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The Tracer Study of the Reaction of Diphenyl Sulfone-1-^{14}C with Elemental Sulfur Using a Convenient Degradative Method

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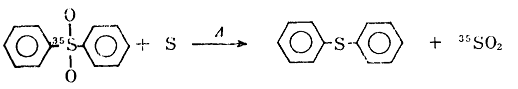
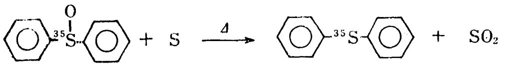
The reaction of diphenyl sulfone with elemental sulfur to give diphenyl sulfide and sulfur dioxide at above 300°C was investigated using diphenyl sulfone-1-^{14}C. By the degradation of the product, diphenyl sulfide-x-^{14}C, it was found that no migration of sulfide group took place. β-Naphthyl phenyl sulfone was also subjected to the same reaction, and not only β-naphthyl phenyl sulfide but also di-β-naphthyl sulfide and diphenyl sulfide were found among the products. These observations appear to indicate the reaction to be a rather simple displacement reaction that involves the initial attack of polymeric sulfur radical chain at C-1 bearing sulfonyl function.

Krafft and Vorster[1] showed that diphenyl sulfone reacts with elemental sulfur to form diphenyl sulfide and sulfur dioxide at elevated temperature. The mechanism of this reaction was recently investigated using ^{35}S-labeled compounds.[2] It was shown to involve the initial S–C bond cleavage of the sulfone and the subsequent replacement of sulfone group by elemental sulfur as shown by Eq. (1). The reaction of diphenyl sulfoxide with elemental sulfur proceeds through a simple reduction involving the cleavage of S–O bond as shown by Eq. (2). The difference between the above two reactions seem to be due to the fact that the force constant of the S–O bond of the sulfoxide is appreciably lower than that of the sulfone.[3]



(1)



(2)

We have extended the reaction with elemental sulfur to dibenzyl[4] and dibutyl[5] sulfones or sulfoxides. We have also studied the reaction of diphenyl sulfone and sulfoxide with diphenyl disulfide,[6] and found that in each case the weakest bond of the respective compound is cleaved by elemental sulfur radical chain at the initial stage of the reaction. An important remaining question is if there is any cross-over of phenyl group between diphenyl sulfone or sulfide during the reaction. If there is any cross-over of the phenyl group, the possibility of migration of the sulfide group arises, since the attack of polymeric sulfur radical chain at *o*- or *p*-position of diphenyl sulfone could eventually give rise to the sulfide.

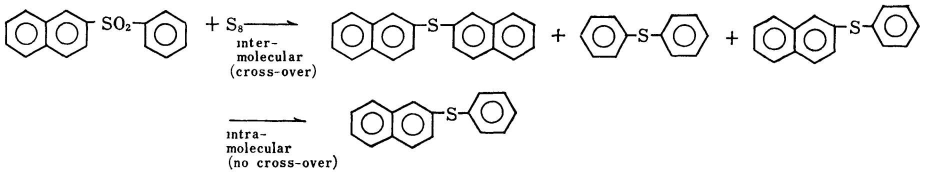
Thus, we have carried out a few critical experiments such as cross-over and ^{14}C tracer, by allowing β-naphthyl phenyl sulfone and diphenyl sulfone-1-^{14}C to react with elemental sulfur. We also examined the possibility of using the photolysis of diphenyl sulfone for a convenient method of degradation. This paper gives a detailed account and implications of these observations.

Results and Discussion

Reaction of β-Naphthyl Phenyl Sulfone with Sulfur. In order to examine the possibility of intermolecular cross-over of phenyl group in the reaction of diphenyl sulfone with sulfur, β-naphthyl phenyl sulfone was employed for the reaction. The reaction was carried out with equimolar amounts of the sulfone and elemental sulfur at a high temperature. The identification and analysis of the products were performed by means of gas chromatography.

If the reaction proceeded *via* an intermolecular process involving complete rupture of aryl-sulfur bonds, both diphenyl sulfide and β-dinaphthyl sulfide should be obtained among the products. If it proceeded without any cross-over of two aryl groups, β-naphthyl phenyl sulfide would be the sole product. (Eq. (3)).

Actually, from the product analysis, both diphenyl and di-β-naphthyl sulfides were obtained in 8% and 10% yields, respectively, along with β-naphthyl phenyl sulfide in 21% yield. Apparently the result indicates that there is some cross-over of aryl groups during the reaction, though the non-cross-over process is the predominant one.



(3)

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[1] F. Krafft and W. Vorster, *Ber.*, **26**, 2813 (1893).

[2] S. Oae and S. Kawamura, This Bulletin, **36**, 163 (1963).

[3] C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press Inc., New York (1962), p. 66.

[4] W. Tagaki, S. Kiso, and S. Oae, This Bulletin, **38**, 414 (1965).

[5] S. Kiso and S. Oae, *ibid.*, **40**, 1722 (1967).

[6] S. Oae, Y. Tsuchida, and H. Nakai, *ibid.*, **44**, 451 (1971).

TABLE 1.

Activity of diphenyl sulfone	Condition	Sulfide[a)] formed	Sulfone recovered	% of rearrangement[b)]
3020 cpm/mg	310°C, 1 hr	38.2%	26.6%	4.7%
3540 cpm/mg	320°C, 1 hr	45.7%	20.6%	5.7%

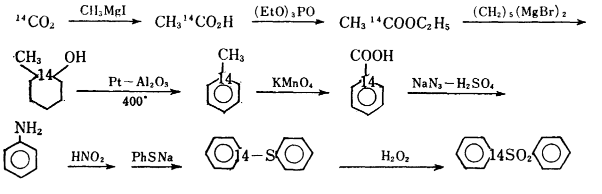
a) Assayed by transformation into diphenylsulfone. The yield was determined by means of the isotope dilution technique.
b) Calculated by Eq. (6).

TABLE 2.

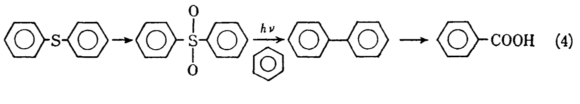
Activity of diphenyl sulfone	Condition	Yield of biphenyl	Activity of biphenyl	Activity of benzoic acid	% of rearrangement
4.62×10^5 dpm/mmol	15 hr, r.t. 0.3 g in 100 m*l* of benzene	27%	4.65×10^4 dpm/mmol	3.70×10^4 [a)] dpm/mmol	0.6%

a) Employed diphenyl sulfone the activity of which was originally placed in 80.2% at 1-position.

Reaction of Diphenyl Sulfone-1-^{14}C with Sulfur. The synthesis of diphenyl sulfone-1-^{14}C is outlined below.

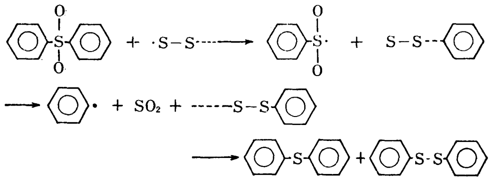


Diphenyl sulfone-1-^{14}C thus obtained was reacted with an equimolar amount of elemental sulfur at 310—320°C in nitrogen stream. Both the yield of diphenyl sulfide-*x*-^{14}C formed and diphenyl sulfone-*x*-^{14}C recovered were determined by the isotope dilution method. The degradation of diphenyl sulfide-*x*-^{14}C was carried out by the covenient process mentioned below (Eq. (4)). The results are shown in Table 1.



(4)

The result reveals that the amount of the ^{14}C rearrangement remains nearly the same in spite of the change of the reaction condition, though a slight difference is observed in the yield of diphenyl sulfide formed. Thus, the reaction of diphenyl sulfone with elemental sulfur appears to be a direct displacement reaction of the sulfone group by elemental sulfur, since the ratio of the rearrangement remains only about 5%. Besides diphenyl sulfide, a small amount of diphenyl disulfide and polymeric substance were formed in the reaction. Both the tracer experiments and previous results, suggest that the replacement of the sulfone group with sulfur atom involves the initial attack of sulfur biradical[7)] on the carbon atom bearing sulfone group, followed by the cleavage of C–S bond of the sulfonyl radical and the subsequent attack on another sulfone by polymeric sulfur chain biradical, giving rise to diphenyl sulfide and diphenyl disulfide. Thus a rough sketch of the overall reaction may be illustrated as shown below. (Eq. (5)).



(5)

Previously, the degradation of ^{14}C-labeled diphenyl sulfone was carried out by means of a rather tedious way of the initial alkaline fusion of the sulfone,[8)] followed by subsequent cleavage of phenol obtained.

Recently, it has been reported by Kharasch and Khodair that the photolysis of diphenyl sulfone in benzene at room temperature gave biphenyl in a good yield upon irradiation with 2537 Å light.[9)]

In order to test the possibility of using this reaction for a simple convenient degradation, diphenyl sulfone-1-^{14}C was subjected to photolysis to see whether or not the original activity at ^{14}C remains at the same position. The result of the degradation reveals that all the activity remains at the carboxyl carbon of benzoic acid (corresponding to 1-position of diphenyl sulfone) as shown in Table 2. The low yield of biphenyl appears to be caused by the use of low efficient irradiation. Biphenyl formed by the photolysis was diluted with an aliquot of inactive biphenyl and then oxidized by CrO_3 in acetic acid. The activity of benzoic acid thus obtained was compared with that of biphenyl. The percentage rearrangement of the activity at 1-position of the sulfide or the sulfone was calculated by the following equation.

$$\left(1-\frac{\text{Activity of benzoic acid}}{\text{Activity of biphenyl}}\right)\times 100 \qquad (6)$$

Thus, the photolysis of diphenyl sulfone in benzene was found to proceed through the mechanistic route proposed earlier by Kharasch and Khodair[9)] as shown by

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[7)] It is known that elemental sulfur behaves as a biradical chain at high temperatures and diphenyl sulfide is obtained together with by-products such as diphenyl disulfide, when a mixture of benzene and sulfur is heated at 350°C. W. A. Pryor, "Mechanism of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York (1962), p. 8; H. B. Glass and E. E. Reid, *J. Amer. Chem. Soc.*, **51**, 3428 (1929).

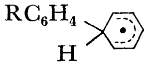
[8)] S. Oae and N. Furukawa, This Bulletin, **39**, 2260 (1966).

[9)] N. Kharasch and A. I. A. Khodair, *Chem. Commun.*, **1967**, 98.

Eq. (7).

$$RC_6H_4SO_2C_6H_4R \longrightarrow RC_6H_4\cdot + RC_6H_4SO_2\cdot$$

$$RC_6H_4\cdot + C_6H_6 \longrightarrow$$



(A)

$$\begin{array}{lll}(A) + RC_6H_4SO_2\cdot \longrightarrow & RC_6H_4C_6H_5 + RC_6H_4SO_2H\ (?) & \\ \quad (\text{or } RC_6H_4\cdot) & (\text{or } RC_6H_5) & \\ \quad (\text{where } R{=}H \text{ or } CH_3) & & (7)\end{array}$$

According to this mechanism no rearrangement of the activity at 1-position should take place during photolysis of the sulfone. Therefore, the photolysis of diphenyl sulfone is a quite suitable and convenient method for the degradation.

Experimental

Preparation of Diphenyl Sulfone-1-^{14}C. Diphenyl sulfone-1-^{14}C was synthesized through 9 steps starting from barium carbonate-^{14}C. The synthetic method was described elsewhere.[10]

Reaction of Diphenyl Sulfone-1-^{14}C with Sulfur. The reaction was carried out in the same way as for the previous cases:[2] diphenyl sulfone-1-^{14}C, (0.005 mol), was thoroughly mixed with 0.005 g atom of elemental sulfur in a Claisen-flask, which was quickly placed in a pre-heated metal-bath, nitrogen gas being passed through the reaction flask. The reaction started at 310 or 320°C (metal-bath temperature) and sulfur dioxide evolved was trapped in several traps cooled with dry-ice - acetone. After the reaction mixture was kept at around 310 or 320°C for 1 hr, it was dissolved in benzene into which known amount of inactive diphenyl sulfide and the sulfone was added in order to determine their yields by means of the isotope dilution method. When a clear benzene solution was concentrated, crystals of the sulfone deposited and were recrystallized from *n*-hexane - benzene two or three times. Diphenyl sulfide obtained was also repeatedly distilled until it became transparent, then was converted into diphenyl sulfone for ^{14}C-counting.

Reaction of β-Naphthyl phenyl Sulfone with Sulfur. The reaction was carried out in the same way as in the reaction of diphenyl sulfone-1-^{14}C with sulfur. Identification of the products was performed by means of gas chromatography (High Vacuum Silicon at 250 or 300°C).

The Degradation of Diphenyl Sulfide-x-*^{14}C.* Photolysis of the sulfone in benzene was carried out in the same way as that by Kharasch and Khodair:[9] photolysis of the sulfone (0.3 g) was carried out in 100 m*l* of benzene at room temperature for 15 hr, and gave biphenyl in 27% yield together with tarry by-products. The reaction mixture was treated with carbon disulfide, and a part dissolved in it was diluted with 0.5 g of inactive biphenyl. An aliquot (about 0.1 g) of the crude biphenyl was purified by sublimation and the rest was dissolved in 5 m*l* of acetic acid. To this solution was added a solution of 5 g of anhydrous chromic acid in 2 m*l* of water and 5 m*l* of acetic acid dropwise with stirring at 70—75°C. Carbon dioxide evolved during the oxidation. After the addition was complete, the contents of the flask was stirred for 1/2 hr at 70—75°C. The reactant was then quenched into 40 m*l* of water and extracted with ether. The ether layer was washed with water three times to remove acetic acid and then re-extracted with 5% alkali solution. The crude benzoic acid thus obtained was purified by sublimation. The benzoic acid was obtained in about 20% yield. Both benzoic acid and biphenyl were employed for counting of ^{14}C activity.

Measurement of the Activities. All the compounds were counted by a liquid scintillation counter (TEN), in toluene solution using POPOP as a scintilator.

We wish to thank Dr. M. Hamada and Dr. T. Nakabayashi of the Radiation Center of Osaka Prefecture for their advice, and for affording facilities for the measurement of the activities.

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[10] S. Oae, N. Furukawa, M. Kise, and M. Kawanishi, This Bulletin, **39**, 1212 (1966).