Rate Constants k$_1$ *and* k$_d$ *for the Reaction of* $TsNCl^-Na^+$ *with* MeSPh.—The reaction was conducted at pH 8·05 and followed to 70% conversion, with starting concentrations $[S]_0 = 6{\cdot}38 \times 10^{-4}$—$5{\cdot}00 \times 10^{-3}$ and $[C]_0 = 5{\cdot}14 \times 10^{-4}$—$1{\cdot}5 \times 10^{-3}$M. A typical [C] against t plot for a single run is given in Figure 1. By using a series of such plots as well as equation (23), the diagram shown in Figure 2 was constructed so as to estimate k_1 and k_d. As indicated by the straight line in Figure 2, the reaction followed equations (22) and (23) and the approximate values k_1 0·108 l mol^{-1} s^{-1} and k_d 0·092 l mol^{-1} s^{-1} could be estimated.†

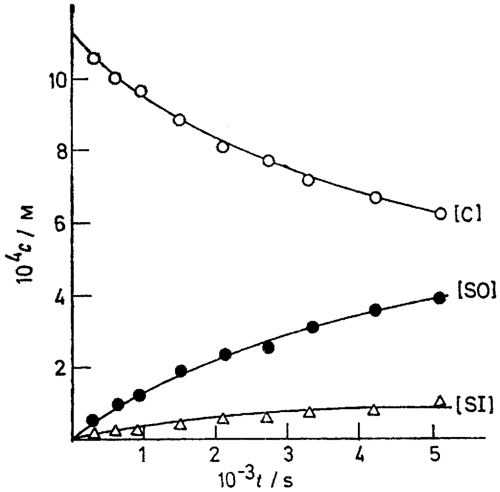

FIGURE 1 [C], [SI], and [SO] against t plots for the reaction of $TsNCl^-Na^+$ with MeSPh {$[S]_0 = 6{\cdot}38 \times 10^{-4}$M, $[C]_0 = 1{\cdot}11 \times 10^{-3}$M; 20°; solvent 1 : 1 (v/v) water–ethanol; pH 8·05}

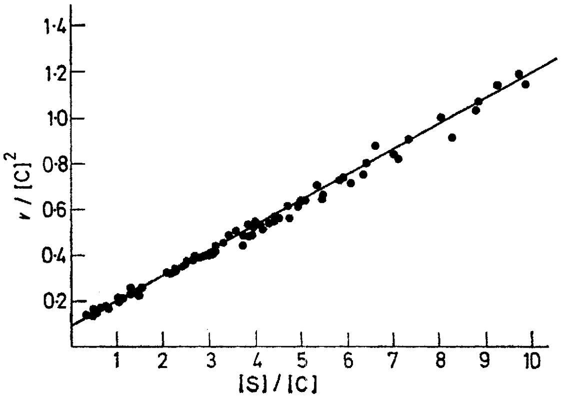

FIGURE 2 Determination of rate constants k_1 and k_d by graphical method for the reaction of $TsNCl^-Na^+$ with MeSPh [20°; solvent 1 : 1 (v/v) water–ethanol; pH 8·05]

Since the measured rate data do not show any significant deviation from the straight line even in the final

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* Here $[SA] = [SA]_0 + [SA]_t$; $[SA]_t$ represents the concentration of $ArSO_2NH_2$ formed in the course of the reaction. This is equivalent to [SO], *i.e.* to the concentration of R^1R^2SO which can be measured polarographically.

† In a buffered solution of pH 8·05, $k_1 + k_d = 0{\cdot}200$ l mol^{-1} s^{-1}. The sum of the rate constants, $k_1 + k_d = k$ was also measured with equal starting concentrations of the reactants. Applying the rate equation $v = k[C]^2$ [*cf.* equation (22)] $k = 0{\cdot}203 \pm 0{\cdot}006$ l mol^{-1} s^{-1} was obtained. Starting concentrations $[S]_0 = [C]_0$ were chosen within the range of $5{\cdot}2$—$51{\cdot}3 \times 10^{-4}$M.

phase of the reaction, equation (22) seems to work well up to 70% conversion. Thus the inequality, $k_{-d}[SA] \leqslant k_2[S]$, assumed for the initial phase must be correct even if concentrations [S] and [SA] have become comparable. This means that $k_{-d} \leqslant k_2$ is also valid at pH 8·05.

Under these circumstances the integrated form of equation (22) can be employed to refine the numerical values of k_1 and k_d. The average values $k_1 = 0{\cdot}1064 \pm 0{\cdot}0017$ l mol^{-1} s^{-1} and $k_d = 0{\cdot}0987 \pm 0{\cdot}0041$ l mol^{-1} s^{-1} obtained by use of computer techniques are in a good agreement with those determined by graphical methods.

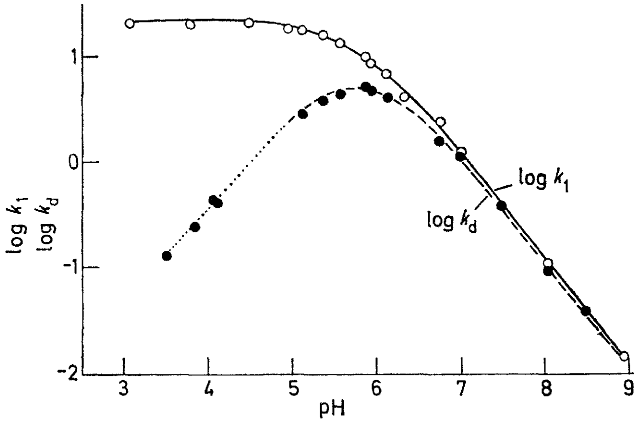

FIGURE 3 pH dependence of rate constants k_1 (——) and k_d (— — —) in the reaction of TsNCl$^-$Na$^+$ with MeSPh [20°; solvent 1 : 1 (v/v) water–ethanol; (· · · ·) in the k_d against pH plot as measured by investigating the disproportionation of chloramine T by the method of Higuchi *et al.*[15]]

The k_1 and k_d data indicate that two parallel simple steps must be considered as rate determining in the Mann–Pope reaction. The consumption of chloramine T is due partly to the direct conversion of sulphide, partly to the formation of dichloramine T intermediate. In a fast reaction dichloramine T reacts almost exclusively with sulphide and this reaction is not disturbed by $TsNH_2$ whose concentration is increasing in the course of the reaction. Since at pH 8·05 the numerical values of k_1 and k_d are nearly identical, TsNHCl and $TsNCl_2$ take an equal part in the conversion of MeSPh.

pH *Dependence of rate constants* k_1 *and* k_d. Equation (22) proved to be valid not only for reactions conducted at pH 8·05 but for those carried out at various pH values in the region 3—9. In sixteen different runs k_1 and k_d values were determined and plotted against pH (Figure 3). The curves for k_1 and k_d are consistent with equations (18) and (19), respectively, k_1 values following the dissociation curve of TsNHCl and nearing a limit in the acidic region (pH < 4·5), and k_d values showing a maximum at a pH which corresponds to the pK_a value of TsNHCl (5·76).*

The rapid consumption of chloramine T is favourable for the preparation of sulphimides or sulphoxides by the Mann–Pope reaction. Since both k_1 and k_d control the reaction, a maximum rate can be attained when the reaction is conducted in a weakly acidic solvent where $k_1 + k_d$ has a maximum value. This is in accordance with earlier preparative observations. The dependence of rate constants on pH indicates that TsNHCl and $TsNCl_2$ only participate equally in converting MeSPh if pH > pK_a. In strongly acidic solvents TsNHCl reacts with the sulphide substrate practically alone.

Calculation of Rate Constants k_1' *and* k_d' *for the Reaction of* TsNHCl *with* MeSPh *and* TsNCl$^-$, *respectively*.—Using equations (18) and (19) as well as the k_1 and k_d values recorded in Figure 3, rate constants k_1' and k_d' independent of pH were calculated for reactions (4) and (5), respectively, conducted in buffered 1 : 1 (v/v) water–ethanol at 20°. The average values k_1' 21·7 ± 1·0 l mol^{-1} s^{-1} and k_d' 20·3 ± 0·9 l mol^{-1} s^{-1} † were obtained indicating that the reactivity of TsNHCl toward the nucleophiles MeSPh and TsNCl$^-$ is nearly the same.

Activation parameters. The dependence of rate constants k_1 and k_d on temperature (10—40°) was measured in buffered solutions at pH 8·05. The experimental data fit the Arrhenius equation. Rate constants k_1' and k_d' independent of pH were calculated in the usual way. At 40° k_1' and k_d' were found to be considerably different (68·8 and 92·8 l mol^{-1} s^{-1}, respectively).‡ At higher temperatures the reaction of TsNHCl with TsNCl$^-$ (disproportionation) is more effective than that with MeSPh. A $\Delta H^‡$ value of 9·8 kcal mol^{-1} and $\Delta S^‡$ −18·9 cal mol^{-1} K^{-1} (20°) were found for the reaction of TsNHCl with MeSPh [equation (4) with rate constant k_1'], while $\Delta H^‡$ 13·3 kcal mol^{-1} and $\Delta S^‡$ −7·2 cal mol^{-1} K^{-1} (20°) were found for the reaction of TsNHCl with TsNCl$^-$ [equation (5) with rate constant k_d']. Although $\Delta H^‡$ for reaction (5) is relatively high, disproportionation is preferred at 40°, owing to the favourable entropy term.

Determination of Rate Constant k_2 *for the Reaction of* $TsNCl_2$ *with* MeSPh.—Applying the indirect method to measure k_2, the reaction of TsNCl$^-$Na$^+$ and MeSPh was conducted in a weakly alkaline medium containing a large excess of $TsNH_2$ (Table 1; $[SA]_0/[S]_0$ = 50—150). Since k_{-d} relating to the retardation of the Mann–Pope reaction depends upon pH [equation (20)], the similarity of $k_{-d}[SA]$ with the term $k_2[S]$ independent of pH was ensured by choosing an appropriately alkaline solvent. Using graphical method a typical diagram shown in Figure 4 was constructed from data obtained at pH 8·95.

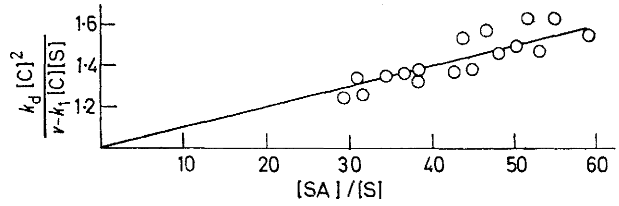

FIGURE 4 Determination of rate constant k_2 by graphical method for the reaction of $TsNCl_2$ with MeSPh [20°; solvent 1 : 1 (v/v) water–ethanol; pH 8·95]

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* K_a for TsNHCl was measured in 1 : 1 (v/v) water–ethanol at 20° by the method of Morris *et al.*[13]

† The same value (k_d' 20·9 l mol^{-1} s^{-1}) was found when the equilibrium disproportionation of chloramine T was investigated by the method of Higuchi *et al.*[15] in buffered 1 : 1 (v/v) water–ethanol at 20°.

‡ The pK_a value for TsNHCl is 5·62 at 40°.

The points in Figure 4 are seen to be almost linear * indicating that equation (24) works well. Starting from the approximate values of k_2 (Table 1), the k_2 values best fitting the experimental [C] against t plots were computed by iteration. The data obtained by graphical methods and by computer techniques are in good agreement and are independent of pH (Table 1).

TABLE 1

Rate constants k_2 calculated by graphical methods and iteration for the reaction of $TsNCl_2$ with MeSPh

$[SA]_o = 5{\cdot}0 \times 10^{-2}$M; 20°; solvent 1 : 1 (v/v) water–ethanol, 0·05M-KH_2PO_4–K_2HPO_4 buffer

pH	$10^3[C]_o$/ M	$10^3[S]_o$/ M	$10^{-5}k_{-d}$/ l mol^{-1} s^{-1} [a]	$10^{-7}k_2$/ l mol^{-1} s^{-1} [b]	$10^{-7}k_2$/ l mol^{-1} s^{-1} [c]
8·95	2·06	1·45	7·93	7·9	7·38
	2·07	1·73			6·76
	2·06	1·19			8·23
	1·09	1·09			8·01
8·50	1·04	0·86	2·82	7·1	9·87
	1·04	0·86			5·44
	1·03	0·57			9·00
	0·57	0·57			6·92
	1·05	0·51			5·15
8·05	0·60	0·28	1·03	7·2	6·57
	0·61	0·61			8·86
	1·08	0·66			7·18
Average				7·4	7·5 ± 1·7

[a] Calculated by equation (20). $k_{-d}' = 2 \times 10^8$ l mol^{-1} s^{-1} was determined by the method of Higuchi *et al.*[15] The dissociation constant for $TsNH_2$ was measured by the u.v. spectrophotometric method at 246 nm; $pK_a^{SA} = 11{\cdot}35$. [b] Determined by graphical method. [c] Calculated by iteration.

Although the very high value of k_2 does not exceed that of k_{-d}' (Table 1), the inequality $k_2 \gg k_{-d}$ is valid for the whole pH range investigated (3—9). This explains why in the Mann–Pope reaction $TsNCl_2$ is only consumed by MeSPh, and $TsNH^-$ being in low concentration cannot compete with MeSPh. On the other hand, the inequality $k_2 \gg k_1'$ is also valid. The $k_2 : k_1'$ ratio of $3{\cdot}5 \times 10^6$ shows that $TsNCl_2$ is more reactive toward MeSPh than TsNHCl by six orders of magnitude.

The reaction of $TsNCl^-$ with MeSPh cannot be detected even in strongly alkaline solutions, although the numerical values of k_1 and k_d are rather low in this case. Thus, the order of reactivity for *N*-chloro-derivatives of $TsNH_2$ toward MeSPh corresponds to that of chlorinating activity and can be written as follows: $TsNCl_2 \gg TsNHCl \gg TsNCl^-$.

Substituent Effects.—While varying the groups Ar, R^1, and R^2, the reaction of $ArSO_2NCl^-Na^+$ with R^1R^2S was investigated similarly to that of $TsNCl^-Na^+$ with MeSPh. The kinetic equations (21)—(24) were found to be applicable for all cases and, when feasible, rate constants k_1', k_d', and k_2 were determined for the reactions (4)—(6). On the basis of the quantitative data obtained the structural factors controlling these reactions may be discussed.

Reaction of $TsNCl^-Na^+$ *with* XC_6H_4SMe. Reactions were carried out with sulphides containing an electron-donating or -withdrawing group. Solvents of different pH were employed to ensure suitable reaction rates and $k_1 : k_d$ and $k_{-d} : k_2$ ratios for the determination of rate constants.

The measured k_1 and k_d data, together with the calculated k_1' and k_d' rate constants, are listed in Table 2.

TABLE 2

Rate constants for the reaction of $TsNCl^-Na^+$ with XC_6H_4SMe

20°; solvent 1 : 1 (v/v) water–ethanol, 0·05M-KH_2PO_4–K_2HPO_4 buffer

X	σ	k_1 [a]/l mol^{-1} s^{-1}	k_d [a]/l mol^{-1} s^{-1}	k_1'/l mol^{-1} s^{-1}	k_d'/l mol^{-1} s^{-1}
p-MeO	−0·268	2·12	0·1	416	19·9
p-Me	−0·170	0·525	0·103	103	20·4
m-Me	−0·069	0·219	0·100	43·0	19·9
H	0			21·7 [b]	20·3 [b]
m-MeO	+0·115	0·050	0·093	9·79	18·4
p-Cl	+0·227	0·013	0·098	2·54	19·3
m-Cl	+0·373	0·587 [c]	0·065 [c]	0·589	22·1

[a] Rate constants k_1 and k_d were determined in a solution of pH 8·05. [b] See text. [c] Since $k_1 \ll k_d$ at pH 8·05, the rate constants were measured in a solution of pH 3·23 (in 0·05M-Britton–Robinson buffer).

k_d', which relates to the disproportionation of chloramine T, is obviously not affected by a change in the sulphide used. Applying the Hammett equation with the usual σ constants (Table 2) and the k_1' data, ρ_1^X −4·25 (r 0·965) † was calculated for the reaction of TsNHCl with XC_6H_4SMe substrates [equation (4)]. The markedly negative ρ_1^X value shows that electron-donating groups cause a considerable increase in the reactivity of XC_6H_4SMe toward TsNHCl. This is consistent with a significant positive polarity of the sulphur atom in the transition state and with the formation of a chlorosulphonium ion intermediate.‡

TABLE 3

Rate constants k_2 for the reaction of $TsNCl_2$ with XC_6H_4SMe

$[SA]_o = 5 \times 10^{-2}$M; 20°; solvent 1 : 1 (v/v) water–ethanol, 0·05M-KH_2PO_4–K_2HPO_4 buffer

X	σ	pH [a]	k_{-d} [b]/ l mol^{-1} s^{-1}	k_2/ l mol^{-1} s^{-1}
H	0	8·95	$7{\cdot}93 \times 10^5$	$7{\cdot}5 \times 10^7$
m-MeO	+0·115	8·69	$4{\cdot}30 \times 10^5$	$2{\cdot}5 \times 10^7$
p-Cl	+0·227	8·05	$1{\cdot}03 \times 10^5$	$1{\cdot}5 \times 10^7$
m-Cl	+0·373	8·05	$1{\cdot}03 \times 10^5$	$4{\cdot}0 \times 10^6$
m-NO_2	+0·710	6·60 [c]	$3{\cdot}42 \times 10^3$	$3{\cdot}1 \times 10^5$
p-NO_2	+0·778	6·29 [c]	$1{\cdot}75 \times 10^3$	$8{\cdot}4 \times 10^4$

[a] Rate constant k_2 was measured in a solution with the given pH. [b] Calculated by equation (20) with $k_{-d}' = 2 \times 10^8$ l mol^{-1} s^{-1}. [c] The measurement was carried out in 0·05M-Britton–Robinson buffer.

The k_2 values obtained experimentally are given in Table 3, where the pH values of solvents used, together with rate constants k_{-d} found for the given media, are also shown. k_2 Data indicate that electron-withdrawing

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* The relatively high deviations can be attributed to the application of an indirect measuring method and to the inaccuracy in graphical differentiation.

† For σ^+ constants, $r = 0{\cdot}756$.

‡ A similar ρ value (−3·2) has been found [17] for the oxidation of XC_6H_4SMe with bromine proceeding *via* an $(XC_6H_4)MeSBr^+$ intermediate.

[17] U. Miotti, G. Modena, and L. Sedea, *J. Chem. Soc.* (*B*), 1970, 802.

groups markedly decrease the reactivity of XC_6H_4SMe toward $TsNCl_2$ [*cf.* equation (6)]. This is also reflected in the reaction constant ρ_2^{X} $-3{\cdot}56$ (r 0·995). Since ρ_2^{X} does not essentially deviate from ρ_1^{X} it may be assumed that both $TsNCl_2$ and TsNHCl convert XC_6H_4SMe primarily to a chlorosulphonium ion.

The numerical values of k_1 and k_d show that in weakly alkaline solutions XC_6H_4SMe with an electron-donating group are predominantly converted by TsNHCl ($k_1 > k_d$), while those having an electron-withdrawing group are chlorinated mostly by $TsNCl_2$ ($k_d > k_1$).

Reaction of $YC_6H_4SO_2NCl^-Na^+$ *with* MeSPh. Reactions were carried out with $YC_6H_4SO_2NCl^-Na^+$ salts having electron-donating or -withdrawing group. The measured k_1 and k_d data, as well as the calculated k_1' and k_d' rate constants are listed in Table 4. For calculations, the pK_a values of $ArSO_2NHCl$ were measured by the method of Morris *et al.*[13] as recorded in Table 4. Applying the Hammett equation with the usual σ constants (Table 4) and the k_1' data, ρ_1^{Y} $+1{\cdot}76$ (r 0·998) was calculated for the reaction of $YC_6H_4SO_2NHCl$ with MeSPh [*cf.* equation (4)]. From the positive ρ_1^{Y} constant it follows that electron-withdrawing groups enhance the reaction. This is consistent with considerable negative polarity of the nitrogen atom of Cl^+ donating *N*-chlorosulphonamide in the transition state and with the formation of a $YC_6H_4SO_2NH^-$ ion. A similar substituent effect has been observed in the equilibrium dissociation of $YC_6H_4SO_2NHCl$ and $YC_6H_4SO_2NH_2$ to produce hydrogen ions (*cf.* Table 4 and ref. 18 respectively). For these acids, ρ $+1{\cdot}68$ (r 0·988) and $+1{\cdot}41$ [18] can be calculated from K_a and σ values. Apparently, in all three cases the substituent effect of the Y group is transmitted to the reaction centre by the SO_2 group.

TABLE 4

Rate constants for the reaction of $YC_6H_4SO_2NCl^-Na^+$ with MeSPh

20°; solvent 1 : 1 (v/v) water–ethanol, 0·05M-KH_2PO_4–K_2HPO_4 buffer

Y	σ	k_1 [a]/ l mol^{-1} s^{-1}	k_d [a]/ l mol^{-1} s^{-1}	$YC_6H_4SO_2NHCl$ pK_a	k_1'/ l mol^{-1} s^{-1}	k_d'/ l mol^{-1} s^{-1}
p-MeO	−0·268	0·099	0·134	5·93	13·1	17·9
p-Me	−0·170	0·106	0·099	5·76	20·8	19·5
H	0	0·112	0·058	5·50	39·8	20·6
p-Cl	+0·227	0·109	0·023	5·11	95·0	20·0
p-NO_2	+0·778	0·130	0·010 [b]	4·18	965	74·2 [b]

[a] Determined in a solution of pH 8·05. [b] Since $k_1 > k_d$, the experimental error is large.

The numerical values of k_1 and k_d indicate that in weakly alkaline solutions MeSPh is converted predominantly by $YC_6H_4SO_2NHCl$ when Y is an electron-withdrawing group ($k_1 > k_d$). On the other hand, under similar conditions the extent of participation of TsNHCl and $TsNCl_2$ (Y = Me) in converting MeSPh has been found to be about the same ($k_1 \sim k_d$).

In disproportionation reaction of type (5), Y exerts opposite effects on the electrophilic–nucleophilic pair of reactants $YC_6H_4SO_2NHCl$ and $YC_6H_4SO_2NCl^-$. For example, an electron-withdrawing group enhances the reactivity of $YC_6H_4SO_2NHCl$ and, at the same time, decreases that of $YC_6H_4SO_2NCl^-$. Thus the rate constant k_d' does not change significantly when Y in $YC_6H_4SO_2NCl^-Na^+$ is replaced by another substituent (Table 4).

Reaction of $TsNCl^-Na^+$ *with* RSPh. Alkyl phenyl sulphides react with chloramine T in the same way as methyl phenyl sulphide. The rate constants k_1' 21·7, 38·8, and 51·1 l mol^{-1} s^{-1} were measured for the reactions of MeSPh, Pr^{i}SPh, and Bu^{t}SPh, respectively. From these preliminary results (*cf.* ref. 19) it may be concluded that the reactivity of a sulphide toward TsNHCl [*cf.* equation (4)] is somewhat increased by the $+I$ effect of the alkyl group. On the other hand, electrophilic Cl^+ addition to the sulphur atom of the sulphide seems not to be hindered markedly by a large alkyl group.

Reaction of $TsNCl^-Na^+$ *with* RSMe. It is well known that dialkyl sulphides react readily with chloramine T. This has been supported by the preliminary results of kinetic measurements (*cf.* ref. 19). The equation $v = k_1[S][C]$ was found to be valid [*cf.* equation (22); $k_1 \gg k_d$], and k_1' 27,000, 43,800, and 51,150 l mol^{-1} s^{-1} were determined for reactions involving Me_2S, Pr^{i}SMe, and Bu^{t}SMe, respectively. The inequality $k_1' \gg k_d'$ indicates that TsNHCl reacts much more readily with alkyl methyl sulphides than with its conjugate base [*cf.* equations (4) and (5)]; in fact alkyl methyl sulphides are converted only by TsNHCl. The inductive and steric effects of the alkyl groups on the reactivity of alkyl methyl sulphides are similar to those observed in the case of alkyl phenyl sulphides.

Reaction of $TsNCl^-Na^+$ *with* Ph_2S. Since diphenyl sulphide is a poor nucleophile compared with alkyl phenyl and dialkyl sulphides, it seems likely that TsNHCl formed in the solution of chloramine T reacts much more readily with its conjugate base than with Ph_2S, *i.e.* $k_d' \gg k_1'$ [*cf.* equations (5) and (4), respectively). This involves the inequality $k_d \gg k_1$ for the usual pH range (3—9) of kinetic measurements. If in this case $k_{-d}[SA] \ll k_2[S]$ is also valid, the reaction of chloramine T with Ph_2S will follow the simple rate equation $v = k_d[C]^2$ [*cf.* equation (22)]. As expected, this equation proved to be valid in the pH range 3·8—6·8; k_d values go through a maximum with changing pH. From the measured k_d data the usual k_d' value (20·8 ± 0·6 l mol^{-1} s^{-1}) was obtained. From the inequality $k_d \gg k_1$ it follows that Ph_2S is converted only by $TsNCl_2$. Obviously, these

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[18] G. Dauphin, A. Kergomard, and M. Veschambre, *Bull. Soc. chim. France*, 1967, 3395.

[19] F. Ruff, K. Komoto, N. Furukawa, and S. Oae, unpublished results.

considerations may be applied to the derivatives of Ph_2S with electron-withdrawing substituents.

The simple rate equation $v = k_d[C]^2$ does not work for pH > 7, since $TsNCl_2$ reacts not only with Ph_2S but with $TsNH_2$ formed in the reaction. Starting from this observation, the rate constant k_2 relating to the reaction of Ph_2S with $TsNCl_2$ [*cf.* equation (6)] was measured. Eight runs were carried out in solvents of pH 6—6·5 containing a large excess of $TsNH_2$ ($[SA]_0/[S]_0 = 50$) and $k_2 = (4{\cdot}79 \pm 0{\cdot}52) \times 10^4\,\mathrm{l\,mol^{-1}\,s^{-1}}$ was obtained. This means that the reactivity of Ph_2S toward $TsNCl_2$ is 1570 times smaller than that of MeSPh, in accordance with the order of nucleophilicity of the sulphides.

TABLE 5

Sulphimide–sulphoxide product distribution for the reaction of $TsNCl^-Na^+$ with MeSPh. Dependence of product distribution on chlorinating agents, $[S]_0 : [C]_0$ ratio, reaction temperature, and pH of solvent

solvent: 1 : 1 (v/v) water–ethanol; 0·05M-Britton–Robinson buffer

						[SI]/[SO] Product distribution	
	pH	T/°C	$10^3[S]_0$/M	$10^3[C]_0$/M	$\frac{k_1[S][C]}{k_d[C]^2}$	Sulphimide (mol %)	Sulphoxide (mol %)
1	8·05	20	0·5	0·5	1·07	18	82
2	8·05	20	0·5	0·5 [a]	~0	17	83
3	8·05	20	1·17	1·17	1·07	23	77
4	8·05	20	5·00	0·52	10·3	24	76
5	8·05	10	1·13	1·13	1·44	20	79
6	8·05	20	1·17	1·17	1·07	23	77
7	8·05	30	1·15	1·15	0·72	18	82
8	8·05	40	1·09	1·09	0·74	19	81
9	9·85	20	1·0	1·0	1·07	23	77
10	8·42	20	1·0	1·0	1·03	24	76
11	8·05	20	1·0	1·0	1·07	23	77
12	6·99	20	1·0	1·0	1·10	24	76
13	5·95	20	1·0	1·0	1·86	26	74
14	4·52	20	1·0	1·0	27·1	24	76
15	3·17	20	1·0	1·0	436	22	78

[a] $TsNCl_2$ was used instead of $TsNCl^-Na^+$.

Reaction of $TsNCl^-Na^+$ *with* $(p\text{-}MeOC_6H_4)_2S$. By replacing the *para*-hydrogen atoms in Ph_2S with methoxy-groups, the nucleophilicity is increased. The reaction involving $(p\text{-}MeOC_6H_4)_2S$ and chloramine T was investigated in buffered (pH 3·25) water–ethanol solution and, as expected, rate equation (22) described the reaction. From the measured k_1 ($0{\cdot}47\ \mathrm{l\,mol^{-1}\,s^{-1}}$) and k_d ($0{\cdot}08\ \mathrm{l\,mol^{-1}\,s^{-1}}$)[*] data, the pH-independent rate constants k_1' 0·47 and k_d' $26{\cdot}0\ \mathrm{l\,mol^{-1}\,s^{-1}}$, respectively, were obtained. On the basis of the rate data, it may be concluded that derivatives of Ph_2S containing electron-donating substituents are converted by both $TsNCl_2$ and TsNHCl.

Reactive Intermediates and Product-controlling Steps.— The kinetic experiments discussed above have shown that R^1R^2S is converted either by $ArSO_2NHCl$ or by $ArSO_2NCl_2$. In general, the conversion of sulphides to sulphimides and sulphoxides is due to both these species; under certain circumstances, however, one of them may predominate.

The substituent effects observed in both chlorination steps can be correlated with the formation of $R^1R^2SCl^+$ and $ArSO_2NQ^-$ (Q = H or Cl). Product analysis showed the product distribution [SI]/[SO] to be practically independent of the species converting the sulphide. This supports the idea that either of the chlorinating agents transforms R^1R^2S into a common $R^1R^2SCl^+$ reactive intermediate from which both $R^1R^2SNSO_2Ar$ and R^1R^2SO are formed in parallel steps.

Thus, the product distribution was found not to change when in buffered (pH 8·05) water–ethanol solution MeSPh reacted with dichloramine T instead of chloramine T (Table 5). Similarly, the product distribution was practically independent of $[S]_0/[C]_0$ with $[S]_0 > [C]_0$ as well as both temperature and pH (Table 5). In all three series of reactions the ratio $k_1[S][C] : k_d[C]^2$, *i.e.* the percentage of TsNHCl and $TsNCl_2$ intermediates in converting the sulphides was quite different for each run.[†]

The product-controlling steps summarized in Scheme 2 are nucleophilic displacements on $R^1R^2SCl^+$, and they presumably involve sulphurane intermediates.[‡] Analysis showed that the products may form in three different ways (Scheme 3), and these fast steps are influenced by steric and substituent effects, by the starting concentrations as well as by solvent and salt effects.

(a) Reactions involving R^1R^2S with bulky R^1 groups yield a relatively large amount of sulphimide while the yield of sulphoxide is unusually small (Table 6). This provides direct evidence for two parallel S_N displacements on $R^1R^2SCl^+$ with different steric requirements (courses A and B in Scheme 3). In course A the sulphurane intermediate is formed from the tight ion-pair. Here ' front-

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[*] In the acid region k_1 is a maximum, while k_d is considerably decreased (*cf.* Figure 3).

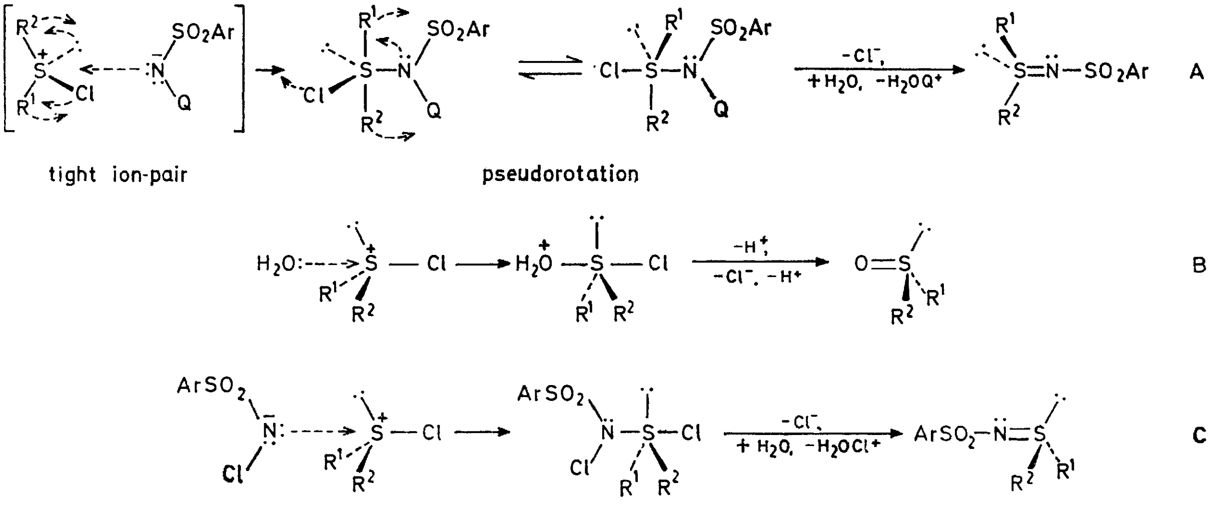
[†] It should be mentioned that in experiments conducted with the same starting concentrations, not only the $k_1[S][C] : k_d[C]^2$ ratios were different but, necessarily, the total concentrations of the reactive intermediate $TsNCl_2$ and TsNHCl as well as the compositions of the buffered solutions containing nucleophilic anions.

[‡] *Cf.* ref. 20. A stable sulphurane was prepared by Kapovits *et al.*[20] from the reaction of 2,2′-thiodibenzoic acid and chloramine T.

[20] I. Kapovits and A. Kálmán, *Chem. Comm.*, 1971, 649; C. R. Johnson and J. J Rigau, *J. Amer. Chem. Soc.*, 1969, **91**, 5398; D. Swern, I. Ikeda, and G. F. Whitfield, *Tetrahedron Letters*, 1972, 2635.

side attack ' by the *N*-nucleophile * is less hindered by bulky R^1 groups than the usual [22] ' back-side attack ' of water in course B.

(b) More sulphimide is produced when a phenyl group in the sulphide is replaced by an electron-donating alkyl substituent or an aryl group by a less electron-withdrawing aryl substituent (Table 6). The electrophilicity of the sulphur atom in $R^1R^2SCl^+$ is obviously diminished by a donor group, and such chlorosulphonium ions seem to react more readily with $ArSO_2NQ^-$ anions than with less nucleophilic water molecules.



SCHEME 3

TABLE 6

Sulphimide–sulphoxide product distribution for the reaction of $ArSO_2NCl^-Na^+$ with R^1R^2S. Dependence of product distribution on steric and substituent effects

$[S]_0 = [C]_0 = 10^{-3}$M; 20°; solvent unbuffered 1 : 1 (v/v) water–ethanol

	R^1R^2S		$YC_6H_4SO_2NCl^-Na^+$	[SI]/[SO] Product distribution	
	R^1	R^2	Y	Sulphimide (mol %)	Sulphoxide (mol %)
1	Me	Me	*p*-Me	48	*a*
2	Pr^i	Me	*p*-Me	66	*a*
3	Bu^t	Me	*p*-Me	75	*a*
4	Me	Ph	*p*-Me	41	59
5	Pr^i	Ph	*p*-Me	60	40
6	Bu^t	Ph	*p*-Me	89	11
7	Me	Me	*p*-Me	48	*a*
8	Me	Ph	*p*-Me	41	59
9	Ph	Ph	*p*-Me	38	62
10	Me	*p*-$MeOC_6H_4$	*p*-Me	50	50
11	Me	Ph	*p*-Me	41	59
12	Me	*m*-$MeOC_6H_4$	*p*-Me	41	59
13	Me	*p*-ClC_6H_4	*p*-Me	40	60
14	Me	*m*-ClC_6H_4	*p*-Me	39	61
15	Me	Ph	*p*-MeO	46	54
16	Me	Ph	*p*-Me	41	59
17	Me	Ph	H	38	62
18	Me	Ph	*p*-Cl	35	65

[a] Dialkyl sulphoxide products cannot be determined polarographically.

Electron-donating groups in $YC_6H_4SO_2NCl^-Na^+$ increase the nucleophilicity of the anion. This explains why somewhat more sulphimide was formed when $YC_6H_4SO_2NCl^-Na^+$ with a donating group was used as reactant (Table 6).

(c) In agreement with the preparative work, the yield of sulphimide can be increased by increasing the starting concentrations $[S]_0 = [C]_0$ or at least that of the chloramine $[C]_0$ (Table 7). In a more concentrated medium $ArSO_2NCl^-$ anions as very good nucleophiles (*cf.* ref. 23) compete markedly with water molecules in converting $R^1R^2SCl^+$ to produce sulphimides (course C in

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* Substitution reactions on a three-co-ordinate sulphur atom involving sulphurane intermediates with radial–apical entering and leaving groups are known.[21]

[21] B. W. Christensen, *Chem. Comm.*, 1971, 597; T. J. Maricich and V. L. Hoffman, *Tetrahedron Letters*, 1972, 5309.

[22] E. Ciuffarin and A. Fava, *Progr. Phys. Org. Chem.*, 1968, **6**, 81.

[23] F. E. Hardy, *J. Chem. Soc.* (*B*), 1971, 1899; J. H. Beale, *J. Org. Chem.*, 1972, **37**, 3871.

Scheme 3). When $ArSO_2NCl^-$ reacts with $R^1R^2SCl^+$, *N*-chloro-derivatives of acid-conjugate sulphimides are formed. These intermediates are very strong chlorinating agents * giving positive chlorine to water molecules or sulphonamides [*cf.* equations (12) and (13)].

TABLE 7

Sulphimide–sulphoxide product distribution for the reaction of $TsNCl^-Na^+$ with MeSPh. Dependence of product distribution on starting concentrations

	$10^3[S]_o$/M	$10^3[C]_o$/M	[SI]/[SO] Product distribution Sulphimide (mol %)	Sulphoxide (mol %)
1 [a]	0·18	0·18	30	70
2 [a]	1·00	1·00	41	59
3 [a]	8·06	8·06	61	39
4 [b]	0·52	0·52	18	82
5 [b]	1·17	1·17	23	77
6 [b]	5·12	5·12	29	71
7 [b]	9·88	9·88	34	66
8 [b]	1·06	10·7	41	59

[a] 20°; Solvent unbuffered 1 : 1 (v/v) water–ethanol. [b] 20°; Solvent 1 : 1 (v/v) water–ethanol, 0·05M-KH_2PO_4–K_2HPO_4 buffer (pH 8·05).

On the other hand, the product distribution does not depend on $[ArSO_2NH_2]$, even if sulphonamide is present in large excess. $ArSO_2NH_2$ being a very weak acid, the concentration of its nucleophilic base-conjugate is negligible.

(d) The product distribution [SI]/[SO] is strongly affected by the composition of the water–ethanol solvent, as shown in Figure 5. This may be due to the different stability of the ion-pair intermediates and to the different reactivity of solvating water molecules in solvents of different polarity. Apparently, there is an analogy between the solvolysis of chlorosulphonium ions and that of carbonium ions studied by Ingold *et al.*[25] The product distribution is similarly controlled by the water content of the solvent which also contains another nucleophile ($ArSO_2NQ^-$ and N_3^-, respectively †).

TABLE 8

Sulphimide–sulphoxide product distribution for the reaction of $TsNCl^-Na^+$ with MeSPh. Dependence of product distribution on the composition and concentration of the buffer

$[S]_o = [C]_o = 10^{-3}$M; 20°; solvent 1 : 1 (v/v) water–ethanol

Buffer	pH	$k(= k_1 + k_d)$/ l mol^{-1} s^{-1} Measured [a]	Calculated [b]	[SI]/[SO] Product distribution Sulphimide (mol %)	Sulphoxide (mol %)
0·1M-Phosphate	8·00	0·226	0·239	18	82
0·025M-Phosphate	8·10	0·179	0·190	22	78
0·1N-Succinate	7·23	1·30	1·353	23	77
0·05N-Succinate	7·45	0·771	0·831	26	74
0·2M-Borate	7·45	0·786	0·831	31	69

[a] Determined by the use of rate equation $v = k[C]^2$. [b] Calculated from equations (18) and (19) with k_1' 21·7 l mol^{-1} s^{-1} and k_d' 20·3 l mol^{-1} s^{-1}, respectively.

(e) Somewhat less sulphimide is formed when a salt (NaCl, $LiClO_4$) is added to the solvent. The increase of the ionic strength from 0·0011 to 0·138 decreases the yield of MePhSNTs from 41 to 31%. Evidently, the combination of two oppositely charged ions to form primarily a neutral sulphurane intermediate and then sulphimide, is affected unfavourably by the increase in ionic strength (*cf.* Scheme 3).

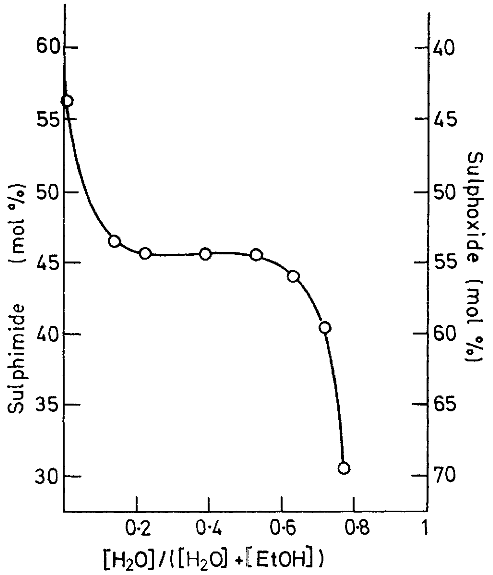

FIGURE 5 Dependence of sulphimide–sulphoxide product distribution on the composition of water–ethanol in the reaction of $TsNCl^-Na^+$ with MeSPh ($[S]_o = [C]_o = 10^{-3}$M; 20°)

In a Mann–Pope reaction carried out in buffered solutions more sulphoxide is produced than in the case of buffer-free solvents (Table 8). This may be due to the salt effect of the buffer, but buffer anions may also act as nucleophiles catalysing the solvolysis of chlorosulphonium ions.[26]

While the composition and concentration of a buffer do not affect the rate constants k_1 and k_d for the rate-controlling steps (4) and (5), respectively, these factors influence the product-controlling steps (Table 8).

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* This follows [16] from the low pK_a values of $\mathrm{MeAr\overset{+}{S}NHSO_2Ar}$ (between −1·88 and −3·00 [24].)

† The nucleophilic activity of $ArSO_2NCl^-$ is as high as that of N_3^-.[23]

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EXPERIMENTAL

Materials.—Sulphides, sulphoxides, sulphimides, and *sodium* salts of *N*-chloroarenesulphonamides used for kinetic measurements and product analysis were prepared by known methods. The purity was checked by analysis, spectroscopic methods, and t.l.c.

Bis-(4-*methoxyphenyl*) *Sulphide*.—This compound was prepared from bis-(4-methoxyphenyl)sulphoxide by the method of Granoth *et al.*[27] The crude product was recrystallized from MeOH (85%), m.p. 46°.[28]

Methoxyphenyl Methyl Sulphoxides.—These compounds were prepared from methoxyphenyl methyl sulphides by the procedure of Leonard *et al.*[29] Sulphide (1 g, 6·4 mmol) was dissolved in dioxan (20 ml) and the cold (0°) solution was added dropwise to a cold (0°) solution of $NaIO_4$ (1·36 g, 6·4 mmol) in water (30 ml). The mixture was stirred for 24 h at 0°, filtered, concentrated to 25 ml, and subjected to continuous extraction with chloroform (50 ml). From the chloroform extract the solvent was removed and the residue was distilled at reduced pressure; yields 0·74 g (68%) and 0·89 g (82%), b.p. 102—103° at 0·05 [30] and 94—95° at 0·05 mmHg [31] for the *meta*- and *para*-isomer, respectively.

Methyl Nitrophenyl Sulphoxides.—*S*-Methyl-*S*-nitrophenyl-*N*-*p*-tolylsulphonylsulphimide (2 g) and aqueous 20% HCl (20 ml) were heated on a water-bath for 20 min. The hot solution was filtered and the solvent was removed under reduced pressure. The residue was triturated with aqueous 5% NaOH (20 ml), filtered (*para*-isomer) or submitted to continuous extraction with chloroform (60 ml) (*meta*-isomer); from the chloroform extract the solvent was removed. The crude products were recrystallized from ethanol; yields 0·69 g (48%) and 0·78 g (54%), m.p. 115—116° [31] and 149—150° [31] for the *meta*- and *para*-isomer, respectively.

Solvents.—1 : 1 (v/v) Water–ethanol solvent was prepared from deionized water and 96% ethanol purified by fractional distillation. Buffered solutions (0·025—0·2M) were prepared from phosphate, borate, succinate, and Britton–Robinson buffers. pH Values were measured on a Radelkisz (Budapest) OP 204 instrument. The glass electrode was calibrated with standard buffers at pH 4·01, 6·99, and 9·15. The rate constants k_2 were measured in solvents containing 0·05M-$TsNH_2$.

Kinetics.—Two analytical methods were elaborated to follow the Mann–Pope reaction. One (a) was based on the fast and quantitative reaction of $ArSO_2NCl^-Na^+$ (not consumed by sulphide) with I^- to give I_2. Iodine and the products (sulphimide and sulphoxide) were measured by spectrophotometric and polarographic methods, respectively. The change in the absorbance of the reaction mixture was registered for method (b) which was based on spectrophotometry.

(a) *Iodometric and polarographic method*. Solutions were prepared from R^1R^2S and $ArSO_2NCl^-Na^+$ reactants with concentrations (10^{-2}—10^{-4}M) twice as high as required for the reaction mixture. Equal volumes of the pre-equilibrated (10—40 ± 0·03°) solutions were mixed in a jacketted flask. Samples were poured into 1 : 1 (v/v) water–ethanol containing KI (in 50-fold excess) and HCl (enough to ensure pH 2·5 with the buffer capacity taken into account).* The solutions obtained were divided into two parts and the concentration of iodine as well as those of sulphimide and sulphoxide were determined separately.

Using one part of the solutions, the concentration of iodine ($\leqslant 5 \times 10^{-4}$M) † was measured (±0·5%) by differential spectrophotometry on a Beckman model DU spectrophotometer at 353 nm (ε 23,000; cell length 1—10 mm).[26,32] In these circumstances $ArSO_2NCl^-Na^+$ was quantitatively reduced by I^-,[33] and the amount of the iodine liberated proved to be unaffected by the sulphide content of the solution.

Sulphimides and sulphoxides were measured polarographically.[2,34,35] Both compounds can be reduced on a dropping mercury electrode; the wave heights are proportional to the concentration. The polarographic measurements can be affected by the presence of iodine which can react with sulphide although this reaction is very slow in acidic media containing I^- ions.[26] Therefore ascorbic acid (two equiv.) was added to reduce iodine.

One part of the iodine-free solution was diluted with an equal volume of Britton–Robinson buffer in 1 : 1 (v/v) water–ethanol, and the concentration of sulphimide was measured at pH 4·5 (for MePhSNTs $E_{\frac{1}{2}} = -0{\cdot}600$ V).‡ The other part was mixed with an equal volume of 0·2N-H_2SO_4 in the same solvent, and the concentration of sulphoxide was determined at pH 1 (for MePhSO $E_{\frac{1}{2}} = -0{\cdot}900$ V).‡ Using solutions of suitable pH values, either of the products (sulphimide or sulphoxide) could be measured selectively. Control experiments showed that, under the given circumstances, sulphimides did not hydrolyse to sulphoxides,[36] and the latter compounds were not reduced by iodide ions.[37]

Polarograms were recorded on a Radelkisz (Budapest) OH 102 polarograph in a jacketted cell thermostatted at 20 ± 0·1°. For the polarographic measurements an AgCl reference electrode was used. Solutions were deaerated with 99·99% nitrogen. Calibrations were carried out with sulphimide and sulphoxide solutions of known concentration. The measurements were accurate to within ±3%.

(b) *Spectrophotometric method*. Relatively fast reactions ($k_1 > 2$ l mol^{-1} s^{-1}) involving MePhS and $TsNCl^-Na^+$ can be followed spectrophotometrically. The absorbances of the reactants and the products differ significantly at 286 nm; ε 700, 400—700,§ 60, and 20 were found for MeSPh, $TsNCl^-Na^+$, MePhSNTs, and MePhSO, respectively. The actual absorbance of the reactants is proportional to their concentration and can be calculated from the measured values [equation (25) where A, A_t, A_0, and A_p are the

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* Reaction mixtures containing at least 50% ethanol may be acidified with mineral acids.

† The Bouguer–Lambert–Beer law is valid in this concentration range.

‡ Referred to a saturated calomel electrode.

§ Depending upon the pH of the reaction mixture.

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absorbances for the reactants at time t, for the reaction mixture at the same time, for the reaction mixture at $t = 0$, and for the reaction mixture containing only products, respectively]. Equation (25) is valid for $[S]_o = [C]_o$, but the

$$A = A_o - (A_o - A_t)/[1 - (A_p/A_o)] \qquad (25)$$

condition $[S]_o \neq [C]_o$ can also be taken into account without difficulty. Measurements were taken on a Unicam SP 700 spectrophotometer equipped with a constant temperature cell holder.

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