1038. *Action of Alkali Metals on Organic Sulphur Compounds. Part II.*[1] *The Cleavage of Diphenyl Sulphide by Potassium in Ethereal and Hydrocarbon Solvents.*

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Diphenyl sulphide is cleaved by potassium in 1,2-dimethoxyethane and hydrocarbon solvents with the primary formation of phenyl and thiophenoxide anions, and phenyl radicals. The cleavage is mainly anionic in 1,2-dimethoxyethane whereas in benzene 50% of the reaction proceeds by a one-electron radical mechanism.

In Part I[1] we showed quantitatively that thioanisole is cleaved mainly by a two-electron process in various organic solvents. In benzene, however, a small percentage of the reaction seemingly proceeded by a one-electron radical mechanism. Diphenyl sulphide is also easily cleaved by potassium in the same solvents, and our qualitative and semi-quantitative observations are shown in Table 1. The amounts of the compounds formed have been mainly determined by measuring the peak areas of vapour-phase chromatograms, so that the reported values are only approximate. Specific corrections, however, have been made for the results with benzene. We have also made measurements in chlorobenzene, the result of which are discussed below. The stoicheiometry of the reaction in 1,2-dimethoxyethane and in benzene has also been determined, using the method

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[1] Part I, *J.*, 1963, 2857.

TABLE 1.

Product of reaction of potassium with diphenylsulphide in various solvents.

Solvent	Products	Moles of product/100 moles of thioether consumed	
(MeO·CH$_2$)$_2$	Benzene	80—90	
	Biphenyl	4—5	
	Thiophenol	90—100	
			[a]
C$_6$H$_6$	Biphenyl + dihydrobiphenyl[b]	23 (4 : 1)	11 (16 : 1)
	Dibenzothiophen	0·5—1	10
	Thiophenol	90	71
	Benzoic acid	—	1
	Resins	[c]	[d]
		[a]	
Toluene	Benzene	15	
	Biphenyl + dihydrobiphenyl	2·2	
	Diphenylmethane	1·8	
	Bibenzyl	1·5	
	Dibenzothiophen	trace	
	Phenylacetic acid	32	
	Thiophenol	73	
	Resins	[d]	

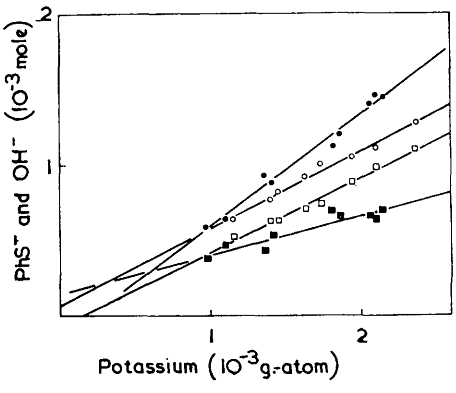
[a] After carboxylation of the reaction mixture with CO$_2$. [b] The figures in parentheses represent the approximate ratio of biphenyl to dihydrobiphenyl. [c] Small amount of unidentified resins. [d] Large amount of unidentified acidic resins.

TABLE 2.

Stoicheiometry of the cleavage of diphenyl sulphide by potassium in 1,2-dimethoxyethane and benzene.

Solvent	PhS$^-$: K	OH$^-$: K
(MeO·CH$_2$)$_2$	0·51 ± 0·03	0·49 ± 0·03
PhH	0·74 ± 0·03	0·25 ± 0·03

described in Part I.[1] The Figure shows the yields of products obtained with various amounts of potassium. The slopes of the lines are shown in Table 2, with probable errors of 5%. The ratios represent the number of moles of thiophenoxide ion and hydroxyl ion formed for each g.-atom of potassium consumed in the reaction. These results are best illustrated by the two reaction paths shown. The stoicheiometry in 1,2-dimethoxyethane shows that the reaction of diphenyl sulphide with potassium is mainly a two-electron cleavage [path (1) or (2) (3) in the Scheme] followed by the formation of a thiophenoxide ion and a phenyl carbanion which reacts with the solvent.* A small



Yield of hydroxide (squares) and thiophenoxide (circles) formed in the cleavage of diphenyl sulphide, as a function of potassium consumed, in 1,2-dimethoxyethane (open symbols) and benzene (full symbols) as solvent.

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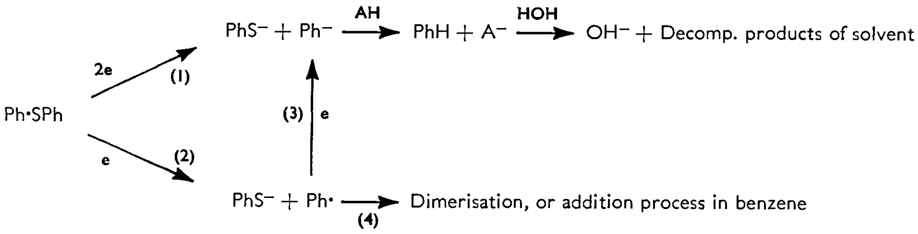
* The benzene detected in the products arose through attack on the solvent rather than by the decomposition of phenyl anion by alcohol in the working-up procedure, since (*a*) carboxylation of the filtered reaction mixture yielded no benzoic acid while gas-chromatographic analysis showed the expected amount of benzene, and (*b*) when water was used to hydrolyse the reaction mixture, gas-chromatographic analysis showed the expected amount of methanol. The action of the phenyl anion on 1,2-dimethoxyethane is thus presumably similar to that of the methyl anion discussed in Part I.[1]

fraction of the diphenyl sulphide is also cleaved by a radical mechanism as is demonstrated by the presence of biphenyl in the product. It seems reasonable to assume that 3—8% of the diphenyl sulphide is cleaved according to this scheme [path (2) below].



In benzene, the amount of phenyl radicals which becomes free of the metal surface is much larger and the stoicheiometric ratios can be accounted for by assuming that 49 ± 6% of the diphenyl sulphide is cleaved by a one-electron process. The amount of biphenyl found as product is in good agreement with the above value, within the experimental error. The dihydrobiphenyl * was thought to be formed mainly by the subsequent action of potassium on biphenyl, as was confirmed by a separate experiment, using pure biphenyl and potassium in benzene. The possible direct action of phenylpotassium on benzene [2] might also play some significant part in the formation of dihydrobiphenyl, depending on the reaction time. Luttringhaus *et al.*[3] described the action of phenylsodium on diphenyl sulphide at 70° in benzene, obtaining a 40% yield of dibenzothiophen. It seems reasonable to consider a similar reaction of phenylpotassium with diphenyl sulphide to account for the production of dibenzothiophen. We have no satisfactory explanation for the increased yield of dibenzothiophen found after carboxylation of the reaction mixture on solid carbon dioxide. In this respect, concordant observations were made on two separate experiments on a preparative scale. The minute yield of benzoic acid probably reflects the interaction of phenylpotassium with diphenyl sulphide and benzene. One can conclude, from the results in Table 1, that about 20% of the consumed diphenyl sulphide reacted without cleavage to produce acidic compounds after carboxylation.

In toluene, one might tentatively say that *ca.* one molecule in ten of diphenyl sulphide undergoes a one-electron cleavage. Our results are best described by the following equations:

$$\begin{aligned} \mathrm{Ph\cdot + Ph{\cdot}CH_3} &\longrightarrow \mathrm{PhH + Ph{\cdot}CH_2\cdot\ (or\ CH_3{\cdot}C_6H_4\cdot)} \\ \mathrm{Ph\cdot + Ph{\cdot}CH_2\cdot} &\longrightarrow \mathrm{Ph{\cdot}CH_2{\cdot}Ph} \\ \mathrm{2Ph{\cdot}CH_2\cdot} &\longrightarrow \mathrm{Ph{\cdot}CH_2{\cdot}CH_2{\cdot}Ph} \\ \mathrm{2Ph\cdot} &\longrightarrow \mathrm{Ph{\cdot}Ph} \end{aligned}$$

It is widely known [4] that phenyl radicals, generated by the thermal decomposition of benzoyl peroxide in solution, react with the solvent rather than dimerise. Dannley and Zatemsky [5] obtained a mixture of diphenylmethane and methylbiphenyls in toluene; these authors did not mention the presence of either biphenyl or bibenzyl. A different reaction-course might, however, be expected in our case owing to the essentially heterogenous character of the reaction.

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* It is evident that the side-reaction of potassium with biphenyl *decreases* the real PhS⁻ : K ratio. However, we estimate that the apparent stoicheiometric relation found in this work differs from the actual one by a constant *negative* term smaller than the experimental error (short reaction time).

[2] Morton and Lanpher, *J. Org. Chem.*, 1958, **23**, 1639.

[3] Luttringhaus, Wagner-v. Säaf, Sucker, and Borth, *Annalen*, 1945, **557**, 46.

[4] Walling, " Free Radicals in Solution," Wiley, New York, 1957, p. 482 and references therein.

[5] Dannley and Zaremsky, *J. Amer. Chem. Soc.*, 1955, **77**, 1588.

We had expected to find some 4-chlorobiphenyl[6] in the reaction of diphenyl sulphide with potassium in chlorobenzene. However, after 115 hr., less than 1% of the initial sulphide had been cleaved to form thiophenol, but about 40% of this sulphide (if not thiophenoxide) had reacted in some other manner. The predominant interaction must have taken place between chlorobenzene and potassium, as was demonstrated by comparison of the results with those of a blank experiment in which diphenyl sulphide was absent. In both cases, benzene, biphenyl, resinous residues, and potassium chloride were obtained in about the same amounts.

It is concluded that the cleavage of diphenyl sulphide by potassium is mainly anionic in 1,2-dimethoxyethane, whereas 50% of the reaction proceeds by a one-electron radical mechanism in benzene. In toluene, probably not more than 10% of the reaction proceeds by the latter mechanism.

EXPERIMENTAL

Some of the materials and methods have been described in Part I.[1] Diphenyl sulphide (Fluka " purum ") was distilled before use (b. p. 145—146°/12 mm.; n_D^{20} 1·6328). Analyses by gas-liquid chromatography (g.l.c.) were carried out on a Perkin-Elmer 116H Fraktometer, the reaction-mixtures being separated on a column of Apiezon grease (Perkin-Elmer Q). Although many different experiments were carried out in each of the solvents mentioned, only typical experiments are reorted below.

(i) *Reaction in* 1,2-*Dimethoxyethane*.—Diphenyl sulphide (0·080 mole) was added portionwise to a suspension of potassium (0·160 g.-atom) in 1,2-dimethoxyethane (200 ml.). The mixture, which assumed a blue-green colour, was stirred for 24 hr.* at room temperature. The excess of potassium (*ca.* 1%) was decomposed with methanol, water was added, and the mixture extracted with ether. The ether layer was washed with 2N-sodium hydroxide, dried, and the major part of the volatile products distilled at atmospheric pressure. Both the volatile fraction (b. p. <85°) and the residue were further fractionated by g.l.c. Benzene was obtained with an overall yield of *ca.* 0·065 mole. Biphenyl (0·004—0·005 mole) was identified in the residue by comparison with an authentic sample. About 8% of the biphenyl appeared as dihydrobiphenyl. No diphenyl sulphide was detected and no further peak appeared on the chromatogram at 240°. The aqueous layer was titrated potentiometrically with 0·1N-hydrochloric acid and showed only two waves, corresponding to hydroxide and thiophenoxide ion (0·074 mole). A little diphenyl disulphide (0·002 mole) was separated from the aqueous layer by filtration. Parallel titration of the thiophenol with 0·1N-iodine solutions gave results identical with those of the potentiometric method.

(ii) *Reaction in Benzene*.—With the same quantities of reactants and solvent as in (i), the mixture was stirred with glass chips for 3 days in a securely stoppered flask. The unreacted potassium (*ca.* 0·025 g.-atom) was determined on the basis of the hydrogen gas evolved after careful deomposition of the metal with isopropyl alcohol. The mixture was then worked up as above and the fractions were examined by g.l.c. Biphenyl (0·015 mole), dihydrobiphenyl (0·0037 mole), and dibenzothiophen (0·0005 mole) were identified. No unreacted diphenyl sulphide was detected and only a minute peak, representing less than 0·5% of the initial sulphide, remained unidentified. The aqueous phase was acidified with 2N-sulphuric acid and extracted with ether. After distillation of the solvent, only thiophenol (about 0·070 mole) was detected in the residue by g.l.c.

In another experiment, we observed that when the final reaction-mixture was filtered from benzene and taken up in 1,2-dimethoxyethane under nitrogen, a green solution was formed which displayed the characteristic nine-line paramagnetic resonance spectrum of the biphenyl radical anion.[7]

* It was shown in other experiments that 50% of the diphenyl sulphide reacted in *ca.* 2—3 hr.

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[6] Hey, *J.*, 1934, 1966.

[7] de Boer, *J. Chem. Phys.*, 1956, **25**, 190. The above result corroborates a previous observation made by Tesch and Hoffmann (Stamford Laboratory of the American Cyanamid Co.) on the appearance of the biphenyl radical-anion spectrum after potassium had reacted with diphenyl sulphide in 1,2-dimethoxyethane.

Carboxylation of the reaction-products in benzene. Diphenyl sulphide (0·065 mole) and potassium (0·11 g.-atom) in benzene (160 ml.) were allowed to react for 16 hr. The mixture was carboxylated and treated as described in Part I. Thiophenol (0·041 mole) and a resinous acidic residue (4·3 g.) were found in the aqueous layer. Benzoic acid (40 mg.), m. p. and mixed m. p. 121—122°, was obtained from the acidic resin by sublimation. A colourless amorphous solid separated on dissolving the resin in a few ml. of benzene; this product decomposed at 310° without melting and remained unidentified. Biphenyl (0·006 mole), dihydrobiphenyl (0·0004 mole), dibenzothiophen (0·0058 mole), and unreacted diphenyl sulphide (0·008 mole) were found in the organic " neutral " fraction. Dibenzothiophen was isolated by fractional crystallisation from ethanol after chromatographic purification of a benzene solution of the neutral residue on a short column of aluminium oxide; the colourless needles had m. p. and mixed m. p. 99—99·5° (Found: C, 78·5; H, 4·25; S, 17·75. Calc. for $C_{12}H_8S$: C, 78·2; H, 4·4; S, 17·4%).

(iii) *Reaction in Toluene.*—Diphenyl sulphide (0·06 mole) and potassium (0·12 g.-atom) in toluene (150 ml.) were allowed to react for 21 hr. at room temperature. After carboxylation on solid carbon dioxide, the reaction-mixture was worked up as described for the reaction in benzene. The neutral organic layer was roughly separated by distillation into a low- and a high-boiling fraction which were examined by g.l.c. Benzene (*ca.* 0·015 mole) was identified in the volatile fraction. The high-boiling fraction was shown to contain biphenyl and dihydrobiphenyl (0·0011 mole), diphenylmethane (possibly containing a mixture of methylbiphenyl isomers) (0·0009 mole), bibenzyl (0·0007 mole), diphenyl sulphide (0·012 mole), and traces of dibenzothiophen. All these compounds were identified by comparison with authentic samples. In the aqueous layer, the thiophenoxide was oxidised with a 0·5N-iodine solution and the resultant disulphide (0·037 mole) removed by ether extraction. An oily residue (4 g.), which solidified at room temperature, was extracted with ether from the remaining aqueous solution after acidification. Recrystallisation of the residue from water afforded phenylacetic acid (0·015 mole), m. p. and mixed m. p. 77—78°.

(iv) *Reaction in Chlorobenzene.*—A mixture of diphenyl sulphide (4·5 g.) and potassium (1·7 g.) in chlorobenzene (60 ml.) (run A), and a separate suspension of potassium (1·7 g.) in chlorobenzene (60 ml.) (run B), were stirred in tightly stoppered flasks for 115 hr. The reaction-mixtures were worked up in the usual manner. In the aqueous layers from both runs A and B, chloride was titrated with 0·1N-silver nitrate, using potassium chromate as indicator; the thiophenoxide was determined iodometrically in run A. The organic layers were examined by g.l.c. after a preliminary vacuum distillation to separate them from tarry residues. The following products (in g., run A figure first) were found (potassium consumed 1·64, 1·62): recovered diphenyl sulphide 2·92, —; benzene 0·71, 0·79; biphenyl 0·75, 0·39; thiophenol 0·01, —; potassium chloride 2·94, 288; resins 2·12, 1·40.

Quantitative Determinations.—The apparatus and method are essentially the same as those described in Part I.[1] Reaction-times were arbitrarily varied from 5 to 18 hr. in 1,2-dimethoxyethane, and from 20 to 24 hr. in benzene. The measurements were made with different concentrations of diphenyl sulphide (0·07—0·11 mole/l. in 1,2-dimethoxyethane; 0·07—0·17 mole/l. in benzene) and with different diphenyl sulphide to potassium ratios (in 1,2-dimethoxyethane: 0·5—2·5; in benzene: 0·5—1·1 moles of diphenyl sulphide/g.-atom of potassium).

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