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The Reaction of Elemental Sulfur with Organic Compounds. VI.[1] ^{35}S-Tracer Study of Aromatic Displacement Reaction of Thianthrene, Phenoxathiin, Dibenzothiophene and Their Oxidation Compounds by Sulfur

Shigeru OAE, Shigeo MAKINO, and Yoshiyuki TSUCHIDA
Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka

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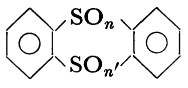
We reported on aromatic displacement reactions which take place when diphenyl sulfide, diphenyl sulfone,[2] and halobenzenes[3] are heated with elemental sulfur at elevated temperature as follows.

$$\mathrm{Ph^{35}SPh + S \longrightarrow Ph^{35/2}SPh + {}^{35/2}S} \qquad (1)$$

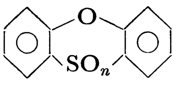
$$\mathrm{Ph^{35}SO_2Ph + S \longrightarrow PhSPh + {}^{35}SO_2} \qquad (2)$$

$$\mathrm{PhX + S \longrightarrow PhS_xPh + S_xX_2} \qquad (3)$$

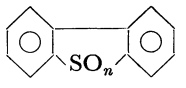
It is of interest that these three reactions essentially involve displacement of aromatic substituents (sulfonyl, sulfide groups and halogen) by a sulfur atom of elemental sulfur without any rearrangement or migration.[4] We have extended the investigation to reactions of elemental sulfur with a few polycyclic aromatic sulfur compounds, *i.e.*, thianthrene (**1**), phenoxathiin (**4**), dibenzothiophene (**7**), and their oxidation compounds (sulfones **2**, **5**, **8** and sulfoxides **3**, **6**, **9**). This paper will describe the reactions in detail.



1: $n=0$, $n'=0$
2: $n=2$, $n'=2$
3: $n=0$, $n'=1$



4: $n=0$
5: $n=2$
6: $n=1$



7: $n=0$
8: $n=2$
9: $n=1$

Sulfur Exchange Reaction of 1, 4, and 7 with Elemental Sulfur. The results of the tracer experiments using ^{35}S-labeled compounds are shown in the table. The sulfur exchange reaction was found to take place when **1**-^{35}S or **4**-^{35}S was heated with elemental sulfur at above 300°C. Under similar reaction condition **7** did not undergo such reaction, while prolonged heating of the reactant resulted in the formation of a polymer-like substance with evolution of H_2S. This is reasonable since the strength of C–S bond of **7** is increased by the intraresonance stabilization of the thiophene ring to retard the cleavage of C–S bond.

Reactions of 2, 5, and 8 with Sulfur. The reduction of **2** by elemental sulfur to **1** was reported earlier.[5] The reactions of **5** and **8** with elemental sulfur were found to proceed under the usual conditions giving the corresponding reduction compounds **4** and **7** respectively. The results of the tracer experiments of these reactions are also shown in the table. We see that the sulfonyl group in all the sulfones **2**, **5**, and **8** was replaced by sulfur atom of elemental sulfur in the main path of the reaction. The fact that these three reactions do not proceed *via* a simple reduction, namely the S–O bond cleavage of the sulfonyl group, can be attributed to the large bond strength of S–O bond in these sulfones.[6]

TABLE 1. ^{35}S-TRACER EXPERIMENT

Reactant ($\times 10^5$ cpm/mmol)	Product ($\times 10^5$ cpm/mmol)	Displacement of sulfur (%)	Reaction condition	Yield of product (%)
1 (5.23)[a]	**1** (4.44)	85.2	320°C 2 hr	69
4 (9.72)[a]	**4** (3.51)	72.0	330°C 2 hr	93
7 (8.87)[a]	**7** (0.015)	0.17	330°C 2.5 hr	14
2 (1.76)	**1** (0.34)	80.7	345°C 2.5 hr	66
5 (1.97)	**4** (0.21)	89.2	335°C 3 hr	18
8 (7.69)[a]	**7** (6.63)	87.0	320°C 2 hr	38
3 (8.97)	**1** (8.16)	9.0	250°C 30 min	75
6 (1.92)	**4** (1.90)	1.0	250°C 30 min	80
9 (7.67)[a]	**7** (0.012)	0.2	250°C 30 min	51

a) Radioactivity of elemental sulfur-35. In these reactions nonactive reactants (**1**, **4**, **7**, **8**, and **9**) were reacted with radio active elemental sulfur.

Reactions of 3, 6, and 9 with Sulfur. We carried out the reduction of the sulfoxides **3**, **6**, and **9** which have a weaker S–O bond than that of sulfone.[6] These sulfoxides were found to be reduced to the corresponding sulfides at somewhat lower temperatures than for the sulfones. The tracer experiments (Table) clearly suggest the reaction to be a simple reduction (S–O bond cleavage).

Mechanism of the Reaction. Sulfur is known to undergo homolytic cleavage of S–S bond at an elevated temperature and to exist as a mixture of many allotropes S_2, S_3, S_4, *etc.*[7] In these aromatic displacement reactions these allotropes of sulfur, which are expected to be active radical species, seem to be actually involved in the initial attack on the aromatic carbon atom bearing sulfur atom, although the subsequent steps are still unclarified. A plausible mechanistic pathway is as follows.

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[6] It is known that the force constant of S–O bond in sulfone 9.5×10^5 dyn/cm, is appreciably higher than that of sulfoxide (7.5×10^5 dyn/cm); C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, Inc., New York (1962), p. 66.

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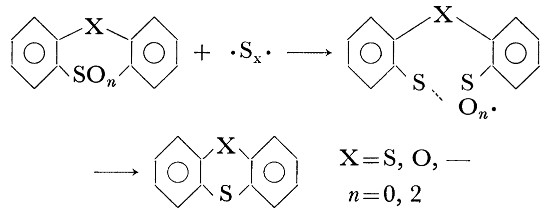

X = S, O, —

n = 0, 2

Experimental

Materials. Compounds **1**, **4**, and **7** were prepared by the usual method. **1**, mp 155°C (lit,[8] 159°C); **4**, mp 56.5°C (lit,[9] 57.5—58°C); **7**, mp 96°C (lit,[10] 99°C).

Radioactive **1**, **4**, and **7**. A mixture of **1** (3.04 g) and radioactive sulfur (0.90 g) was heated for 2 hr at *ca.* 330°C. The resulting mixture was poured into 10% aqueous NaOH solution and refluxed for 3 hr to remove elemental sulfur. The water insoluble **1**-^{35}S was filtered and recrystallized from methanol. Compound **4**-^{35}S was prepared similarly by the sulfur exchange reaction of **4** with radioactive elemental sulfur.

Radioactive **2**, **3**, **5**, and **6** were prepared by oxidation of **1**-^{35}S or **4**-^{35}S with a required amount of 30% H_2O_2 in acetic acid. **2**-^{35}S, mp above 300°C (lit,[11] 324°C); **3**-^{35}S, mp 137.5°C (lit,[12] 143°C); **5**-^{35}S, mp 143°C (lit,[13] 147—148°C); **6**-^{35}S, mp 150.5—151°C (lit,[13] 158—159°C).

Compounds **8** and **9** were similarly prepared from **7**. **8**, mp 227.5—228°C (lit,[14] 230°C); **9**, mp 185.5°C (lit,[15] 188°C).

*Reactions of **1**—**9** with Elemental Sulfur.* The reactions were carried out by the following general procedure. A mixture of 1 mmol of aromatic sulfur compound and 1 matom of sulfur (2 matom in the case of the reactions of **1** and **2**) was placed in a glass tube and heated in a metal bath. The resulting mixture was poured into 10% aqueous NaOH solution and refluxed for several hours. After cooling, the water insoluble precipitate was filtered and passed through a column elution chromatography (silica gel, hexane) and then recrystallized from alcohol for counting of activity.

Counting of Radioactivities. The activities of all the compounds were counted by TEN liquid scintillation counter in toluene solution using POPOP as a scintillator.

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