Tracer Study of the Reactions of Diphenyl Sulfone and Diphenyl Sulfoxide with Diphenyl Disulfide[1]

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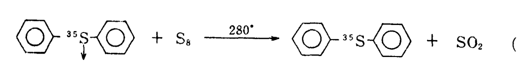
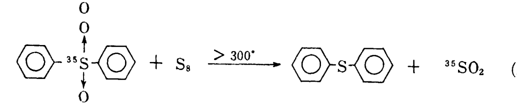
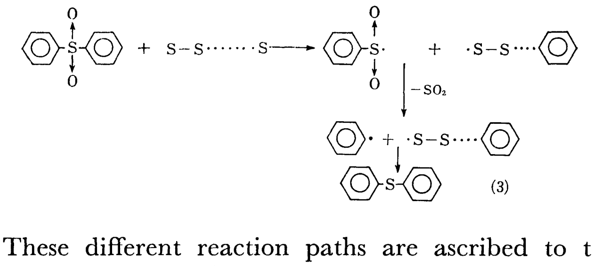
Diphenyl sulfoxide and diphenyl sulfone were found to react with diphenyl disulfide at elevated temperatures, forming in both reactions diphenyl sulfide and sulfur dioxide. On the basis of ^{35}S and ^{14}C tracer experiments, these reactions were found to proceed through quite different mechanistic routes, *viz.*, S–O bond fission in the case of sulfoxide and C–S bond fission in sulfone. The reactions apparently proceed through the attack of the thiyl radical on the sulfoxide and sulfone functions. Further mechanistic details of the reactions are discussed.

Diphenyl sulfoxide[2] and diphenyl sulfone[3] are known to react with elemental sulfur at elevated temperatures to yield diphenyl sulfide and sulfur dioxide.


(1)


(2)

We found through radio-active sulfur-35 tracer experiments that these two reactions, though yielding the same products, proceed through different mechanistic routes (Eqs. (1) and (2)).[2] In the case of sulfoxide the reaction is a straightforward reduction to give sulfide by the abstraction of labile oxygen atom with elemental sulfur. In the reaction of diphenyl sulfone, however, the sulfur atom of the sulfonyl group is replaced by that of elemental sulfur, apparently initiated by the attack of biradical chain of polymeric sulfur to cleave the C–S bond followed by the extrusion of sulfur dioxide and the formation of the sulfide (Eq. (3)).



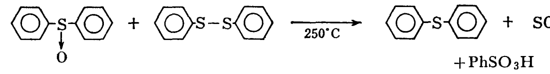
These different reaction paths are ascribed to the weaker bond strength of the S–O bond of the sulfoxide than that of sulfone. However, further mechanistic details of these reactions are not well understood, mainly because of the complicated nature of elemental sulfur at elevated temperatures.

Diphenyl sulfone is known to react with diphenyl disulfide at elevated temperatures to form diphenyl sulfide and sulfur dioxide.[3] We found that diphenyl sulfoxide also reacts with disulfide similarly. The reactions appear to serve as simple model reactions for making detailed mechanistic study of the reactions with elemental sulfur.

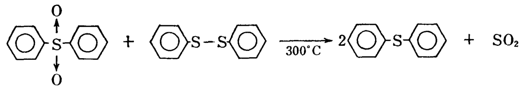
We have investigated the reactions of diphenyl sulfoxide and sulfone with diphenyl disulfide and present in this paper a detailed account of our investigation.

Results and Discussion

Diphenyl sulfoxide reacts nearly explosively with diphenyl disulfide at 250°C under nitrogen atmosphere giving diphenyl sulfide, sulfur dioxide, and a small amount of benzenesulfonic acid as shown in the following equation.


(4)

The reaction of diphenyl sulfone with diphenyl disulfide was shown by Kraft and Vorster to give diphenyl sulfide and sulfur dioxide in about 75% yield at about 300°C, a higher temperature than that for the reaction with sulfoxide.


(5)

^{35}S-Tracer Experiments. ^{35}S-tracer technique was very useful for showing that the reactions of sulfoxide and sulfone with elemental sulfur proceed through different mechanistic routes, and we have examined the reactions of sulfoxide and sulfone with diphenyl disulfide using sulfur-35 labeled diphenyl sulfoxide and diphenyl sulfone. The specific activities

Table 1. Tracer experiments

	Reactant cpm/mg	Product cpm/mg	Product / Reactant	Condition
I	8844[b]	7677[a]	86.8%	250°C (about 5 min)
II	22100[c]	481[a]	2.2%	310°C (30 min)
III	5250[a]	11[d]	0.0%	250°C (1 hr)
IV	2647[c]	507[a]	19.2%	310°C (30 min)

I: $Ph^{35}SOPh+PhSSPh$, II: $Ph^{35}SO_2Ph+PhSSPh$
III: $PhSOPh+Ph^{35}SPh$, IV: $PhSO_2Ph\text{-}^{14}C+PhSSPh$
a) Activity of formed sulfide (counted after being converted to sulfone).
b) Sulfoxide (counted after being converted to sulfone).
c) Sulfone.
d) Recovered sulfoxide.

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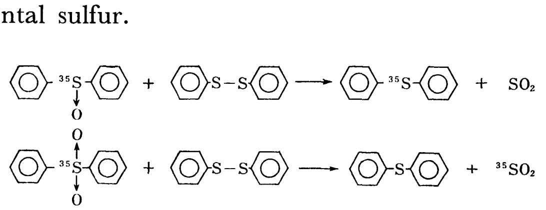
[1] Paper XXXV on Sulfoxide.
[2] S. Oae and S. Kawamura, This Bulletin, **36**, 163 (1963).
[3] F. Kraft and W. Vorster, *Ber.*, **26**, 2813 (1893).

of the reactants and the products were then counted, and the results are tabulated in Table 1.

Inspection of the data reveals that replacement of sulfur atom does not take place in the reaction of the sulfoxide (Eq. (6)) and the reaction is a reduction proceeding through the S–O bond fission.

In the case of the sulfone, the activity of the sulfide formed was only 2.2% of that of the original sulfone. As will be shown later, 19.2% of the sulfide resulted from the sulfone and the rest from diphenyl disulfide under this reaction condition. Nevertheless, these results suggest that replacement of sulfur atom occurs during the reaction, and not the S–O bond but the C–S bond of the sulfone is cleaved in the main path.

The results from the two tracer experiments are similar to those obtained from the reactions with elemental sulfur.



(6)

(7)

These different modes of reaction can be interpreted in terms of the difference of the bond strengths of the S–O linkages of the respective compounds. It is known that the force constant of the S–O bond in the sulfone calculated from the infrared data, 9.5×10^5 dyne/cm,[4a] is appreciably higher than that of the sulfoxide (7.0×10^5 dyne/cm). Thus, unlike the sulfoxide group, the sulfur-oxygen bond in the sulfone group is not easily cleaved.[4b]

Mechanism of the Reaction of Diphenyl Sulfoxide with Diphenyl Disulfide. Two mechanisms are conceivable for the relatively facile S–O bond cleavage of sulfoxide as shown in Fig. 1, the homolytic reductive cleavage of the sulfoxide bond induced by the benzenethiyl radical formed by the thermal dissociation of the sulfur-sulfur bond of diphenyl disulfide (path A), and the nucleophilic reaction between the sulfoxide and the disulfide (path B). The fact that the reaction temperature (250°C) is high enough to dissociate diphenyl disulfide into the corresponding radical[5] and that the reaction proceeds nearly explosively suggests the free radical chain mechanism to be more favorable.

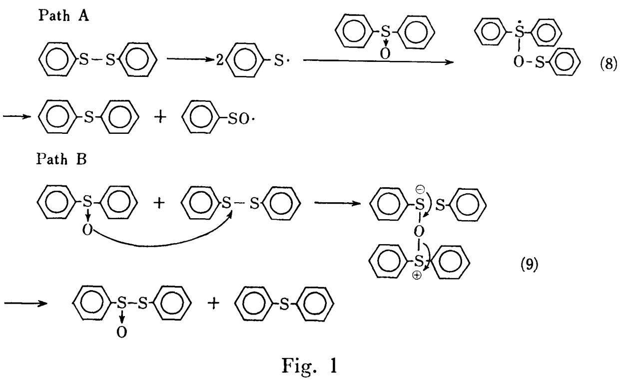
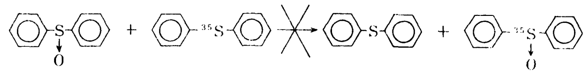


Fig. 1

Evidence to support path A may be found in the following observations. (1) Apparently, oxygen acts as an inhibitor. When nitrogen gas was not passed through the reaction system to sweep oxygen before heating, either a prolonged induction period was observed for this reaction or the reaction did not occur at all. (2) If the reaction proceeds through path B, it is reasonable to consider that an oxygen exchange reaction takes place between diphenyl sulfoxide and diphenyl sulfide as in the case with disulfide. However, by the ^{35}S tracer experiment no such exchange reaction was found to take place (Table 1). (3) A free radical induced reductive cleavage of semi-polar *N*-oxide bond has been reported.[6]



(10)

In view of these observations, the cleavage of the sulfoxide seems to proceed through the former path (path A) involving the attack of the benzenethiyl radical on the sulfoxide oxygen.

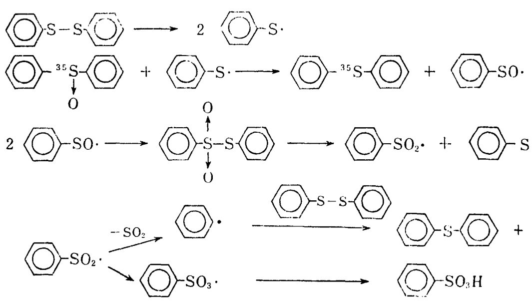


Fig. 2

The overall mechanism of the reaction is thus illustrated in Fig. 2. Phenylsulfinyl radical, PhSO·, has been considered to be rather long-lived[7] and known to undergo dimerization to give the corresponding thiolsulfonate.[7,8] However, thiolsulfonate thus formed would dissociate into $PhSO_2$· and PhS· radicals at these reaction temperatures. Desulfonylation[9] and disproportionation[10] of $PhSO_2$· radical have been known to occur readily. Desulfonylation of phenylsulfonyl radical leads to the formation of SO_2 and phenyl radical which would immediately be converted to diphenyl sulfide by the chain transfer reaction with diphenyl disulfide. By disproportionation both $PhSO_3$· and PhSO· radicals would result. Formation of a small amount of benzenesulfonic acid in the products may be rationalized on the basis of hydrogen abstraction with $PhSO_3$· radical.

According to this mechanism, the first step of the

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[4] a) These values are of alkyl sulfoxides and sulfones, C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, Inc., New York (1962), p. 66. b) *ibid.*, p. 132.

[5] a) G. Leandri and A. Tundo, *Ann. Chim.* (Rome), **44**, 63 (1954); *Chem. Abstr.*, **49**, 4563 (1955). b) J. G. D. Brandt and J. R. Davidson, *J. Chem. Soc.*, **1956**, 15.

[6] N. Inamoto, *Yuki Gosei Kagaku Kyokai Shi*, **17**, 174 (1959).

[7] S. Oae and K. Ikura, This Bulletin, **38**, 58 (1965).

[8] R. M. Topping and N. Kharasch, *Chem. Ind.* (London), **1961**, 178.

[9] For the decomposition of phenyl benzenthiolsulfonate; F. Kraft and O. Steiner, *Ber.*, **34**, 564 (1901).

[10] J. L. Kice and N. A. Favstritsky, *J. Org. Chem.*, **35**, 114 (1970).

reaction in Fig. 2 will afford radioactive sulfide, and the subsequent desulfonylation of thiolsulfonate will afford the nonactive sulfide. Thus, the specific activity of diphenyl sulfide formed will be reduced substantially as compared to the activity of the original sulfoxide. This is consistent with our experimental result (Table 1).

Mechanism of the Reaction of Diphenyl Sulfone with Dephenyl Disulfide. It is known that at these temperatures for the reaction of sulfone (300°C) diphenyl disulfide dissociates into a pair of benzenethiyl radicals, which then attack the original diphenyl disulfide, eventually giving rise to diphenyl sulfide and elemental sulfur in several steps.[11]

(11)

Since the reaction occurs nearly spontaneously at higher temperatures than that with diphenyl sulfoxide, the reaction of the sulfone with the disulfide is considered to proceed through a free radical process.[2] The following three paths involving the C–S bond fission are conceivable for the initial step of the reaction of diphenyl sulfone and diphenyl disulfide (Fig. 3), A) the attack of benzenethiyl radical formed from diphenyl disulfide at the sulfone function, B) the initial decomposition of diphenyl disulfide into the sulfide and polymeric sulfur, which in the subsequent step attacks the sulfone, C) both mechanisms occur concurrently.

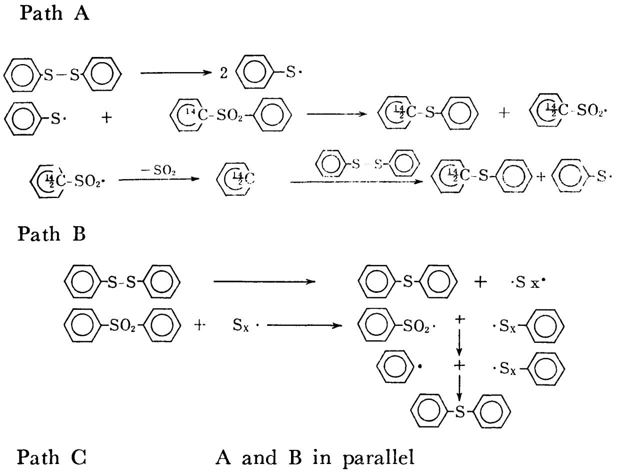

Fig. 3

In order to examine the possibility of the three conceivable mechanistic pathways, we first tried the reaction of diphenyl sulfone with bis(p-chlorophenyl)-disulfide, but this procedure was unsuccessful because of unexpected side reactions giving rise to many complicated products including chlorobenzene *etc.* Thus we adopted the reaction of carbon-14 labeled diphenyl sulfone with the disulfide. If the reaction proceeds through path A, the specific activity of the sulfide formed should be one half of that of the original sulfone at any time during the course of the reaction. The result given in Table 1 reveals that the sulfide formed has an activity corresponding to 19.2% of the original sulfone. This indicates that the mechanism A can be excluded. Of the two mechanisms B and C, the latter seems to be adequate on the basis of the following observations.

$$\underset{1.0}{\mathrm{PhSSPh}} \xrightarrow[21\ \mathrm{min}]{302^\circ\mathrm{C}} \underset{0.45}{\mathrm{PhSPh}} + \cdot\mathrm{Sx}\cdot \qquad (12)$$

$$\underset{1.0}{\mathrm{PhSO_2Ph}} + \underset{1.0}{\cdot\mathrm{Sx}\cdot} \longrightarrow \underset{0.10}{\mathrm{PhSPh}} + \mathrm{SO_2} \qquad (13)$$

$$\underset{1.0}{\mathrm{PhSO_2Ph}} + \underset{1.0}{\mathrm{PhSSPh}} \longrightarrow \underset{0.68}{\mathrm{PhSPh}} + \mathrm{SO_2} \quad (\times 10^{-3}\ \mathrm{mol}) \qquad (14)$$

Diphenyl disulfide, 1.0×10^{-3} mol, gave 0.45×10^{-3} mol of the sulfide and elemental sulfur at 302°C for 21 min, and equimolar (1.0×10^{-3} mol) amounts of the sulfone and elemental sulfur gave 0.10×10^{-3} mol of the sulfide under the same condition. If the reaction of the sulfone with the disulfide were to proceed through path B, the total amount of the sulfide formed should be less than $(0.45+0.1)\times10^{-3}=0.55\times10^{-3}$ mol, when equimolar (1.0×10^{-3} mol) amounts of the sulfone and the disulfide were reacted. However, 0.68×10^{-3} mol of the sulfide is actually formed.

The results cannot be explained on the assumption that the reaction proceeds through path B. Thus, it is reasonable to consider that both mechanisms A and B exist, namely, the attack of both benzenethiyl radical and the radical chain of elementary polymeric sulfur take place on the sulfone. Thus, the reaction of the sulfone proceeds through mechanism C.

Experimental

Diphenyl sulfide-^{35}S was prepared by Friedel-Crafts' reaction of benzene with radioactive sulfur in the presence of aluminium chloride according to the method[2] previously reported.

Diphenyl sulfoxide-^{35}S was prepared by the usual bromine oxidation of ^{35}S-labeled diphenyl sulfide.[12] From 4.6 g of the sulfide, the sulfoxide-^{35}S (mp 70.5°C) was obtained in 66% yield after repeated recrystallization from benzene-hexane.

Diphenyl sulfone-^{35}S was prepared by oxidizing diphenyl sulfide-^{35}S with potassium permanganate in glacial acetic acid. From 2.0 g of the sulfide, the sulfone-^{35}S (mp 123°C) was obtained in 80% yield.

Diphenylsulfone-1-^{14}C was prepared according to the procedure described elsewhere.[13]

Reaction of Diphenyl Sulfoxide with Diphenyl Disulfide. Diphenyl sulfoxide, 2.02 g, was thoroughly mixed with 1.09 g of diphenyl disulfide in a Claisen-flask and heated to about 100°C in order to melt the reactants. Dry nitrogen gas was bubbled through the liquid reaction mixture to remove any residual air. Then the flask was quickly put in a preheated silicon bath. In ten minutes the reaction took place nearly explosively and dark colored solution was formed with evolution of sulfur dioxide which was trapped in a few traps cooled with methanol - dry ice. The products were distilled *in vacuo*, and the distillate and the residue thus obtained were analyzed

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[11] C. Graebe, *Ann. Chem.*, **174**, 189 (1874).

[12] S. Oae, Y. Ohnishi, S. Kozuka, and W. Tagaki, This Bulletin, **39**, 364 (1966).

[13] S. Oae and N. Furukawa, *ibid.*, **39**, 2260 (1965).

by gas-liquid and column-elution chromatography, respectively. The distillate was found to be diphenyl sulfide alone. From the residue benzenesulfonic acid and a small amount of tarry substance were separated. Benzenesulfonic acid was identified as its thiouronium salt which has the same melting point and infrared spectrum as that of the authentic sample. The ^{35}S-tracer experiment was carried out similarly. The original sulfoxide having the specific activity of 8844 cpm/mg (converted to the sulfone) was treated with ordinary diphenyl disulfide. Diphenyl sulfide obtained was distilled repeatedly, usually two or three times, and then converted to diphenyl sulfone by the usual method (7677 cpm/mg).

Exchange Reaction of Diphenyl Sulfide-^{35}S and Diphenyl Sulfoxide. A mixture of diphenyl sulfide-^{35}S (5250 cpm/mg, converted to the sulfone), 1.03 g, and ordinary diphenyl sulfoxide, 1.12 g, was treated in the same way as in sulfoxide with disulfide. The reaction time was prolonged to 1 hr. After cooling the sulfide was distilled and the recovered sulfoxide was washed with *n*-hexane and recrystallized twice and the activity was counted (1.0 cpm/mg).

Reaction of Diphenyl Sulfone-^{35}S with Diphenyl Disulfide. Diphenyl sulfone-^{35}S (22100 cpm/mg), 1.09 g, was mixed with ordinary diphenyl disulfide, 1.09 g, in a Claisen flask and was put in a preheated air bath while nitrogen gas was passed through the reaction flask. After about 30 min, the flask was cooled down to room temperature and diphenyl sulfide formed was distilled *in vacuo* three times, and then converted to diphenyl sulfone by the usual method (481 cpm/mg).

Reaction of Diphenyl Sulfone-1-^{14}C with Diphenyl Disulfide. The reaction was carried out in the same way as in diphenyl sulfone-^{35}S. Diphenyl sulfone-1-^{14}C and diphenyl sulfide formed (converted into the sulfone) was found to have the activities of 2647 cpm/mg and 507 cpm/mg, respectively.

Estimation of the Conversions. The decomposition reaction of diphenyl disulfide was carried out at 302°C in degassed sealed tube in which 1.0×10^{-3} mol of the disulfide was placed with no solvent. A sealed tube was taken out from the silicon oil bath and cooled down to room temperature. The contents were then diluted with benzene to 10m*l* and the amount of diphenyl sulfide was determined by gas-liquid chromatography with biphenyl as an internal standard.

Conversion of the reactions of diphenyl disulfide (1.0×10^{-3} mol) and elemental sulfur (1.0×10^{-3} g atom) with diphenyl sulfone (1.0×10^{-3} mol) was determined similarly.

Counting of Radioactivities. The activities of all the compounds were counted by Packard Tri-Carb liquid scintillation counter, in toluene solution using POPOP as scintillator.

We are grateful to Dr. S. Kawamura of the Radiation Center of Osaka Prefecture, who kindly performed the counting of specific activities.