BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 2260—2263 (1966)

The Mechanism of the Alkaline Fusion of Diphenylsulfone[1]

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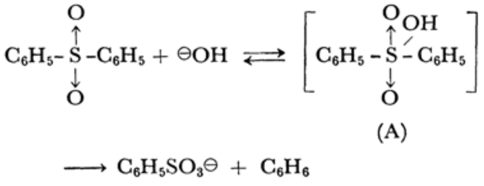
(Received February 7, 1966)

Diphenylsulfone-1-^{14}C was treated with fused potassium hydroxide at 300°C for 7 hr. in a sealed metal tube. The yield of phenol, as determined by the isotope dilution technique, was found to be almost quantitative. The distribution of ^{14}C in the resulting phenol was determined by degradating it by the usual method. Practically all the activity of ^{14}C in the phenol was found at the position 1, which corresponded to the originally-labeled position in the diphenylsulfone-1-^{14}C used. This indicates that the mechanism of the alkaline fusion of diphenylsulfone proceeds thruogh a simple S_N2-type mechanism, not the elimination-addition mechanism.

The treatment of diphenylsulfone with potassium hydroxide at a high temperature was first performed several decades ago by Otto,[2] who claimed to have obtained diphenyl and phenol as the main final products of the reaction. Many years later, Ingold and Jessop[3] studied the reaction more precisely; they observed that the main products of this reaction were benzene and benzenesulfonic acid. From the product analysis, they suggested that the mechanism of the reaction involved the primary attack of the hydroxide ion on the sulfur atom, thus expanding the valence shell to decet and forming an incipient complex that collapsed immediately to form the sulfonic acid and benzene, as is shown below.



$$C_6H_5-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-C_6H_5 + {}^{\ominus}OH \rightleftarrows \left[C_6H_5-\overset{\overset{O\ \ OH}{\uparrow\ /}}{\underset{\underset{O}{\downarrow}}{S}}-C_6H_5\right] \longrightarrow C_6H_5SO_3^{\ominus} + C_6H_6$$

(A)

Although the hypothesis of valence-shell expansion in the sulfur atom is very attractive in view of the many well-elucidated examples in other reactions,[4] it has to be tested with more rigorous experiments. We have previously investigated this reaction using ^{18}O-labeled potassium hydroxide[5] in order to test Ingold's mechanism; we found that there was no simultaneous ^{18}O incorporation in diphenyl sulfone during the reaction. This suggested that the reaction was a simple synchronous S_N2-type displacement reaction at the sulfur

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1) Phenols and Phenolic Esters. XII.

2) R. Otto, *Chem. Ber.*, **19**. 2425 (1886).

3) C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, **1930**, 708.

4) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York (1962).

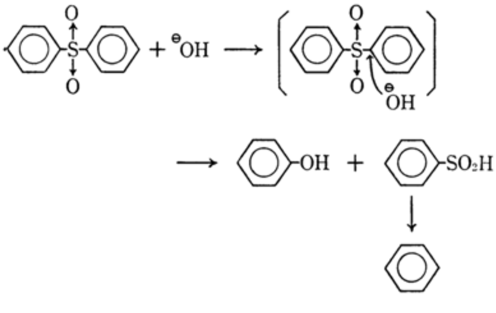
5) D. R. Christman and S. Oae, *Chem. & Ind.*, **1959**, 1251.

atom. However, all these past experiments do not give any hint as to the mechanism of the formation of phenol.

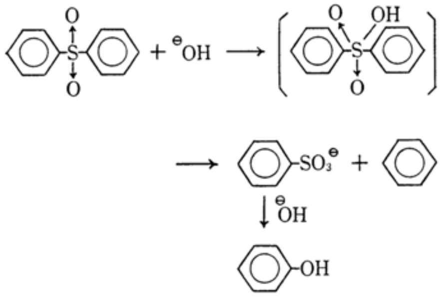
A question still remains whether phenol is formed directly by the nucleophilic attack on the sulfone group by the hydroxide anion (Mechanism I), or through the initial formation of benzenesulfonic acid, followed by substitution with the hydroxide anion (Mechanism II). Moreover, in such strong alkaline conditions as were used in the reaction, the elimination-addition mechanism involving a benzyne-type intermediate[6] also has to be considered (Mechanism III).

The three different mechanisms conceivable for the reaction may be summarized as follows:

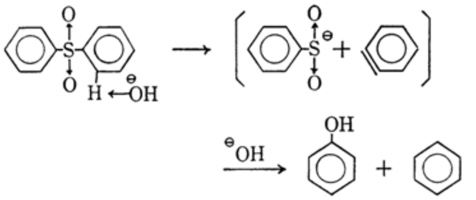
I. Simple S_N2-type mechanism:



II. Through-sulfonic-acid mechanism:



III. Elimination-addition mechanism:



Both the mechanisms I and III involve the formation of phenol and sulfinic acid, which eventually give benzene and which are quite reasonable since benzenesulfinic acid is known to decompose to benzene when treated with molten alkali at a relatively low temperature.[7] According to the mechanism II, benzene is formed, together with benzenesulfonic acid, which is then converted directly to phenol through a simple S_N2-type mechanism.[8] In this paper, we wish to present a detailed account of the mechanistic investigation of the alkaline fusion of diphenyl sulfone using the sulfone labeled with ^{14}C at position 1 of the benzene ring. When the reaction proceeds through the mechanism I or II, the ^{14}C activity in the phenol will be found only at the 1 position, whereas if the reaction proceeds through the mechanism III, half of the total ^{14}C activity in the phenol may be expected to be found at the 1 position, while the remaining 50% should be distributed equally between the 2 and 6 positions.

Results and Discussion

Diphenyl sulfone-1-^{14}C was synthesized according to the following scheme (Fig. 1):

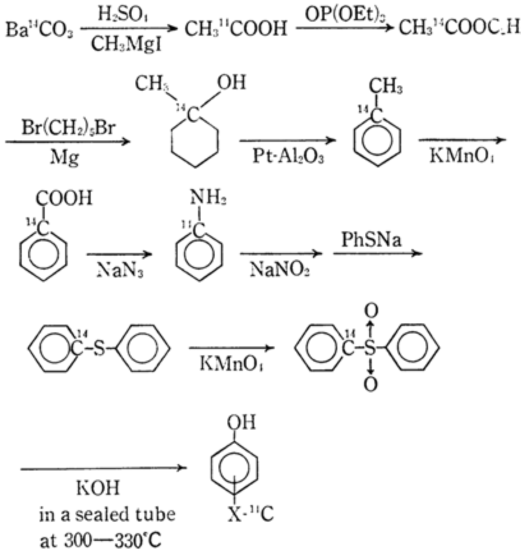


Fig. 1.

The method of degrading phenol is illustrated schematically in Fig. 2. A detailed account of the scheme has been presented elsewhere.[8] The yield of phenol was determined by the conventional isotopic dilution technique, which will be described in detail in the Experimental section.

The results of the degradation of the resulting phenol are shown below:

The results clearly indicate that all the ^{14}C activities of the phenol were found at position 1 of the sulfone where ^{14}C was originally labeled. This

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[6] See, for example, J. D. Roberts, H. E. Simmons, Jr., C. A. Carlsmith and C. W. Vaughan, *J. Am. Chem. Soc.*, **75**, 3290 (1953).

[7] R. Otto, *Ann*, **145**, 322 (1868).

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

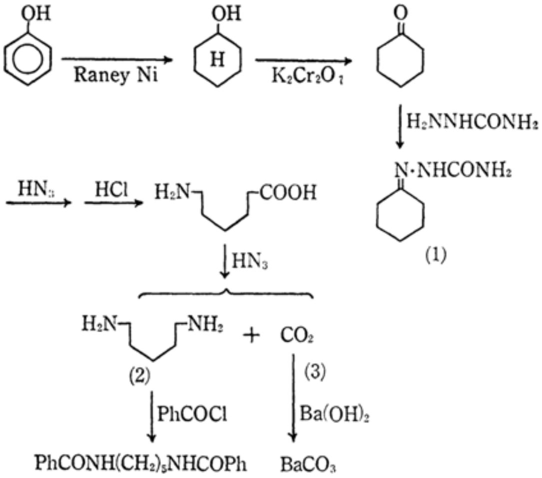
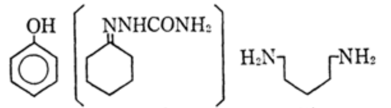
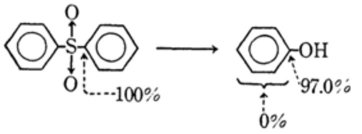


Fig. 2.

TABLE I. COUNTING DATA



	(1)	(2)	BaCO$_3$ (3)
c. p. m.	625 (729)[a]	0	4215 (703)[b]
%	100	0	96.4
c. p. m.	426 (497)[a]	—	2903 (484)[b]
%	100	—	97.4



a, b) The counts were corrected for background. The counts were recalculated as follows; for example, $625 \times 7/6 = 729$ and $4215 \times 1/6 = 703$.

excludes the elimination-addition mechanism involving a benzyne-type intermediate, since the mechanism requires half of the ^{14}C activities to be at the position 1, while the remaining half are divided equally between the two ortho positions.

Now that the mechanism III is excluded from the ^{14}C tracer experiment, the next problem is to make a choice between the mechanisms I and II. Earlier works related to nucleophilic substitutions on various aryl arylsulfonates suggest that the hydroxide ion prefers to attack the sulfone group rather than the aryl carbon.[9,10] Although a reaction in a fused alkali may be somewhat different from that in aqueous media, the same trend of nucleophilic selectivity would be found in both reactions, since the negative hydroxide ion attacks the positively-charged sulfur atom of the sulfone group more readily than the neutral benzene carbon. Moreover, the successful isolation of benzenesulfonic acid in the reaction by Ingold and his group, as well as by us, appears to suggest strongly that the hydroxide ion preferentially attacks at the sulfone group, as is illustrated by mechanism II.

Experimental

The Preparation of Diphenylsulfone

Aniline-1-^{14}C.—Aniline-1-^{14}C was synthesized starting from barium carbonate-^{14}C through 7 steps. The synthetic method has been described previously.[8]

Diphenylsulfide-1-^{14}C.—Thiophenol (3.0 g.) was dissolved in 40 ml. of a 20% potassium hydroxide solution. To this solution there was added benzenediazonium chloride-1-^{14}C prepared from 1.9 g. of aniline and 1.7 g. of sodium nitrite in 8 ml. of water, with the temperature kept at 70°C with vigorous stirring. After the addition had been completed, the mixture was stirred for 2 more hr. at the same temperature. Then the solution was extracted with ether. The ether solution was washed with water and dried over magnesium sulfate. After the ether had been evaporated, the residue was distilled under reduced pressure. Diphenylsulfide-1-^{14}C (2.8 g.) was thus obtained in a 76% yield (b. p. 124°C/3 mmHg).

Diphenylsulfone-1-^{14}C.—Diphenylsulfide-1-^{14}C (2.8 g.) was oxidized with 4.4 g. of potassium permanganate in 15 ml. of acetic acid. After the addition of potassium permanganate, the reaction mixture was warmed on a water bath for 1 hr. at 50°C. Then the mixture was quenched with a large amount of water. To this solution sulfur dioxide gas was introduced in order to decompose the excess potassium permanganate. The precipitate was then filtered and washed with water. The crude diphenylsulfone was recrystallized from *n*-hexane - benzene. The yield was 2.6 g. in a 81% yield (m. p. 128°C).

The Alkaline Fusion of Diphenylsulfone-1-^{14}C.—Diphenylsulfone-1-^{14}C (1.00 g.) was fused with 3.0 g. of potassium hydroxide in a small nickel tube which had a cork stopper equipped with a capillary tube to collect the benzene evolved. The tube was immersed in a potassium nitrate salt bath at the initial temperature of 240°C. Then the temperature was raised gradually to 300—330°C, at which temperature the reaction tube was kept for 7 hr. The reaction began at 250°C. After cooling, the reaction mixture was dissolved in water. To this mixture authentic phenol was added as a carrier. The mixture was acidified with concentrated hydrochloric acid, and then steam-distilled. The distillate was saturated with sodium chloride and extracted with ether, and the etheral solution was dried over magnesium sulfate. After the ether had evaporated off, the residue was distilled; phenol-*x*-^{14}C boiling at above 180°C was thus collected. The yield was determined by the isotope dilution method using the equation:

$$xS_0 = (a - x)S \qquad x = \frac{aS}{S_0 - S}$$

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[9] C. A. Bunton and Y. F. Frei, *J. Chem. Soc.*, **1956**, 3240.

[10] S. Oae and R. Kiritani, This Bulletin, **38**, 765 (1965).

where x is the unknown weight of the phenol produced, where S_0 and S are the ^{14}C activities in the initial and diluted phenol respectively, where S_0 represents the activity of the diphenyl sulfone-1-^{14}C available in the reaction, and where a is the authentic, weighed amount of pure phenol for dilution.

From the experimental figure (S_0: 9738 c. p. m.; S: 1448 c. p. m; a: 2.22 g.), x was calculated to be 0.39 g. (91% of the theoretical yield).

The Degradation of Phenol-*x*-^{14}C..—The degradation of phenol-*x*-^{14}C was carried out following a method described previously.[8)]

The counting of ^{14}C was performed according to the conventional Van-Slyke wet combustion method. The activities were measured for cyclohexanonesemicarbazone, barium carbonate and dibenzoyl pentamethylenediamine, with pellets of these samples weighing 132 mg., 181 mg., and 218 mg. respectively. The measurements of ^{14}C was performed with an Aloka 2π-gas flow G. M. counter, using Q-gas as the counting gas. The data are shown in Table I.