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,¹ dialkyl disulphides with sulphur in the

¹ G. R. Levi and A. Baroni, *Atti accad. Lincei*, 1929, 9, 772. ² H. E. Westlake, jun., H. L. Laquer, and C. P. Smith, *J. Amer. Chem. Soc.*, 1950, 72, 436. presence of amines,² Bunte salts with disodium disulphide,³ thiols with sulphur,⁴ and alkyl bromides with sodium thiosulphate.³ I describe here the reduction ³ B. Milligan, B. Saville, and J. M. Swan, *J. Chem. Soc.*, 1963, 3608.

⁴ 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 $^{\circ}$ 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 $^{\circ}$ C

	Deceta	nto luo mol		% Yield of the products ^a	
	Reactants/mmol		Time/		
	SO_2	$Et_{3}N$	day	RSSR	RSSSR
EtSH	20	2	3	72	28
	100	2	3	66	28
	4 0	20	1	40	17
Pr ⁿ SH	20	2	3	69	25
	100	2	3	69	27
	40	20	1	56	11
(0 °C)	20	2	2 months	63	25
(40 °Ć)	20	2	0.5	69	25
Bu ⁿ SH	20	2	3	72	25
	100	2	3	70	27
	40	20	1	71	8
. 100			0 5 / 1		

" 100 \times (mol of product)/0.5 \times (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.

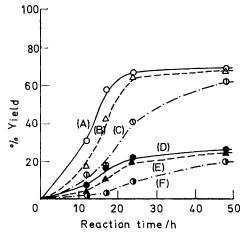


FIGURE 1 The concurrent formation of disulphide and trisulphide in the reaction of sulphur dioxide with n-propanethiol in the presence of triethylamine at 25 °C; initial amounts: PrSH, 40 mmol; SO₂, 20 mmol; Et₃N, 2 mmol. Curves (A) (B), and (C), yield of disulphide; (D), (E), and (F), yield of trisulphide; (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).

$$RSSR \longrightarrow 0.5 RSSSR + 0.5 RSR$$
 (1)

$$SO_2 + 4RSH \longrightarrow 2RSSR + S + 2H_2O$$
 (2)

$$RSSR + S \longrightarrow RSSSR$$
 (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.² 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

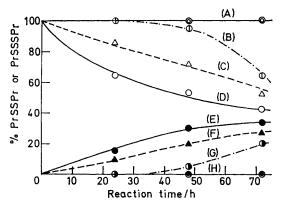
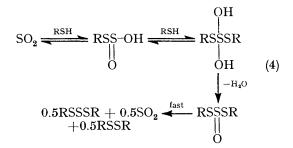


FIGURE 2 The reaction of di-n-propyl disulphide with elemental sulphur in the presence of triethylamine and sulphur dioxide at 25 °C; initial amounts: PrSSPr, 14 mmol; SO₂, 20 mmol; Et₃N, 2 mmol. Curves (A)—(D), 100 × [PrSSPr]_l/[PrSSPr]_o; (E)—(H), 100 × [PrSSPr]_l/[PrSSPr]_o; (D) and (E), without BQ; (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 diand 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.

Polysulphide exchange reactions have been investigated and both radical and ionic mechanisms have been proposed for them.^{2,5,6} The reaction conditions in the present study are different from those in these reports; the reaction is considered to be catalysed by a sulphur dioxide-triethylamine adduct since ten times as much sulphur dioxide as triethylamine is used. Since an induction period has been observed in similar reactions proceeding entirely by a radical mechanism ⁷⁻⁹ and in view of the above-mentioned special situation in the present study the present polysulphide exchange reaction must proceed mainly through a radical mechanism.

The fact that only a small retardation effect was observed in the reaction of sulphur dioxide with the thiols does not necessarily indicate a non-radical mechanism. However, the work of Field et al.,¹⁰ and Wallace et al.,¹¹ suggests that formation of an unstable intermediate catalysed by a sulphur dioxide-triethylamine adduct and its decomposition [equation (4)] are possible.



Formation of an unstable intermediate as in equation (4) is analogous to that in the reaction of carbonyl groups with thiols.¹²⁻¹⁴ The intermediate in these reactions decomposes to give an alkyl dithiosulphite, which rapidly decomposes to di- and tri-sulphides. Primary alkyl dithiosulphites have been reported to be unstable and to decompose easily to give equal amounts of di- and tri-sulphides.¹⁰ Even with this mechanism, a retardation effect by BQ can operate. Donbavand and Mockel have reported radical ion formation in a mixture of sulphur dioxide and triethylamine,¹⁵ and it is thus probable that BQ consumes the radical ion which catalyses the reaction.

If disulphide and trisulphide formation is due to the occurrence of reaction (4), the product should contain equal amounts of di- and tri-sulphides. However, as shown in the Table, the product consists of di- and trisulphides in a ratio of ca. 7:3. This fact suggests the

⁵ E. N. Gur'yanova, Vulkanizatsiya Resin Sbornik, 1954, 101

(Chem. Abs., 1958, **52**, 4227c). ⁶ C. D. Trivette, jun., and A. Y. Coran, J. Org. Chem., 1966, **31**, 100.

⁷ S. G. Foord, J. Chem. Soc., 1940, 48. ⁸ G. V. Schulz and H. Kammerer, Chem. Ber., 1947, **80**, 327.

⁹ P. D. Bartlett, G. S. Hammond, and H. Kwart, Discuss. Faraday Soc., 1947, 2, 342.
 ¹⁰ L. Field and W. B. Lacffield, J. Org. Chem., 1966, 31, 3555.

- ¹¹ T. J. Wallace and J. J. Mahon, J. Amer. Chem. Soc., 1964, 86, 4099.
 - ¹² E. Fromm, Annalen, 1889, 253, 135.
 ¹³ T. Posner, Ber., 1900, 33, 3165.

¹⁴ A. Recsei, Ber., 1927, 60, 1420.

existence of another route for the formation of the disulphides. In the formation of disulphides by the reaction of thiols with metal oxides the presence of thivl radicals has been suggested.¹⁶ Disulphide formation by a radical mechanism is conceivable to some extent in the present case also.

Another particular feature of the reaction of sulphur dioxide with thiols is that the product composition is independent of the reactant composition, as shown in the Table. Increase in the amount of sulphur dioxide does not lead to a corresponding increase in the yield of the trisulphides. The composition of the products in the reaction of sulphur dioxide with olefins or epoxides has been reported to be almost independent of the reactant composition,¹⁷⁻²⁰ and there have been several discussions of this behaviour.^{21,22} Although these reactions are between relatively simple components, no widely accepted explanation for constancy of the product composition has vet been established. A full explanation of such behaviour in the present case is being investigated.

For the reactions with high amine concentrations, transformation of disulphide into trisulphide appears to occur to small extent (Figure 3). In these cases the total yield of di- and tri-sulphides was less than 100% (Table). The reasons for this behaviour are not yet clear.

The reaction of 1,1-dimethylethanethiol with sulphur dioxide under the above-mentioned condition is very slow, and isolation of the product was not attempted. The reaction of benzenethiol with sulphur dioxide under similar conditions, was about ten times faster than that of n-alkanethiols. However, attempted isolation of diphenyl trisulphide was unsuccessful for the reasons mentioned by Field et al.¹⁰

Pyridine and picoline in place of triethylamine had a similar catalytic activity.

EXPERIMENTAL

Analyses .-- All analyses of reaction mixtures were performed on a Yanagimoto type G-8-T gas chromatograph. Analysis of disulphides and trisulphides using both a 0.7 m SE-30, 15% on Chromosorb W column, at 110 °C, and a 4.5 m ethyleneglycol adipate polyester, 20% on Chromosorb W column, at 125 or 140 °C, gave similar results so decomposition of the di- and tri-sulphides during analysis can be neglected. For quantitative analyses hexamethylbenzene was used as an internal standard.

General Procedure .--- Reactions were carried out in a 50 ml glass pressure vessel. The reaction vessel containing the

¹⁵ M. Donbavand and H. Mockel, Z. Naturforsch, 1973, 28a, 1258; 1974, 29b, 742. ¹⁶ T. J. Wallace, J. Org. Chem., 1966, **31**, 1217.

¹⁷ E. M. Fettes and F. O. Davis, in 'High Polymers,' ed. N. G. Gaylord, vol. 13, part III, Interscience, New York, 1962, p. 225. J. Schaefer, Macromolecules, 1968, 1, 111.

¹⁹ M. Matsuda, F. Akiyama, and Y. Hara, Kobunshi Ronbunshu, 1975, 32, 660.

²⁰ K. Soga, I. Hattori, J. Kinoshita, and S. Ikeda, J. Polymer Sci., Polymer Chem. Edn. 1977, 15, 745.
 ²¹ M. Matsuda, M. Iino, T. Hirayama, and T. Miyashita, Macro-

molecules, 1972, 5, 240.

²² R. E. Cais and J. H. O'Donnell, *Macromolecules*, 1976, 9, 279. R. E. Cais, J. H. O'Donnell, and F. A. Bovey, *ibid.*, 1977, 10, 255.

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: δ 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 C₄H₁₀S₂: C, 39.3; H, 8.25; S, 52.5%). Diethyl trisulphide: δ 1.39 (3 H, t, J 7 Hz) and 2.87 (2 H, q, J 7 Hz); ν_{max} . 475s cm⁻¹ (S-S) (Found: C, 31.2; H, 6.5; S, 62.0%. Calc. for C₄H₁₀S₃: C, 31.1; H, 6.5; S, 62.3%). Di-n-propyl disulphide: δ 1.01 (3 H, t, J 7 Hz, Me), 1.73 (2 H, sextet, J 7 Hz, SCH₂CH₂Me), and 2.66 (2 H, t, J 7 Hz, SCH₂Et) (Found: C, 47.9; H, 9.6; S, 42.5%. Calc. for C₆H₁₄S₂: C, 47.95; H, 9.4; S, 42.7%). Di-n-propyl trisulphide: δ 1.05 (3 H, t, J 7 Hz, SCH₂CH₂Me), 1.82 (2 H, sextet, J 7 Hz, SCH₂CH₂CH₂

Me), and 2.87 (2 H, t, J 7 Hz, SCH₂Et); ν_{max} . 475s cm⁻¹ (S-S) (Found: C, 39.75; H, 7.7; S, 52.9%. Calc. for C₆H₄₁S₃: C, 39.5; H, 7.7; S, 52.75%). Di-n-butyl disulphide: δ 0.97 (3 H, t, J 7 Hz, S[CH₂]₃Me), 1.1—1.9 (4H, m, SCH₂CH₂CH₂Me), and 2.66 (2 H, t, J 7 Hz, SCH₂[CH₂]₂Me) (Found: C, 53.7; H, 10.2; S, 35.6%. Calc. for C₈H₁₈S₂: C, 53.9; H, 10.2; S, 35.95%). Di-n-butyl trisulphide: δ 0.98 (3 H, t, J 7 Hz,

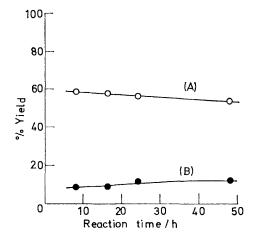


FIGURE 3 The reaction of sulphur dioxide with n-propanethiol in the presence of high concentration of triethylamine at 25 °C; initial amounts: PrSH, 40 mmol; SO₂, 40 mmol; Et₃N, 20 mmol. (A), yield of PrSSPr; (B), yield of PrSSSPr

$$\begin{split} & \mathrm{S}[\mathrm{CH}_2]_2 Me), \ 1.2 & --1.9 \ (4 \ \mathrm{H}, \ \mathrm{m}, \ \mathrm{S}\mathrm{CH}_2\mathrm{C}H_2\mathrm{C}H_2\mathrm{Me}), \ \mathrm{and} \ 2.86 \ (2 \\ & \mathrm{H}, \ \mathrm{t}, \ J \ 7 \ \mathrm{Hz}, \ \mathrm{S}\mathrm{CH}_2[\mathrm{CH}_2]_2\mathrm{Me}); \ \nu_{\mathrm{max}}, \ 475 \mathrm{s} \ \mathrm{cm}^{-1} \ (\mathrm{S}^{-}\mathrm{S}) \quad (\mathrm{Found}: \ \mathrm{C}, \ 45.5; \ \mathrm{H}, \ 8.3; \ \mathrm{S}, \ 45.8\%. \ \ \mathrm{Calc.} \ \mathrm{for} \ \mathrm{C}_8\mathrm{H}_{18}\mathrm{S}_3 \ \mathrm{C}, \ 45.7; \ \mathrm{H}, \ 8.6; \ \mathrm{S}, \ 45.7\%). \ \ \mathrm{Diphenyl} \ \mathrm{disulphide} \ (\mathrm{Found}: \ \mathrm{C}, \ 66.5; \ \mathrm{H}, \ 4.8; \ \mathrm{S}, \ 29.8\%. \ \ \mathrm{Calc.} \ \mathrm{for} \ \mathrm{C}_{12}\mathrm{H}_{10}\mathrm{S}_2 \ \mathrm{C}, \ 66.0; \ \mathrm{H}, \ 4.6; \ 29.4\%). \end{split}$$

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