

## Reduction of Sulphur Dioxide with Thiols. Synthesis of Dialkyl Trisulphides

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The reactions of sulphur dioxide with thiols in the presence of triethylamine have been investigated. Aliphatic thiols gave a mixture of dialkyl disulphide and trisulphide in a ratio of *ca.* 7 : 3, which was independent of the reactant ratio. Addition of 1,4-benzoquinone caused a relatively small retardation. An ionic mechanism is tentatively proposed for the reaction.

DIALKYL TRISULPHIDES have been synthesised by various methods, *i.e.*, reactions of disulphur dichloride with thiols,<sup>1</sup> dialkyl disulphides with sulphur in the

<sup>1</sup> G. R. Levi and A. Baroni, *Atti accad. Lincei*, 1929, **9**, 772.

<sup>2</sup> H. E. Westlake, jun., H. L. Laquer, and C. P. Smith, *J. Amer. Chem. Soc.*, 1950, **72**, 436.

presence of amines,<sup>2</sup> Bunte salts with disodium disulphide,<sup>3</sup> thiols with sulphur,<sup>4</sup> and alkyl bromides with sodium thiosulphate.<sup>3</sup> I describe here the reduction

<sup>3</sup> B. Milligan, B. Saville, and J. M. Swan, *J. Chem. Soc.*, 1963, 3608.

<sup>4</sup> G. F. Bloomfield, *Chem. and Ind.*, 1948, **67**, 14.

of sulphur dioxide with thiols to dialkyl trisulphides in the presence of triethylamine. Although the yields of trisulphides are relatively low, the present study provides information on the mechanism of the reactions of sulphur dioxide.

Although no reaction took place on heating (at 80 °C) or irradiation with u.v. light of a mixture of liquid sulphur dioxide and thiols for a few days, a reaction did occur on addition of triethylamine. Thus, a mixture of these

Yields in the reaction of sulphur dioxide with thiols (40 mmol) in the presence of triethylamine at 25 °C

	Reactants/mmol		Time/day	% Yield of the products <sup>a</sup>	
	SO <sub>2</sub>	Et <sub>3</sub> N		RSSR	RSSSR
EtSH	20	2	3	72	28
	100	2	3	66	28
	40	20	1	40	17
Pr <sup>n</sup> SH	20	2	3	69	25
	100	2	3	69	27
	40	20	1	56	11
	(0 °C)	20	2	2 months	63
(40 °C)	20	2	0.5	69	25
Bu <sup>n</sup> SH	20	2	3	72	25
	100	2	3	70	27
	40	20	1	71	8

<sup>a</sup> 100 × (mol of product)/0.5 × (mol of thiol used).

three compounds, when kept at room temperature for several days, gave dialkyl disulphides and trisulphides, with a corresponding decrease in the amount of sulphur dioxide and the formation of water. Yields of disulphides and trisulphides obtained under various conditions are shown in the Table.

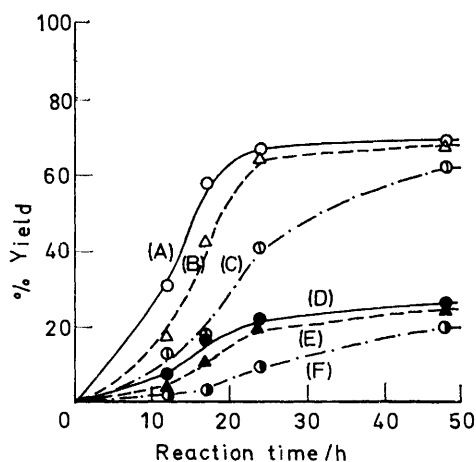


FIGURE 1 The concurrent formation of disulphide and trisulphide in the reaction of sulphur dioxide with n-propanethiol in the presence of triethylamine at 25 °C; initial amounts: PrSH, 40 mmol; SO<sub>2</sub>, 20 mmol; Et<sub>3</sub>N, 2 mmol. Curves (A) (B), and (C), yield of disulphide; (D), (E), and (F), yield of trisulphide; (A) and (D), without BQ; (B) and (E), with 0.4 mmol of BQ; (C) and (F), with 1.2 mmol of BQ

The concurrent formation of disulphides and trisulphides is demonstrated by Figure 1; a relatively small retardation effect in the presence of 1,4-benzoquinone (BQ) is also observed. One might suppose that the trisulphides are not products of the direct reaction of

sulphur dioxide with the thiols but are formed from disulphides through reactions such as in (1), or (2) and (3).



A mixture of a disulphide, triethylamine, and sulphur dioxide did not give any trisulphide or monosulphide after 2 days at 25 °C, so it is clear that reaction (1) does not occur. If sulphur dioxide is reduced to give elemental sulphur as shown in reaction (2), the reaction of a disulphide with elemental sulphur should give the trisulphide.<sup>2</sup> The reaction of di-n-propyl disulphide with elemental sulphur under similar conditions as for the reactions illustrated in Figure 1 was investigated and results are shown in Figure 2. These results indicate that the trisulphide is not produced *via* reactions (2) and (3) but by direct reaction of sulphur dioxide with the thiol, for the following reasons. (i) If the trisulphide is formed

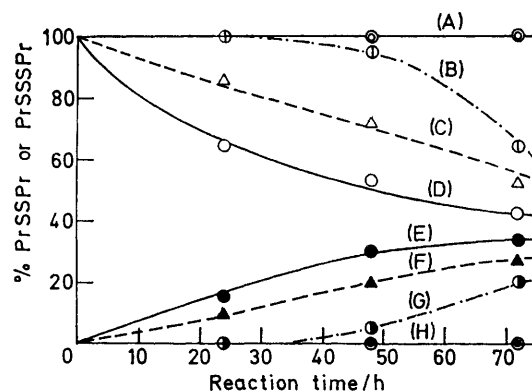


FIGURE 2 The reaction of di-n-propyl disulphide with elemental sulphur in the presence of triethylamine and sulphur dioxide at 25 °C; initial amounts: PrSSPr, 14 mmol; SO<sub>2</sub>, 20 mmol; Et<sub>3</sub>N, 2 mmol. Curves (A)–(D), 100 × [PrSSPr]<sub>t</sub>/[PrSSPr]<sub>0</sub>; (E)–(H), 100 × [PrSSSR]<sub>t</sub>/[PrSSPr]<sub>0</sub>; (D) and (E), without BQ; (C) and (F), with 0.04 mmol of BQ; (B) and (G), with 0.12 mmol of BQ; (A) and (H), with 1.2 mmol of BQ

through reactions (2) and (3), concurrent formation of di- and tri-sulphide (see Figure 1) should not be observed. (ii) For prolonged reaction times in the reactions illustrated in Figure 2 the total yield of disulphide and trisulphide is much less than 100%. However, in the reaction of sulphur dioxide with thiols in the presence of a small amount of amine the total yield is nearly 100% (Table; Figure 1). (iii) Elemental sulphur was not detected in the reaction of sulphur dioxide with thiols by t.l.c. (iv) Comparison of Figures 1 and 2 indicates a greater retardation effect by BQ in the reaction shown in Figure 2 than in that in Figure 1, and a pronounced induction period is observed in Figure 2 but not in Figure 1. When 1.2 mmol of BQ is used in the reaction shown in Figure 2, reaction could not be detected even after 3 days. These differences show that the two reactions must have different mechanisms.



reagents except sulphur dioxide was cooled in liquid nitrogen and degassed *in vacuo*, and sulphur dioxide was introduced. The reaction vessel was then immersed in a thermostat. In the reaction of sulphur dioxide with thiols, the mixture separated into two phases as the reaction proceeded. In contrast, in the reaction of disulphides with elemental sulphur the mixture was heterogeneous throughout. In both cases, at the end of the reaction 30–50 ml of chloroform was added to make a uniform solution, which was analysed by g.l.c.

**Separation and Identification of the Products.**—A mixture of the thiol (0.4 mol), sulphur dioxide (0.2 mol), and triethylamine (0.08 mol) was set aside at room temperature. Within several hours this solution split into two layers. After 6 h the upper layer was separated off, washed ( $\times 3$ ) with water, and distilled under reduced pressure to give pure disulphide and trisulphide.

Tetrasulphides were not detected in the products of the reaction of sulphur dioxide with thiols in the presence of triethylamine. In the reaction of disulphides with sulphur in the presence of sulphur dioxide and triethylamine, unidentified material was formed, in amounts so small that it was not isolated and identified.

The structures of the disulphides and trisulphides isolated were established on the basis of the following data (n.m.r. data are for solutions in carbon tetrachloride and i.r. data for neat liquids).

Diethyl disulphide:  $\delta$  1.32 (3 H, t,  $J$  7 Hz) and 2.66 (2 H, q,  $J$  7 Hz) (Found: C, 39.6; H, 8.1; S, 52.0%. Calc. for  $C_4H_{10}S_2$ : C, 39.3; H, 8.25; S, 52.5%). Diethyl trisulphide:  $\delta$  1.39 (3 H, t,  $J$  7 Hz) and 2.87 (2 H, q,  $J$  7 Hz);  $\nu_{\max}$  475  $cm^{-1}$  (S–S) (Found: C, 31.2; H, 6.5; S, 62.0%. Calc. for  $C_4H_{10}S_3$ : C, 31.1; H, 6.5; S, 62.3%). Di-n-propyl disulphide:  $\delta$  1.01 (3 H, t,  $J$  7 Hz, Me), 1.73 (2 H, sextet,  $J$  7 Hz,  $SCH_2CH_2Me$ ), and 2.66 (2 H, t,  $J$  7 Hz,  $SCH_2Et$ ) (Found: C, 47.9; H, 9.6; S, 42.5%. Calc. for  $C_6H_{14}S_2$ : C, 47.95; H, 9.4; S, 42.7%). Di-n-propyl trisulphide:  $\delta$  1.05 (3 H, t,  $J$  7 Hz,  $SCH_2CH_2Me$ ), 1.82 (2 H, sextet,  $J$  7 Hz,  $SCH_2CH_2-$

Me), and 2.87 (2 H, t,  $J$  7 Hz,  $SCH_2Et$ );  $\nu_{\max}$  475  $cm^{-1}$  (S–S) (Found: C, 39.75; H, 7.7; S, 52.9%. Calc. for  $C_6H_{14}S_3$ : C, 39.5; H, 7.7; S, 52.75%). Di-n-butyl disulphide:  $\delta$  0.97 (3 H, t,  $J$  7 Hz,  $S[CH_2]_3Me$ ), 1.1–1.9 (4 H, m,  $SCH_2CH_2CH_2Me$ ), and 2.66 (2 H, t,  $J$  7 Hz,  $SCH_2[CH_2]_2Me$ ) (Found: C, 53.7; H, 10.2; S, 35.6%. Calc. for  $C_8H_{18}S_2$ : C, 53.9; H, 10.2; S, 35.95%). Di-n-butyl trisulphide:  $\delta$  0.98 (3 H, t,  $J$  7 Hz,

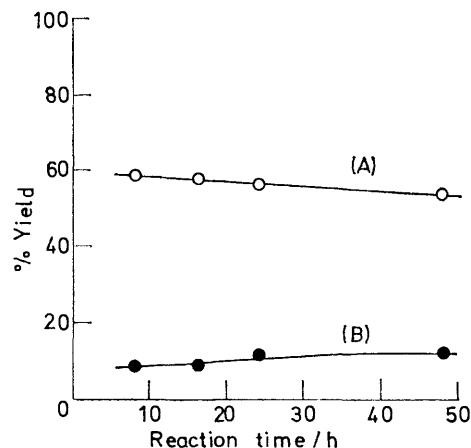


FIGURE 3 The reaction of sulphur dioxide with n-propanethiol in the presence of high concentration of triethylamine at 25 °C; initial amounts: PrSH, 40 mmol;  $SO_2$ , 40 mmol;  $Et_3N$ , 20 mmol. (A), yield of PrSSPr; (B), yield of PrSSSPr

$S[CH_2]_2Me$ ), 1.2–1.9 (4 H, m,  $SCH_2CH_2CH_2Me$ ), and 2.86 (2 H, t,  $J$  7 Hz,  $SCH_2[CH_2]_2Me$ );  $\nu_{\max}$  475  $cm^{-1}$  (S–S) (Found: C, 45.5; H, 8.3; S, 45.8%. Calc. for  $C_8H_{18}S_3$ : C, 45.7; H, 8.6; S, 45.7%). Diphenyl disulphide (Found: C, 66.5; H, 4.8; S, 29.8%. Calc. for  $C_{12}H_{10}S_2$ : C, 66.0; H, 4.6; S, 29.4%).

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