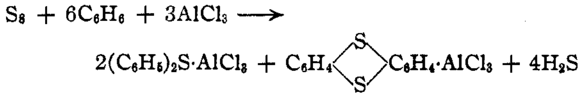
[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Reaction of Sulfur with Benzene in the Presence of Aluminum Chloride

BY GREGG DOUGHERTY AND PHILIP D. HAMMOND

When aluminum chloride is added to a solution of sulfur in benzene, a reaction is apparent at room temperature and is rapid at 80°.[1,2] The products reported are hydrogen sulfide, thiophenol, diphenyl sulfide, diphenylene disulfide or thianthrene and isothianthrene. Böeseken[3] has made the only systematic study of the reaction. In his experiments he varied the amount of benzene while keeping the amounts of sulfur and aluminum chloride constant. The only organic compounds formed in measurable quantities were diphenyl sulfide and thianthrene. The reaction was represented by the equation



$$S_8 + 6C_6H_6 + 3AlCl_3 \longrightarrow 2(C_6H_5)_2S\cdot AlCl_3 + C_6H_4\langle S_2 \rangle C_6H_4\cdot AlCl_3 + 4H_2S$$

Only for a short range, however, do his experimental results approximately fit the equation, that is, a ratio of two moles of diphenyl sulfide to one of thianthrene. Böeseken's experiments show that the yield of diphenyl sulfide is increased and that of thianthrene decreased as the benzene concentration is increased, although at all times the benzene was present in considerable excess.

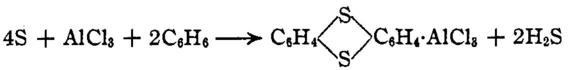
It seemed probable that considerable additional information concerning the mechanism of this reaction could be obtained by carrying out experiments similar to those of Böeseken but varying the amount of aluminum chloride while keeping the amounts of benzene and sulfur constant. In most of the present experiments, 250 cc. of benzene, 32 g. of sulfur and 0.1 to 1 mole of aluminum chloride were refluxed together at 80° for three hours. The products were the same as those noted by Böeseken. When the hydrogen sulfide evolved during a run was measured, it was found to be in no case less than an amount corresponding to the sulfur in the organic compounds. Furthermore, no hydrogen could be detected in the gas evolved during the reaction. It would seem then safe to postulate, as an over-all mechanism for the reaction, a process involving the elimination of one mole of hydrogen sulfide for every atom of sulfur fixed as diphenyl sulfide or thianthrene.

A very interesting observation had to do with the change in the relative quantities of diphenyl sulfide and thianthrene found as the amount of aluminum chloride was varied. This may be seen in Table I.

TABLE I

Run	1	2	3	4
Moles of $AlCl_3$	0.1	0.2	0.3	0.4
Moles of diphenyl sulfide	.032	.062	.147	.215
Moles of thianthrene	.1	.179	.125	.118
Run	5	6	7	8
Moles of $AlCl_3$	0.5	0.6	0.8	1.0
Moles of diphenyl sulfide	.310	.310	.361	0.350
Moles of thianthrene	.068	.068	.046	.053

Both sulfur compounds increased until the aluminum chloride concentration was between 0.2 and 0.3 mole. From that point the yield of diphenyl sulfide increased and that of thianthrene decreased as more aluminum chloride was added until the latter was present in an amount corresponding to 0.8 to 1.0 mole, after which the relative yields of the two compounds remained roughly constant. It was found that an optimum yield of thianthrene was obtained when 0.25 mole of aluminum chloride was used and, under these conditions, 0.183 mole of thianthrene was formed. An equation closely representing the best conditions for the formation of that compound would be therefore as follows



$$4S + AlCl_3 + 2C_6H_6 \longrightarrow C_6H_4\langle S_2 \rangle C_6H_4\cdot AlCl_3 + 2H_2S \qquad \text{(a)}$$

It was found, on the other hand, that if the aluminum chloride content was raised to 0.5 to 1 mole, and the sulfur added gradually to the reaction mixture, the product consisted entirely of diphenyl sulfide. This suggested the equation

$$4S + 2AlCl_3 + 4C_6H_6 \longrightarrow 2C_6H_5\text{—}S\text{—}C_6H_5\cdot AlCl_3 + 2H_2S \qquad \text{(b)}$$

Equation (b) indicates that in some way an excess of aluminum chloride prevents the formation of thianthrene and also that diphenyl sulfide might be an intermediate in the formation of that compound. Krafft and Vorster[4] found that when diphenyl sulfide and sulfur were heated together at 290° without a catalyst, a

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[1] C. Friedel and J. M. Crafts, *Ann. chim.*, [2] **14**, 437 (1888).

[2] M. P. Genvresse, *Bull. soc. chim.*, [3] **15**, 1038 (1896).

[3] Böeseken, *Rec. trav. chim.*, **24**, 221 (1905).

[4] Krafft and Vorster, *Ber.*, **26**, 2813 (1893).

good yield of diphenyl disulfide resulted. This was a useful clue in elaborating a more complete mechanism for the reaction. When 1 mole of diphenyl disulfide, 1 formula weight of sulfur and 1 mole of aluminum chloride were heated in ligroin solution, a nearly quantitative yield of thianthrene resulted. Also, an equally good yield of thianthrene was obtained when 1 mole of diphenyl sulfide, 1 mole of aluminum chloride and 2 formula weights of sulfur were allowed to react under the same conditions. Further, in both cases, an increase in the aluminum chloride content above 1 mole vitiated the result. This fact leads to the conclusion that free sulfur is necessary in these reactions, not an aluminum chloride complex. Such a complex is probably formed and would appear to be the active agent in the formation of diphenyl sulfide but it cannot react further to give thianthrene. The different steps in the whole process may be represented as follows. For diphenyl sulfide

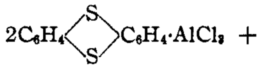
$$S_2 \cdot AlCl_3 + C_6H_6 \cdot AlCl_3 \longrightarrow C_6H_5{-}S{-}S{-}H \cdot AlCl_3 + AlCl_3 \quad (1)$$

$$C_6H_5{-}S{-}S{-}H \cdot AlCl_3 + C_6H_6 \cdot AlCl_3 \longrightarrow C_6H_5{-}S{-}C_6H_5 \cdot AlCl_3 + AlCl_3 + H_2S \quad (2)$$

For thianthrene

$$2C_6H_5{-}S{-}C_6H_5 \cdot AlCl_3 + S_2 \longrightarrow 2C_6H_5{-}S{-}S{-}C_6H_5 \cdot AlCl_3 \quad (3)$$

$$2C_6H_5{-}S{-}S{-}C_6H_5 \cdot AlCl_3 + S_2 \longrightarrow$$



$$2C_6H_4 \left\langle \begin{matrix} S \\ S \end{matrix} \right\rangle C_6H_4 \cdot AlCl_3 + 2H_2S \quad (4)$$

The use of binary compounds of aluminum chloride as reactants and resultants in the above is justified by the work of many investigators. No compound with benzene has ever been isolated but it is always assumed that the two do combine in a feeble way to give a reaction complex. The additive compounds with diphenyl sulfide and thianthrene were isolated by Böeseken.[3] Dissolved in benzene they give to the solution a deep blue color. Equation (1) above is hypothetical. However, it is preferred here to one representing thiophenol as an intermediate. The latter compound was never isolated in the present work although attempts were made to do so. Thiophenol and aluminum chloride do react to give diphenyl sulfide but the reaction is not particularly rapid, so that if it were a step in the process under investigation, one would have expected to find at least small amounts of the compound among the products. The evidence pointed to the existence of a much more active substance in the beginning stage of the reaction.

Experimental

In the experiments in Table I the diphenyl sulfide and thianthrene were isolated as follows: the reaction mixture was decomposed with 250 cc. of cold 10% hydrochloric acid. The benzene layer was washed with water and dried with calcium chloride. The benzene was removed from the dissolved sulfur compounds by distillation. Five hundred cc. of absolute alcohol was added to the mixed sulfur compounds and the thianthrene which separated was filtered off. The filtrate was distilled under reduced pressure, the diphenyl sulfide coming over at 115° at 3 mm. The residue remaining in the flask was also thianthrene and its weight was included in the total yield of thianthrene reported.

Conditions favoring thianthrene formation: a mixture of 40 g. of benzene, 200 cc. of carbon disulfide, 32 g. of sulfur and 33.5 g. of aluminum chloride was refluxed and stirred for twelve hours. The reaction mixture was decomposed, with dilute hydrochloric acid, the carbon disulfide steamed off and the residue taken up in benzene. The benzene extract was treated as above; yield 40 g.

Conditions favoring diphenyl sulfide formation: 134 g. of aluminum chloride was added to 250 cc. of benzene and the mixture was refluxed and stirred while adding slowly, over a period of three hours, 32 g. of sulfur. The heating was continued for three hours more. The reaction mixture was worked up in the usual way; yield 65 g.

Preparation of thianthrene from diphenyl disulfide and sulfur, and diphenyl sulfide and sulfur: stoichiometric amounts of the reactants together with aluminum chloride were heated at 80° in ligroin until the evolution of hydrogen sulfide had nearly ceased (about three hours). The reaction mixtures were decomposed with 10% hydrochloric acid, the ligroin steamed off, the residue dried and recrystallized from acetic acid; yields 95–100% of the theoretical.

Summary

A qualitative and semi-quantitative study of the reaction between benzene and sulfur in the presence of aluminum chloride was made. Under the conditions used, only the products, diphenyl sulfide and thianthrene, resulted and the ratio in which the two were formed was affected markedly by varying the aluminum chloride content. An attempt was made to indicate the probable course of the reaction.

PRINCETON, N. J.

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