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The Reaction of Sulfur Dioxide with Thiols Catalyzed by Boron Trifluoride Etherate. Evidence for a Possible Intervention of Dithiosulfite as a Reaction Intermediate

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The reaction of sulfur dioxide (SO_2) with 1-propanethiol (NPT), 2-propanethiol (IPT), or 2-methyl-2-propanethiol (TBT) catalyzed by boron trifluoride ethrate (BF_3OEt_2) was investigated. The ratios of dialkyl trisulfide to dialkyl disulfide obtained (RSSSR/RSSR) at an early stage of the reaction were larger than 1 for the reaction of TBT and less than 1 for the reaction of NPT or IPT. The reaction of dithiosulfites with BF_3OEt_2 in the presence or absence of thiol was investigated. From a consideration of the similarity of the composition of the sulfides formed in the reaction of dithiosulfites with BF_3OEt_2 to those in the reaction of SO_2 with thiol in the presence of BF_3OEt_2, the possibility of the intervention of dithiosulfite as a reaction intermediate in the reaction of SO_2 with thiol was discussed.

In previous papers it was reported that the reaction of SO_2 with 1-alkanethiols took place in the presence of tertiary amine or acids.[1] The reaction of SO_2 with thiols catalyzed by triethylamine or pyridine proceeded to only a small extent for the reaction of thiols with a secondary alkyl group adjacent to the SH group, and scarcely occurred for the reaction of thiols with a tertiary alkyl group.[2] The reaction mechanism of the reaction of SO_2 with thiols has not yet been elucidated, although a mechanism including dithiosulfite as one of the reaction intermediates has been proposed in previous papers.[1a,c] In the present report it is reported that the reaction of SO_2 with not only 1-alkanethiols, but also with thiols having a secondary or tertiary alkyl group, occurs in the presence of BF_3OEt_2. Also, evidence which suggests the possible intervention of dithiosulfite as one of the reaction intermediates is presented.

Results and Discussion

The yields of the products of the reaction of SO_2 with NPT, IPT, or TBT in the presence of BF_3OEt_2 are shown in Table 1. In this table the ratios of trisulfide to disulfide are calculated, and the decrease in the proportion of trisulfide and the increase in the proportion of disulfide as the reaction proceeds are shown. Since the reason for these changes was considered to be the disproportionation of the trisulfide formed, the reactions of dialkyl trisulfides with BF_3OEt_2 were carried out; the change in the composition with the reaction time is shown in Fig. 1. Contrary to the reported result in the literature that the homolitical disproportionation reaction of dialkyl trisulfide gave equal amounts of dialkyl di- and tetrasulfide,[3] Fig. 1 shows that the value of RSSSSR/RSSR given in the disproportionation by BF_3OEt_2 is in the order of R= *t*-Bu (0.7)>*i*-Pr (0.6)>*n*-Pr (0.3). In the reaction of dialkyl trisulfide with BF_3OEt_2, presumably not only the disproportionation of trisulfide to give di- and tetrasulfide, but also the removal of the sulfur atom from trisulfide to give disulfide preferentially, occurs. It is well known that the removal of sulfur atom from trisulfide to give disulfide occurs in the reaction of trisulfide with triphenylphosphine.[4] Table 1 indicates that the yields of tetrasulfide for the reactions of three sorts of thiols with SO_2 for a prolonged reaction time are in the order of R=*t*-Bu>*i*-Pr>*n*-Pr, which is same as that of the reaction shown in Fig. 1, although, the absolute amount of tetrasulfide is larger in Fig. 1 than in Table 1 because the reactions in Fig. 1 are carried out using pure trisulfide, while in the reactions in Table 1 trisulfide increases as the reaction proceeds. Therefore, the change in the composition of three sulfides during the reaction of SO_2 with thiol may be attributed to the disproportionation reaction of the

Table 1. Yields of the dialkyl sulfides from the reaction of SO_2 with alkanethiols in the presence of BF_3OEt_2 at 25 °C[a)]

RSH	BF_3OEt_2 (mmol)	Reaction time h	RSH (residual) (%)	Sulfides formed[b)]			Total (%)	RSSSR/RSSR
				RSSR (%)	RSSSR (%)	RSSSSR (%)		
n-PrSH	2	72	70.5	15.8	14.4	0	101	0.87
	20	0.4	36.2	33.7	29.5	0	99	0.87
	20	24	4.0	55.1	32.6	2.0	94	0.59
i-Pr	2	72	74.8	13.5	13.5	0	102	1.0
	20	0.4	84.1	7.7	6.0	0	98	0.78
	20	24	8.4	50.5	33.1	3.7	96	0.65
t-BuSH	2	72	79.0	1.0	1.8	6.8	89	1.80
	20	2.2	70.3	7.7	14.7	Trace	93	1.90
	20	48	5.7	39.6	32.2	10.2	88	0.81

a) 40 mmol of thiol and 20 mmol of SO_2 were used. b) 100× (mol of product)/0.5× (mol of thiol used).

Table 2. Yields of the dialkyl sulfides in the reaction of dialkyl dithiosulfites with BF_3OEt_2 in the presence or absence of thiol at 25 °C[a]

Entry	$\mathrm{RS\overset{O}{\overset{\|}{S}}SR}$ (mmol)	RSH (mmol)	BF_3OEt_2 (mmol)	Sulfides formed[b]		
				RSSR (mmol)	RSSSR (mmol)	RSSSSR (mmol)
1	R = Pr^i, 1	2	1	0.95	0.98	Trace
2	Pr^i, 1	0	1	0.44	0.21	0.09
3	R = Bu^t, 1	2	1	0.68	0.96	Trace
4[c]	Bu^t, 1	0	1	0.056	0.28	0.15[d]

a) Average values of two runs for each experiment are listed. The reactions were carried out in 2.9 ml of the CH_2Cl_2 solution. Although all of the dithiosulfite was consumed immediately after the addition of BF_3OEt_2, analyses were done 3 min after the addition of BF_3OEt_2 (The compositions did not depend on when analyses were done for several minutes after addition). b) No polysulfides higher than tetrasulfide were observed. c) Isobutene was identified in the gas over the reaction mixture. d) A explanation of the formation of the considerable amount of tetrasulfide is presented in Ref. 8.

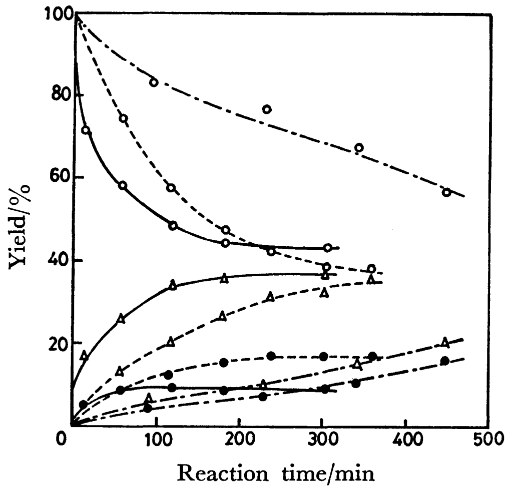
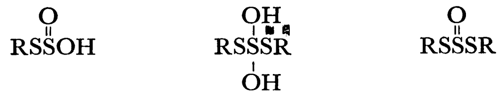


Fig. 1. Disproportionation reaction of dialkyl trisulfides catalyzed by BF_3OEt_2 to give disulfides and tetrasulfides in CH_2Cl_2 at 25 °C. $[RS_3R]=0.33$ mol/l, $[BF_3OEt_2]=0.33$ mol/l. ○: Decrease of RSSSR; △: increase of RSSR; ●: increase of RSSSSR. ——: R=*n*-Pr; -----: R=*i*-Pr; — — — —: R=*t*-Bu. Reactions were carried out in 3.0 ml of CH_2Cl_2 solution. Higher polysulfides than tetrasulfide were scarcely observed.

trisulfide formed. Therefore, the compositions of the products obtained at early stage of the reaction reflect the reaction mechanism of SO_2 with thiol.

The kinetics of the reaction of SO_2 with thiols is hampered by the acceleration of the reaction rate as the reaction proceeds, which disturbs the reaction and prevents it from fitting the first- or second-order rate law.[5] Although, in hope of seeing a signal of the reaction intermediates, the proton NMR of the reaction mixture was measured, there were no paticular signal other than those of the reactant, products, and catalyst. Kice *et al.* have reported that signals of the intermediates of the reaction of selenite with thiols were not observed.[6] Probably the concentration of the intermediates does not build up to a level sufficient to be detected because of the instability (*vide infra*) of the intermediates.

In a previous paper[1a] three sorts of reaction intermediates, I, II, and III, were proposed:

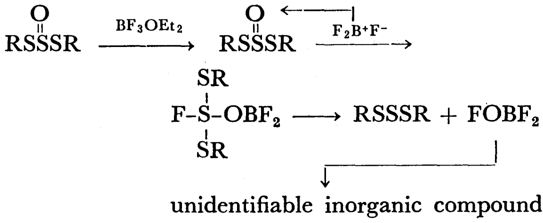


$$\mathrm{RS\overset{O}{\overset{\|}{S}}OH} \qquad \mathrm{RS\overset{OH}{\overset{|}{\underset{OH}{\underset{|}{S}}}}SR} \qquad \mathrm{RS\overset{O}{\overset{\|}{S}}SR}$$

I II III

Although there is no way to synthesize I or II, dithiosulfite(III), which seems to indicate the most stable compounds of the three structures, can be synthesized (dithiosulfite, having a primary alkyl group, can not be synthesized).[7] Since direct proofs (kinetic or spectroscopic observation of the reaction intermediates in the reaction mixture) were impossible, as has been mentioned above, indirect proof of the reaction intermediate, especially dithiosulfite(III), was attempted as follows. If dithiosulfite intervenes as a reaction intermediate, dithiosulfite may react with BF_3OEt_2 and/or thiol. Therefore, the reaction of dithiosulfites with BF_3OEt_2 in the presence or absence of thiol was tried; the results are shown in Table 2. This table indicates that the compositions of the products of the reaction of dithiosulfite with BF_3OEt_2 are similar to the composition at an early stage of the reaction of SO_2 with thiols (see Table 1) in the sense that the value of RSSSR/RSSR is larger than 1 for R=*t*-Bu and close to 1 or a little less than 1 for R=*i*-Pr. This fact suggests the possibility that one of the reaction intermediates is dithiosulfite.

Field and Lacefield have assumed that the lower decomposition velocity of dithiosulfites with a tertiary alkyl group than that of dithiosulfites with a secondary alkyl group could be attributed to a bimolecular decomposition mechanism.[7] Since the reaction of di-*t*-butyl dithiosulfite (TBDS) with TBT or another molecule of TBDS suffers steric hindrance, TBDS would have chance to react with BF_3OEt_2 without being attacked by TBT or another molecule of TBDS. The reduction of sulfoxide by acids such as hydrogen iodide,[9,10] phosphorus trichloride,[11] or phosphorus pentachloride,[12] has been reported to give monosulfide. If a similar reduction mechanism works also for the reaction of this dithiosulfite with BF_3OEt_2, the preferential formation of trisulfide in the reaction of TBDS with BF_3OEt_2 may be explained (Entries 3 and 4 in Table 2):

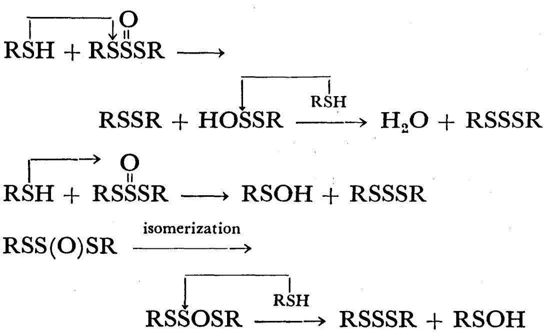


$$\mathrm{RS\overset{O}{\overset{\|}{S}}SR} \xrightarrow{BF_3OEt_2} \mathrm{RS\overset{O}{\overset{\|}{S}}SR} \xrightarrow{F_2B^+F^-} \mathrm{F\text{-}\overset{SR}{\underset{SR}{S}}\text{-}OBF_2} \longrightarrow \mathrm{RSSSR + FOBF_2} \quad (1)$$

$$\downarrow$$

unidentifiable inorganic compounds[13)]

The reaction of IPDS (Entry 1) or TBDS (Entry 3 in Table 2) in the presence of IPT or TBT, respectively, occurs by reaction paths other than Eq. 1 (a part of the TBDS would react with BF_3OEt_2 without being attacked by TBT even in the presence of TBT). The reaction schemes proposed by Kice *et al.* for the reaction of RSSe(O)SR with thiol[6)] are reasonable (2a—c):



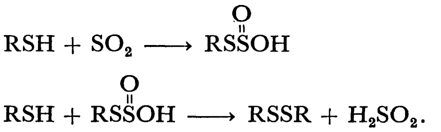
$$\mathrm{RSH + RS\overset{O}{\overset{\|}{S}}SR} \longrightarrow \mathrm{RSSR + HOSSR} \xrightarrow{RSH} \mathrm{H_2O + RSSSR} \quad (2a)$$

$$\mathrm{RSH + RS\overset{O}{\overset{\|}{S}}SR} \longrightarrow \mathrm{RSOH + RSSSR} \quad (2b)$$

$$\mathrm{RSS(O)SR} \xrightarrow{\text{isomerization}} \mathrm{RSSOSR} \xrightarrow{RSH} \mathrm{RSSSR + RSOH} \quad (2c)$$

Kice *et al.* considered that the reaction of thiol with RSSe(O)SR proceeded by a reaction of type 2b or 2c in order to interpret the formation of the thiosulfonic *S*-ester (RSO_2SR), which was considered to be formed from the reaction of RSOH. In the present reaction of SO_2 with thiol, the formation of the thiosulfonic *S*-ester was not observed at all.[14)] Therefore, dithiosulfite probably disappears by means of the process shown in Eq. 2a in the reaction in the presence of thiol. The reaction of TBDS most likely occurs by means of both Eqs. 1 and 2a: It gives a ratio of RSSSR/RSSR larger than 1. For the reaction of IPDS, Eq. 1 would not contribute so much: Instead, Eq 2a would contribute to a large extent.

If, in the reaction of NPT or IPT with SO_2, sulfides form through only the reaction of dithiosulfite (Eq. 2a), an equal amount of di- and trisulfide must form. However, a little larger amount of disulfide than trisulfide forms at an early stage of the reaction of NPT or IPT with SO_2. This fact suggests that a reaction path giving disulfide preferentially also most likely contributes to some extent. One possible reaction path is shown in Eq. 3:



$$\mathrm{RSH + SO_2} \longrightarrow \mathrm{RS\overset{O}{\overset{\|}{S}}OH} \quad (3a)$$

$$\mathrm{RSH + RS\overset{O}{\overset{\|}{S}}OH} \longrightarrow \mathrm{RSSR + H_2SO_2}. \quad (3b)$$

The reduction of SO_2 with 1-alkanethiol in the presence of an equal amount of triethylamine to give disulfide and thiosulfuric acid preferentially[15)] can be explained by means of Eq. 3 (Thiosulfuric acid forms by the reaction of H_2SO_2). A part of the reaction of NPT or IPT with SO_2 most likely passes through Eq. 3, even in the case of a reaction catalyzed by BF_3OEt_2. On the other hand, the reaction of TBT with SO_2 would not pass through Eq. 3, since the attack of TBT on the sulfenyl sulfur of RSS(O)OH (R=*t*-Bu) is suppressed because of steric hindrance between *t*-Bu groups of TBT and RSS(O)OH.

Finally, the aspects of the reaction of thiols with SO_2 catalyzed by BF_3OEt_2 may be summarized as follows. In the reaction of NPT or IPT with SO_2 the dithiosulfite formed decomposes through Eq. 2a, which gives equal amounts of di- and trisulfide. In addition to this reaction path, Eqs. 3a and 3b occur to some extent. Therefore, the value of RSSSR/RSSR at an early stage of the reaction of NPT or IPT with SO_2 is little less than 1. On the other hand, in the reaction of TBT with SO_2, the dithiosulfite formed decomposes through both Eqs. 1 and 2a. In this case, the reactions in Eq. 3 scarcely occur. Therefore, the value of RSSSR/RSSR at an early stage of the reaction of TBT with SO_2 is considerably larger than 1. In the reactions of three sorts of thiols with SO_2 the disproportionation reaction of trisulfide formed to give di- and tetrasulfide takes place as the reaction proceeds, giving a lesser value than 1 of RSSSR/RSSR at a prolonged reaction time.

Experimental

Procedure for the Reaction of SO_2 with Thiols Catalyzed by BF_3OEt_2. The reagents were introduced and the reaction was started by the same method reported in a preceding paper.[1c)] At an appropriate time, 20 ml of dichloromethane, appropriate amounts of hexamethylbenzene (an internal standard for sulfides), and cyclohexane (an internal standard for residual thiol) were added to make a uniform solution, which was then analyzed by means of GLC using SE-30, 15%, on a chromosorb W column.

Separation and Identification of Dialkyl Sulfides. Two mixtures, each of which contains thiol (80 mmol), BF_3OEt_2 (40 mmol), and SO_2 (40 mmol), were allowed to stand for 2 d. The upper layers of the two reaction mixtures thus obtained were combined and washed with water, a dilute alkaline aqueous solution, and water again: They were then dried over anhydrous magnesium sulfate and distilled to give pure di- and trisulfide. The structures of the disulfides and trisulfides isolated were established on the basis of the following data (the date for dipropyl di- and trisulfide were reported in Ref. 3):

Diisopropyl Disulfide: Bp 50—51 °C/6.5 mmHg (1 mmHg≈133.322 Pa) (lit,[16)] 54—55 °C/7.5 mmHg). $\delta(CDCl_3)=1.33$ (6H, d, $J=6.5$ Hz, 2Me), 3.05 (1H, septet, $J=6.5$ Hz, $SC\underline{H}(CH_3)_2$). Found: C, 47.70; H, 8.99; S, 42.25%. Calcd for $C_6H_{14}S_2$: C, 47.95; H, 9.39; S, 42.66%.

Diisopropyl Trisulfide: Bp 78—79 °C/6.5 mmHg (lit,[16)] 75—76 °C/5 mmHg). $\delta(CDCl_3)=1.41$ (6H, d, $J=6.5$ Hz, 2Me), 3.28 (1H, septet, $J=6.5$ Hz, $SC\underline{H}(CH_3)_2$), ν_{max} 500 cm^{-1} (S-S). Found: C, 39.23; H, 7.70; S, 52.30%. Calcd for $C_6H_{14}S_3$: C, 39,52; H, 7.74; S, 52.74%.

*Di-*t*-butyl Disulfide*: Bp 47 °C/1 mmHg (lit,[16)] 64 °C/5.5 mmHg). $\delta(CDCl_3)=1.30$ (s). Found C, 54.24; H, 10.07; S, 35.76%. Calcd for $C_8H_{18}S_2$: C, 53.87; H, 10.17; S, 35.95%.

*Di-*t*-butyl Trisulfide*: Bp 70—71 °C/1 mmHg (lit,[16)] 86 °C/

4 mmHg). δ($CDCl_3$) = 1.38 (s), ν_{max} 500 cm^{-1}. Found: C, 45.59; H, 8.41; S, 45.33%. Calcd for $C_8H_{18}S_3$: C, 45.66; H, 8.62; S, 45.71%.

Isolation of dialkyl tetrasulfides was not attempted, because the yields of tetrasulfide were quite low. Instead, the retention time in the glc of the compounds obtained in this study was compared with that of dialkyl tetrasulfides synthesized by literature method:[17,18] The results showed a good coincidence.

Preparation and Purification of Dithiosulfites. TBDS was synthesized and purified by the method of Field *et al.*[7] The compound purified by chromatography (on Florisil), which had a mp of 48.5—49.5 °C (lit,[7] 48—49.5 °C), NMR δ($CDCl_3$) = 1.56 (singlet) (lit,[7] 1.50) and IR 1105 cm^{-1} (lit,[7] 1110 cm^{-1}) was used for the reaction with BF_3OEt_2 without further recrystallization. IPDS was also synthesized by the same method.[7] Although Field *et al.* using crude IPDS without purification for their decomposition experiment,[7] their purification method using Florigil for TBDS was found to be also effective for IPDS. Purified IPDS (liq) showed NMR signals at δ($CDCl_3$) = 1.51 (doublet, 6H, J = 6.5 Hz) and at 3.66 (septet, 1H, J = 6.5 Hz), IR absorption at 1110 cm^{-1} (lit,[7] 1110 cm^{-1}). The preservation of purified IPDS as a $CDCl_3$ solution (10%) at room temperature for 10 d and at −20 °C for 4 months gave about 50% and only a slight decomposition respectively. Therefore, purified IPDS was used for the reaction with BF_3OEt_2 after preservation in a refrigerator (−20 °C) for a few days.

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5) Several authors have described decompositinn reactions of boron trifluoride with water, such as $2BF_3 + 3H_2O \rightarrow HBF_4 + 2HF + B(OH)_3$ (see A. V. Topchiev, S. V. Zavgorondnii, and Ya. M. Paushikin, "Boron Trifluoride and its Compounds as Catalysts in Organic Chemistry," International Series of Monographs on Organic Chemistry, ed by W. Doering and H. R. Barton, Pergamon Press, London (1957), Vol. 2, p. 46) and the decomposition of BF_3OEt_2 with water to give BF_3 and diethyl ether (see Y. Kawashima, H. Takeo, and C. Matsumura, *Chem. Phys. Lett.*, **57**, 145 (1978); *J. Mol. Spectrosc.*, **78**, 493 (1979)). Presumably water formed by the reduction of SO_2 decomposes BF_3OEt_2, thus resulting in the acceleration of the reaction rate.

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8) Although the origin of the formation of a considerable amount of tetrasulfide in the case of Entry 4 in Table 2 can not be explained on the basis of experimental proof, sulfoxide-sulfenate rearrangement (see E. G. Miller, O. R. Rayner, H. T. Thomas, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4861 (1968) and H. Mizuno, M. Matsuda, and M. Iino, *J. Org. Chem.*, **46**, 520 (1981)) or α-di-sulfoxide-sulfenyl sulfinate rearrangement (see M. M. Chau and J. L. Kice, *J. Am. Chem. Soc.*, **98**, 7711 (1976) and F. Freeman and C. N. Anglestakis, *ibid.*, **103**, 6232 (1981)) suggests the possibility that the following reaction occurs in the reaction of TBDS with BF_3OEt_2 in the absence of TBT:
RSS(O)SR$\rightleftharpoons$RSSOSR or
RSSS(O)R$\rightarrow$RSS· + ·OSR or ·S(O)R
RSS·$\rightarrow$0.5RSSSSR

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13) The treatment of the reaction mixture of TBDS with BF_3OEt_2 with a dilute aqueous sodium hydroxide solution, followed by the separation of aqueous layer and the evaporation of the layer, gave a white solid. IR spectra of this solid showed no contamination of organic compounds. The separation and identification of the inorganic boron compounds formed was unsuccessful.

14) One might suspect that the thiosulfonic *S*-ester was formed in the reaction of SO_2 with thiols, but decomposed after formation. When a mixture of 1 mmol of authentic *S-t*-butyl 2-methyl-2-propanethiosulfonate (for synthetic method: see Ref. 6), 2 mmol of TBT, 1 mmol of BF_3OEt_2, and 25 ml of CH_2Cl_2 was allowed to stand for 2 d at 25 °C, a decrease of only 10% of the concentration of the thiosulfonic *S*-ester was observed. This fact excludes the possibility of the formation of the thiosulfonic *S*-ester.

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