

Mechanism of the Reaction of Dialkyl Sulphides with Bromamine T in Alkaline Medium¹

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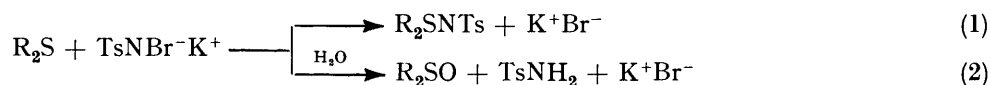
Bromamine T (*p*-MeC₆H₄SO₂NBr⁻K⁺) reacts readily with dialkyl sulphides (R₂S) to yield sulphoxides (R₂SO) and sulphimides (R₂SNTs). The kinetics of the reaction were investigated in buffered alkaline water-methanol solutions. In rate-determining steps HOBr and *p*-MeC₆H₄SO₂NHBr formed in equilibrium reactions convert dialkyl sulphides into bromosulphonium (R₂SBr⁺) intermediates (ρ^* -1.22 and -1.11, ρ_1 -13.3 and -14.4, respectively). Electrophilic additions of Br⁺ to sulphur atom are significantly hindered by the steric effect of *S*-alkyl groups (δ 0.713 and 0.765, ρ_s 0.766 and 0.792, respectively). Products are rapidly formed from bromosulphonium ions by nucleophilic displacement with OH⁻ and *p*-MeC₆H₄SO₂NH⁻ nucleophiles. Product distribution depends on pH and the concentration of *p*-MeC₆H₄SO₂NH₂ but is not influenced markedly by *S*-alkyl groups in sulphides. Results are compared with those obtained earlier for chloramine T.

THE mechanism of the Mann-Pope reaction,² the conversion of sulphides with sodium salts of *N*-chloroarene-sulphonamides, was extensively studied earlier.³⁻⁶ Thus, it is known that TsNHCl (Ts = *p*-MeC₆H₄SO₂), the conjugate acid of chloramine T, converts dialkyl sulphides (R₂S) in a rate-determining step into chlorosulphonium sulphonamidate tight ion-pair intermediates (R₂SCI⁺ TsNH⁻) from which sulphimide (R₂SNTs) and sulphoxide (R₂SO) products are formed by a fast nucleophilic attack of sulphonamidate anion or water on the sulphonium centre.

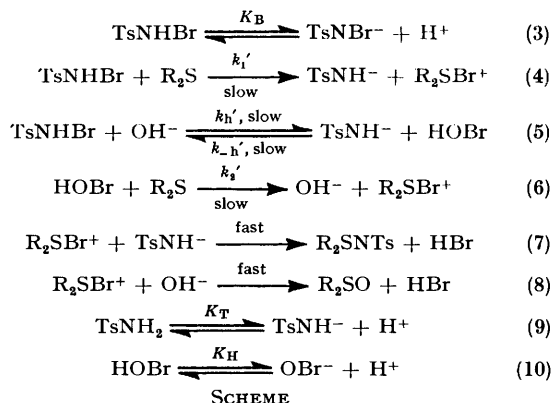
For further understanding the mechanism of reaction between sulphides and *N*-halogeno-compounds, reactions of bromamine T (TsNBr⁻K⁺) with dialkyl sulphides were studied by applying kinetic methods and product analysis (see refs. 3 and 6), and results were compared with those obtained for chloramine T previously.

RESULTS AND DISCUSSION

Mechanism.—In preparative experiments we observed that bromamine T, like chloramine T, reacts readily with dialkyl sulphides in water-methanol solutions yielding sulphimide and an equimolar mixture of sulphoxide and toluene-*p*-sulphonamide products.



For the reactions (1) and (2) we suggest the mechanism shown in the Scheme based on experimental data discussed in the following text.



SCHEME

Rate-determining Steps, Kinetic Equations.†—Dialkyl sulphides are highly reactive toward bromamine T, so the rates of reactions conducted in buffered 1 : 1 (v/v) water-methanol were measurable with the usual kinetic methods only in the alkaline region (*cf.* refs. 3 and 4). In moderately basic solutions (pH < 12) the rates of reactions decreased with the increase of pH, but they did not depend on the ionic strength of the buffer.‡ In contrast to the corresponding reactions of chloramine T, the conversion of sulphides with bromamine T was found not to follow second-order kinetics, $-d[\text{B}]/dt \neq k_1[\text{S}][\text{B}]$. We also observed that the rate of reaction was significantly diminished by addition of TsNH₂ to the reaction mixture (Figure 1), while even a great excess of bromide ions did not retard the conversion of sulphide [both TsNH₂ and Br⁻ are also produced in reactions (1) and (2)]. From the latter observation it follows that the reversible reaction of bromosulphonium and bromide ions (R₂SBr⁺ + Br⁻ \rightleftharpoons R₂S + Br₂)⁷ resulting in the recovery of sulphide may be neglected. Again, the rate decrease caused by TsNH₂ suggests that dialkyl sulphides can be converted not only by TsNHBr but also by HOBr intermediate [reaction (6)] formed from TsNHBr and

OH⁻ in slow equilibrium reaction (5), as well. Hardy and Johnston⁸ gave earlier evidence that HOBr as a brominating intermediate takes a part in the reaction of bromamine T with *p*-nitrophenoxide ion. They showed that in strongly alkaline solutions the equilibrium hydrolysis of bromamine T is shifted to the formation of HOBr, consequently the concentration of HOBr can exceed that of TsNHBr with the increase of pH.

For *strongly alkaline* solutions we supposed that [TsNHBr] \ll [HOBr] if pH > 12, thus only HOBr is responsible for the conversion of sulphides, and TsNHBr as brominating agent may be neglected. Applying the steady-state approximation to HOBr ($d[\text{HOBr}]/dt = 0$)

† Hereinafter [S], [B], and [T] represent stoichiometric concentrations of sulphide, bromamine T, and toluene-*p*-sulphonamide, respectively; pH-dependent and -independent rate constants are distinguished by symbols *k* and *k*'.

‡ See details in Table 1.

equation (11) can be obtained, by taking the steps (3), (5), (6), (9), and (10) in the Scheme into account.

$$-\frac{d[B]}{dt} = \frac{k_h k_2 [B][S]}{k_{-h}[T] + k_2[S]} \quad (11)$$

We found equation (11) to be valid in the pH range 12.45–12.96. Using the differential equation (12) or the

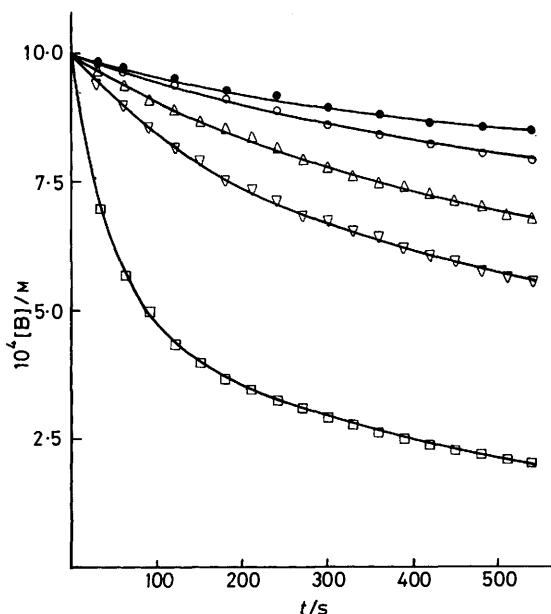


FIGURE 1 $[B]$ against t plots for the reaction of TsNBr^-K^+ with Pr_2S $\{[S]_0 = [B]_0 = 10^{-3}\text{M}$; 20°C ; solvent 1 : 1 (v/v) water-methanol; pH 12.70; $[T]_0 = 0$ and $[T]_0 = 0$, $[\text{Br}^-]_0 5 \times 10^{-3}\text{M}$ (\square); $[T]_0 2.6 \times 10^{-3}\text{M}$ (∇); $[T]_0 5.1 \times 10^{-3}\text{M}$ (\triangle); $[T]_0 10^{-2}\text{M}$ (\circ); $[T]_0 1.97 \times 10^{-2}\text{M}$ (\bullet)}

integral of equation (11) the $k_{-h}/k_h k_2$ and $1/k_h$ expressions were evaluated by least-squares methods (Figure 2, Table 1).

$$\frac{[B]}{-d[B]/dt} = \frac{k_{-h}[T]}{k_h k_2 [S]} + \frac{1}{k_h} \quad (12)$$

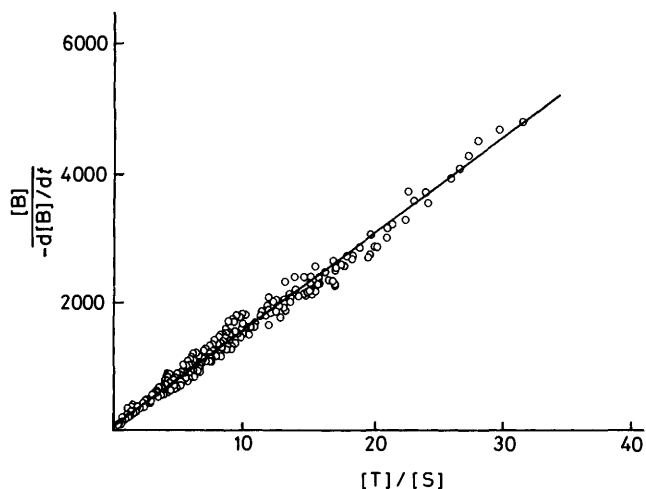


FIGURE 2 Evaluation of $k_{-h}/k_h k_2$ expression from equation (12) for the reaction of TsNBr^-K^+ with Pr_2S [20°C ; solvent 1 : 1 (v/v) water-methanol; pH 12.70]

TABLE 1

Rate constants for the reaction of TsNBr^-K^+ with Pr_2S ; 20°C ; solvent buffered 1 : 1 (v/v) water-methanol

pH	$k_{-h}/k_h k_2$ $^b/s$	k_1/l $\text{mol}^{-1} \text{s}^{-1}$
12.97	145	
12.85	155	
12.70	150 ^c	
12.61	152	
12.45	148 ^c	
11.90	(134)	0.25 ^d
11.70	(124)	0.42
11.50	(112)	0.80
11.25	(92.4)	1.25
10.70	(45.9)	4.10
10.40	(27.4)	10.50

^a Rate constant values are accurate to within $\pm 5\%$. ^b Data in parentheses were calculated from equation (13); see text. ^c The values 150 ± 10 s were obtained when LiClO_4 was added to 0.025 and 0.05M- NaOH solutions (pH 12.45 and 12.70) to adjust the ionic strength to 0.05 and 0.1, respectively. ^d The value $0.26 \text{ l mol}^{-1} \text{ s}^{-1}$ was obtained in 0.025M-Britton-Robinson buffer.

From $k_{-h}/k_h k_2$, however, the value of k_2 cannot be simply calculated because the ratio $k_h : k_{-h}$, *i.e.* the equilibrium constant for the reversible reaction (5) between TsNHBr and OH^- cannot be determined by investigation of the hydrolysis of bromamine T. There is no detectable change in absorption at 332 nm of hypobromite ions when a slightly alkaline (pH 8) solution of bromamine T is basified to pH 13. Consequently, the concentration of hypobromite ions must be small even in highly alkaline solutions.

Nevertheless, $k_{-h}/k_h k_2$ values are useful data for calculating the k_2^{rel} values characterizing the relative reactivities of HOBr toward sulphides [reaction (6); Table 2]. In the given pH range ($[\text{H}^+] \ll K_B, K_T$) $k_{-h}/k_h k_2$ proved to be independent of pH, in accord with expectations based on equation (13) which gives a correlation between pH-dependent and -independent rate constants; the equilibrium constants $K_B = 6.61 \times 10^{-7}$ and $K_T = 8.51 \times 10^{-12}$ were measured in 1 : 1 (v/v) water-methanol at 20°C .

$$\frac{k_{-h}}{k_h k_2} = \frac{k'_{-h} K_T (K_B + [\text{H}^+])}{k'_h k'_2 K_w (K_T + [\text{H}^+])} \quad (13)$$

The rate constant k_h [see reaction (5)] estimated from the intercept of equation (12) can be obtained with less accuracy. In alkaline solutions (pH 10.40–12.97) the value $k_h = 0.02 \text{ s}^{-1}$ is independent of pH, in accordance with equation (14) if $K_B \gg [\text{H}^+]$.

$$k_h = \frac{k'_h K_w}{K_B + [\text{H}^+]} \quad (14)$$

We found that in *moderately alkaline* solutions (pH < 12) the conversion of sulphides does not follow equation (11), suggesting that the concentrations of TsNHBr and HOBr as brominating agents should be commensurable. Starting from reactions (3)–(6), (9), and (10) in the Scheme, and applying again the steady-state approximation for HOBr , rate equation (15) was deduced, and for

TABLE 2

Rate constants for the reaction of TsNBr⁻K⁺ with R₂S; 20 °C; solvent buffered 1 : 1 (v/v) water-methanol

R ₂ S sulphide	$k_{-h}/k_h k_2$ ^a / s	k_2 ^{rel}	k_1 ^b /l mol ⁻¹ s ⁻¹	$10^{-4} k_1'$ / l mol ⁻¹ s ⁻¹	$k_1'^{Br}/$ $k_1'^{Cl}$ ^c	$\Sigma\sigma^*$ ^d	$\Sigma\sigma_I$ ^e	ΣE_s ^d	ΣE_{s1} ^{e,f}
Me ₂ S	91.5	1	1.00	35.0	13.0	0	-0.092	0	-2.48
Et ₂ S	58.2	1.57	1.68	58.8	8.9	-0.20	-0.114	-0.14	-2.62
Pr ₂ S	150	0.61	0.42	14.7	3.2	-0.23	-0.112	-0.72	-3.20
Pr ⁱ ₂ S	134	0.68	0.68	23.8	3.3	-0.38	-0.130	-0.94	-3.42
Bu ₂ S	134	0.68	0.58	20.3	4.4	-0.26	-0.126	-0.78	-3.26
Bu ⁱ ₂ S	770	0.12	0.12	4.2	2.0	-0.25	-0.130	-1.86	-4.34
Bu ^s ₂ S	1 200	0.076	0.045	1.57	2.4	-0.42	-0.138	-2.26	—
(CH ₂) ₄ S	35.8	2.55	1.97	69.0	5.1				
(CH ₂) ₅ S	25.6	3.57	2.40	84.0	7.4				

^a Measured at pH 12.70. ^b Measured at pH 11.70. ^c Reactivity of TsNHBr, as compared to that of TsNHCl, in conversion of sulphides; for the latter, data in ref. 4 (Tables 3 and 4) were taken into account. ^d Ref. 9. ^e Ref. 10. ^f Ref. 11.

the pH range 10.4–11.9 its validity was verified by the use of the differential equation (16) (Figure 3).

$$-\frac{d[B]}{dt} = k_1[B][S] + \frac{k_h k_2 [B][S]}{k_{-h}[T] + k_2[S]} \quad (15)$$

$$\Delta = \frac{-d[B]/dt}{[B]} - \frac{1}{(k_{-h}[T]/k_h k_2[S]) + 1/k_h} = k_1[S] \quad (16)$$

The pH-dependent $k_{-h}/k_h k_2$ values referring to the pH range 10.4–11.9 were calculated from the mean of corresponding data measured between pH 12.45 and 12.97, using equation (13) where $k'_{-h}/k'_h k_2 K_w = 2.32 \times 10^8$ l s mol⁻¹ was taken into account (Table 1).

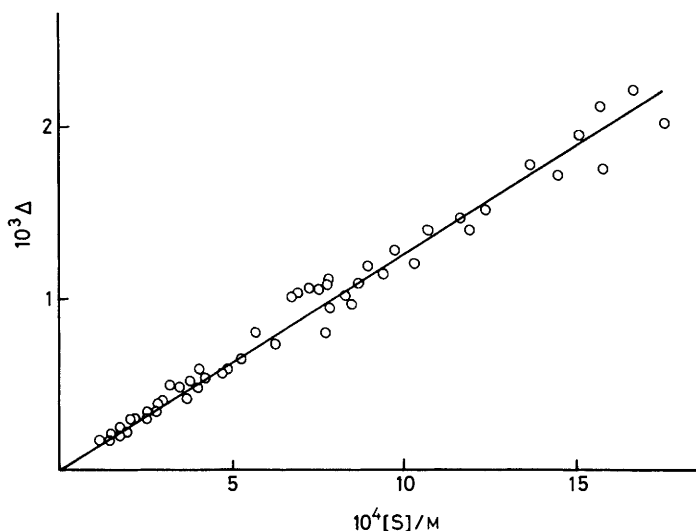


FIGURE 3 Evaluation of rate constant k_1 from equation (16) for the reaction of TsNBr⁻K⁺ with Pr₂S [20 °C; solvent 1 : 1 (v/v) water-methanol; pH 11.25]

The pH-dependent k_1 constants were evaluated from the slope of equation (16) (Table 1 and Figure 3). As expected from equation (17) with $K_B \gg [H^+]$, k_1 values show linear dependence on $[H^+]$ in the pH region 10.4–11.9; $\log k_1 = 1.042$ (pH) + 11.83; $r = 0.997$.

$$k_1 = \frac{k'_1 [H^+]}{K_B + [H^+]} \quad (17)$$

The pH-independent k'_1 rate constants, characterizing reaction (4) between TsNHBr and sulphides, were calculated from equation (17) and are listed in Table 2.

As it appears from numerical values, the reactivity of TsNHBr towards sulphides is considerably higher than that of TsNHCl, and the difference in reactivity of the two halogenating agents depends on the S-alkyl groups, as well (see column k'_1^{Br}/k'_1^{Cl} in Table 2).

Polar and Steric Effects.—Applying the Taft equation,⁹ polar and steric reaction constants were calculated for the reactions of dialkyl sulphides with the halogenating agents TsNHBr, HOBr, and TsNHCl. The validity of the Taft equation was checked both with the original σ^* and E_s constants [equation (18)] and with the recently proposed σ_I ¹⁰ and E_s^e ¹¹ values [equation (19)] listed in Table 2. To clear up the significance of the polar effect of alkyl substituents, a single parameter correlation with E_s^e constants was also tested [equation (20)].

$$\log k = \rho^* \sigma^* + \delta E_s + a \quad (18)$$

$$\log k = \rho_I \sigma_I + \rho_s E_s^e + a \quad (19)$$

$$\log k = \rho_s E_s^e + a \quad (20)$$

Reaction constants are collected in Table 3. The simple correlation of $\log k$ values with E_s^e steric substituent constants is decidedly poorer than if both σ_I and E_s^e values were used. The polar effect of S-alkyl substituents therefore cannot be neglected in explaining the reactivity of dialkyl sulphides towards TsNHBr, HOBr, and TsNHCl. The reaction constants obtained either with the application of σ^* and E_s or with that of σ_I and E_s^e substituent constants have the same sign and their changes show similar trends. On the other hand, the diverse effectiveness of factors controlling the reactivity of TsNHBr and TsNHCl is also revealed from data given in Table 3.

The negative values of ρ^* (or ρ_I) polar reaction constants show that the rate of conversion of sulphides with brominating agents is enhanced by an increasing +I effect of S-alkyl groups. This is consistent with a significant positive polarity of the sulphur atom in the transition state and with the formation of bromosulphonium ion intermediates. A similar intervention of halogenosulphonium intermediates was also assumed earlier in reactions of sulphides with chloroamine T,³⁻⁶ bromine,⁷ iodine,¹² or chlorine.¹³

If we compare the additions of Br⁺ and Cl⁺ to sulphides leading to halogenosulphonium ions, a decreasing effectiveness of the polar factor can be established in the

TABLE 3

Reaction constants calculated by Taft equation for the conversion of R₂S with TsNBr⁻K⁺ or TsNCl⁻Na⁺

		Rate-determining steps		
		R ₂ S + TsNHBr ^a	R ₂ S + HOBr ^b	R ₂ S + TsNHCl ^c
Equation (18)	δ^*	-1.11 ± 0.61	-1.22 ± 0.22	-1.96 ± 0.22
	ρ^*	0.765 ± 0.100	0.713 ± 0.036	0.285 ± 0.037
	ρ^2	0.050	0.037	-0.010
Equation (19)	ρ_1	0.958	0.994	0.966
	ρ_s	-14.36 ± 3.79	-13.27 ± 2.17	-18.38 ± 3.84
	ρ^2	0.792 ± 0.084	0.766 ± 0.048	0.442 ± 0.086
Equation (20)	ρ_s	0.621	0.697	-0.540
	ρ^2	0.976	0.991	0.777
	ρ^2	0.545 ± 0.110	0.538 ± 0.096	0.117 ± 0.099
	ρ^2	1.51	1.52	0.525
	ρ^2	0.861	0.887	0.134

^a k_1 Rate constants are given in Table 2. ^b k_2 Rate constants are given in Table 2. ^c k_1 Rate constants were published in ref. 4.

former case. On the other hand, δ (or ρ_s) steric reaction of Br⁺ than for that of Cl⁺, which can be in part rationalised by the moderate difference in van der Waals radii of bromine and chlorine.

The rates of conversion of cyclic sulphides with brominating agents (TsNHBr, HOBr) are higher than those of open-chain dialkyl sulphides and they do not depend significantly on ring-size. These observations are consistent with a rate-determining Br⁺ addition to the sulphur atom. At the same time, S_N2-type displacement as a rate-controlling process may be here excluded because such a reaction occurring on the sulphur atom of a substrate with a six-membered ring would be much slower than a similar process with a sulphide having a five-membered ring.^{14,15}

Product-controlling Steps and Product Analysis.—The product distribution in reactions of dialkyl sulphides with bromamine T was investigated by varying the alkyl substituents, the starting concentration of TsNH₂ and pH of the 1 : 1 (v/v) water-methanol solvent. Results are summarized in Tables 4 and 5.

TABLE 4

Yield of sulphimide product in the reaction of TsNBr⁻K⁺ with Pr₂S. Dependence of yield on pH and starting concentration of TsNH₂; 20 °C; [S]₀ = [B]₀ = 10⁻³M; solvent buffered 1 : 1 (v/v) water-methanol

pH	10 ² [T] ₀ /M	Yield of Pr ₂ SNTs ^a (mol%)
12.97	0	0
	1.0	3.5
12.70	0	0.5
	0.26	1.5
	0.51	3.0
	0.76	4.5
	1.0	6.5
12.45	2.0	11.5
	0	1.0
11.90	1.0	19
	0	4.0
11.25	1.0	28
	0	6
10.40	1.0	38
	0	12
	1.0	45

^a Data are accurate to within ±2%.

In unbuffered solutions bromamine T, like chloramine T, converts dialkyl sulphides into a mixture of sulphimide and sulphoxide products but product distribution is less affected by the bulkiness of S-alkyl groups or by the ring-size of cyclic sulphides (Table 5; cf. Tables 5 and 6 in ref. 4). In buffered alkaline solutions the formation of the

TABLE 5

Yield of sulphimides in the reaction of TsNBr⁻K⁺ with R₂S. Dependence of yield on S-alkyl groups and the composition of the solvent; 20 °C; [S]₀ = [B]₀ = 10⁻³M; solvent (A) unbuffered 1 : 1 (v/v) water-methanol, [T]₀ 0; (B) buffered 1 : 1 (v/v) water-methanol (pH 12.70), [T]₀ 10⁻²M

R ₂ S sulphide	Yield of R ₂ SNTs ^a (mol%)	
	A	B
Me ₂ S	49 (51)	5.5 (94)
Et ₂ S	55 (45)	6.5 (93)
Pr ₂ S	53 (47)	6.5 (93)
Pr ⁱ ₂ S	55	5.0
Bu ₂ S	52	3.5
Bu ⁱ ₂ S	50	4.1
Bu ⁿ ₂ S	65	7.2
(CH ₂) ₄ S	43	5.5
(CH ₂) ₅ S	56	7.0

^a Data are accurate to within ±2%; yields of R₂SO sulphoxide products measured are given in parentheses.

sulphimide is considerably suppressed (Table 5; cf. ref. 3). As expected, the higher the concentration of OH⁻ the more sulphoxide is formed, whereas the increase of the starting concentration of TsNH₂ favours production of sulphimides (Table 4). All these observations are in agreement with reactions (7) and (8) in the Scheme, supporting the view that both sulphimide and sulphoxide products are formed from the bromosulphonium intermediate in fast S_N reactions effected by TsNH⁻ and OH⁻ nucleophiles, respectively.

To explain the striking observations that steric hindrance is less effective in the formation of sulphimides than in that of sulphoxides, we assumed earlier that the reaction of sulphides with chloramine T involves a rate-controlling step leading to a [R₂SCl⁺ TsNH⁻] tight ion-pair from which sulphimide products can form by a less hindered front-side attack of the internal TsNH⁻

nucleophile on the sulphonium centre, while the sterically more hindered back-side attack of the external H_2O and OH^- nucleophiles may give rise to the formation of sulphoxide.^{3,6} It seems very likely that reaction (4) of dialkyl sulphides with TsNHBr also results in the formation of a bromosulphonium sulphonamidate tight ion-pair $[\text{R}_2\text{SBr}^+ \text{TsNH}^-]$ from which the sulphimide can form in a sterically less hindered way than the sulphoxide. Bromosulphonium ions, however, are produced in the reaction (6) of sulphides with HOBr , too. In this case R_2SBr^+ and OH^- ions are formed together, which obviously favours the subsequent formation of sulphoxide. The production of the sulphimide is here more hindered because TsNH^- can attack on the sulphonium centre only as an external nucleophile. All these may explain why the product distribution observed in the reactions of bromamine T is less markedly influenced by the S-alkyl groups of the sulphide substrate than that found for chloramine T.

EXPERIMENTAL

Materials.—Sulphides listed in Table 2 and the corresponding sulphoxides and sulphimides used in the present study were prepared by known methods and purified by distillation or crystallization. Bromamine T (TsNBr^-K^+ , $2\text{H}_2\text{O}$) was prepared by the method of Roberts.¹⁶

Kinetics.—Kinetic measurements were carried out at 20.00 ± 0.05 °C in 1:1 (v/v) water-methanol solutions. Constant pH values (determined by the method of Bates *et al.*¹⁷) were maintained by 0.05M Britton–Robinson buffer (pH < 12) or 0.025–0.1M NaOH solutions (pH > 12). The influence of the ionic strength was measured by varying the concentration of the Britton–Robinson buffer (0.025–0.05M) at constant pH, or by adding LiClO_4 to NaOH solutions (ionic strength 0.05–0.1). Reactions were followed by measuring the absorption of the reaction mixture at 276 nm. At the given wavelength the absorption of bromamine T (ϵ 790) is much higher than that of the products (TsNH_2 and R_2SNTs , ϵ ca. 80); dialkyl sulphides and sulphoxides do not have significant absorption in this region. Starting concentrations of the reactants were varied between 2×10^{-3} – 5×10^{-4} M.

Product Analysis.—Yields of sulphimides were measured in the reaction mixtures by polarography.¹⁸ In the conversion of Me_2S , Et_2S , and Pr_2S the yields of the corresponding sulphoxides and sulphimides were determined by h.p.l.c. Experimental conditions for chromatography were similar to those applied in our earlier study.⁶ The column was 250×4 mm packed with Hypersil of 6 μm particle size

(Shandon, Great Britain); as eluants (v/v), methanol-ether-pentane (12:75:13) and methanol-ether (8:92) were used for the determination of products obtained from Me_2S and from Et_2S and Pr_2S , respectively. The flow rate was 1 ml min^{-1} ; $10 \mu\text{l}$ of the solution of products (0.2 mg ml^{-1}) were injected. Detection was by u.v. absorption of the effluents at 220 nm.

pK Determinations.—The $\text{p}K_{\text{B}}$ value for bromamine T [equilibrium (3)] was measured by titration¹⁹ using the approximate value of K_{D} obtained for the disproportionation equilibrium ($\text{TsNHBr} + \text{TsNBr}^- \rightleftharpoons \text{TsNBr}_2 + \text{TsNH}^-$) by Hardy and Johnston.⁸ The $\text{p}K_{\text{T}}$ value for TsNH_2 [equilibrium (9)] was determined with spectrophotometric measurement at 246 nm.

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REFERENCES

- 1 Preliminary communication presented at 2nd European Symposium on Organic Chemistry (ESOC II) Stresa, 1981.
- 2 F. G. Mann and W. J. Pope, *J. Chem. Soc.*, 1922, **121**, 1052.
- 3 F. Ruff and Á. Kucsman, *Acta Chim. Acad. Sci. Hung.*, 1969, **62**, 437; 1970, **65**, 107; F. Ruff and Á. Kucsman, *J. Chem. Soc., Perkin Trans. 2*, 1975, 509.
- 4 F. Ruff, K. Komoto, N. Furukawa, and S. Oae, *Tetrahedron*, 1976, **32**, 2763.
- 5 F. Ruff, I. Kapovits, J. Rábai, and Á. Kucsman, *Tetrahedron*, 1978, **34**, 2767.
- 6 F. Ruff, G. Szabó, J. Vajda, I. Kövesdi, and Á. Kucsman, *Tetrahedron*, 1980, **36**, 1631; Gy. Szókán, F. Ruff, and Á. Kucsman, *J. Chromatogr.*, 1980, **198**, 207.
- 7 U. Miotti, G. Modena, and L. Sedeá, *J. Chem. Soc. B*, 1970, 802; U. Miotti and G. Modena, *Boll. Sci. Fac. Chim. Ind. Bologna*, 1969, **27**, 381.
- 8 F. E. Hardy and J. P. Johnston, *J. Chem. Soc., Perkin Trans. 2*, 1973, 742.
- 9 R. W. Taft, in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, p. 556.
- 10 R. W. Taft and L. S. Levitt, *J. Org. Chem.*, 1977, **42**, 916.
- 11 S. H. Unger and C. Hansch, *Prog. Phys. Org. Chem.*, 1976, **12**, 91.
- 12 T. Higuchi and K. H. Gensch, *J. Am. Chem. Soc.*, 1966, **88**, 5486; K. H. Gensch, I. H. Pitman, and T. Higuchi, *ibid.*, 1968, **90**, 2096.
- 13 A. A. Humffray and H. E. Imberger, *J. Chem. Soc., Perkin Trans. 2*, 1981, 382.
- 14 R. Curci, F. DiFuria, A. Levi, and G. Scorrano, *J. Chem. Soc., Perkin Trans. 2*, 1975, 408.
- 15 S. Tamagaki, M. Mizumo, H. Yoshida, H. Hirota, and S. Oae, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2456.
- 16 E. Roberts, *J. Chem. Soc.*, 1923, 2707.
- 17 R. G. Bates, M. Paabo, and R. A. Robinson, *J. Phys. Chem.*, 1963, **67**, 1833.
- 18 M. Vajda and F. Ruff, 'Polarography,' McMillan, New York, 1964, p. 759.
- 19 J. C. Morris, J. A. Salazar, and M. A. Wineman, *J. Am. Chem. Soc.*, 1948, **70**, 2036.