133. *The Hydrogenation of Simple Sulphur Compounds. Part II. Reactions of Carbon Disulphide and Sulphur Dioxide.*

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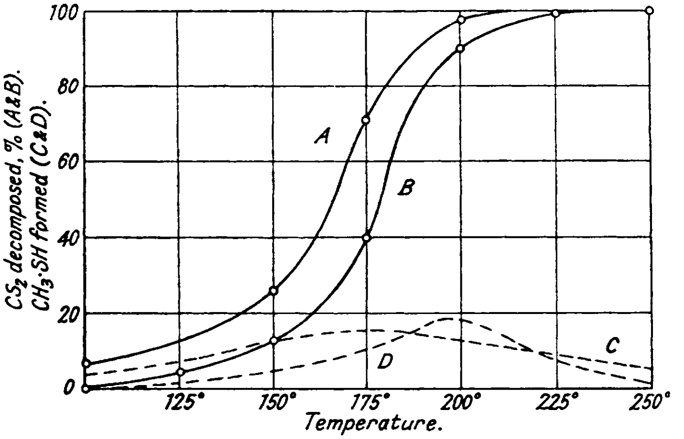
The hydrogenation of carbon disulphide with nickel subsulphide as the catalyst has been investigated at temperatures from 100° to 250°. The reaction is initially of the first order with respect to carbon disulphide, but is vigorously retarded by concentrations of this reagent such that hydrogen is still present in great excess.

The hydrogenation of sulphur dioxide with the same catalyst is also of the first order with respect to that reagent, slight retardation appearing at the higher concentrations. These observations are compared with adsorption data previously described, and the significance of the formation of methylthiol from carbon disulphide is discussed.

THE formation of methylthiol by the catalytic hydrogenation of carbon disulphide is suggested by Sabatier's observations (" Katalyse," 1927, p. 107) although the product was not identified. Evans and Stanier (*Proc. Roy. Soc.*, 1924, *A*, **105**, 626), on the other hand, concluded that the decomposition took place by formation of free carbon and hydrogen sulphide. Randall and Bichowsky (*J. Amer. Chem. Soc.*, 1918, **40**, 368) studied equilibria in the system $SO_2 + 3H_2 = 2H_2O + H_2S$, but no investigations have been described concerning the kinetics of either of these reactions, which form the subject of this communication.

Hydrogenation of Carbon Disulphide.—The catalyst used in these experiments was nickel subsulphide, Ni_3S_2, obtained as described in Part I (preceding paper). About 5 c.c. of catalyst space were used, or 1 c.c. at the highest temperatures, and the catalyst was heated electrically in a hard-glass tube, temperatures being measured by a platinum–platinum-rhodium couple embedded in it. The required mixtures of pure dry hydrogen and carbon disulphide vapour were prepared by use of the carburettor described by Chaplin and Cartwright (*J. Soc. Chem. Ind.*, 1937, **56**, 36T). The reaction products were examined for carbon disulphide, methylthiol, and hydrogen sulphide; the first was determined by alcoholic potash and iodine titration, the second as its silver compound after removal of hydrogen sulphide by iron oxide, and the last two together by silver nitrate. The rate of hydrogen passage was kept at 473 c.c./min., *i.e.*, 1 c. ft./hr., so that it was always present in great excess, and concentrations of sulphur compounds are expressed as mg. per c. ft., which is a convenient unit.

FIG. 1.



Decomposition of CS_2 *by hydrogen.*

A. *Initial* S *content* 8·0 *mg./c. ft.* ; % *of* CS_2 *decomposed.*
B. ,, ,, 20·7 ,, ,, ,,
C. ,, ,, 8·0 ,, *thiol formed.*
D. ,, ,, 20·7 ,, ,, ,,

In Fig. 1 are shown the results at temperatures between 100° and 250°, and in the table are given some further calculations. No attempt was made to determine the order of the reaction with respect to hydrogen, as the catalyst would not persist as Ni_3S_2 under conditions where an excess of carbon disulphide was present. It may be noted that the content of sulphur generally contained in purified coal gas as carbon disulphide is between 12 and 24 mg. per c. ft.

From these results it is evident that the reaction initially approaches the first order with respect to carbon disulphide, but that retardation rapidly sets in as the concentration of that reactant is increased, and after the reaction passes through a stage of apparent zero order, this retardation becomes very pronounced. As the appearance of methylthiol and hydrogen sulphide follows the same course, the retardation cannot be due to those products but must be caused by carbon disulphide itself.

Decomposition of carbon disulphide by hydrogen at 175°.

Inlet CS_2, mg./hr.	CS_2 decomposed, %.	Total CS_2 decomp. per hr., mg.	CH_3·SH formed, mg./hr.	H_2S formed, mg./hr.
9·2	70	6·44	1·51	5·57
22·6	39	8·82	2·86	6·97
36·3	22	8·0	2·75	6·19
48·5	8	3·9	1·84	3·09

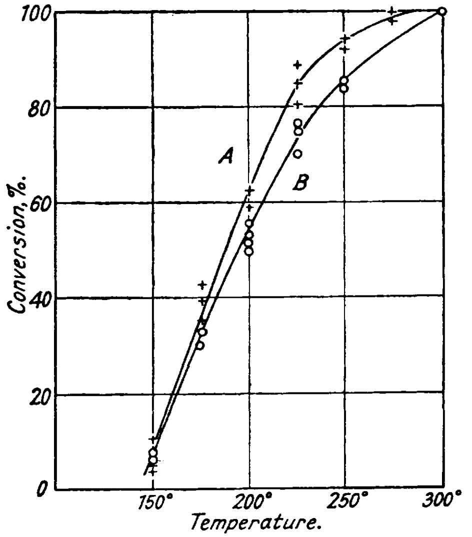
Formation of Methylthiol.—It has been found that the thiol is formed (1) at low temperatures as shown in the table, (2) at high temperature with a deficiency of hydrogen, or (3) at high temperatures with excess hydrogen and high space velocities. Although under condition (2) the catalyst will not remain wholly as Ni_3S_2 (see Part I), there is strong evidence from these observations that methylthiol is the primary hydrogenation product; other partly hydrogenated derivatives of carbon disulphide, such as thioformic acid or thioformaldehyde, cannot be isolated, and there is no evidence for the formation of free carbon.

Methylthiol can be conveniently prepared by passing hydrogen and carbon disulphide vapour in approximately equal volumes over nickel sulphide at 250—300°; 15 g. of catalyst will treat 200 c.c. of gas per minute. The products are freed from hydrogen sulphide by passage through iron oxide, and condensed by cooling with acetone–solid carbon dioxide, and the thiol is purified by fractionation as described in Part I.

In their study of the removal of sulphur compounds from naphtha by catalytic hydrogenation in the presence of nickel sulphide, Elgin, Wilder, and Taylor (*Ind. Eng. Chem.*, 1930, **22**, 1284) concluded that the process took place by formation of nickel sulphide and its reduction to nickel. The present results show that such a mechanism cannot apply to the hydrogenation of carbon disulphide with nickel subsulphide. If the rate-controlling step were the formation of NiS, retardation would not occur with higher carbon disulphide concentrations. Since this is the case, the rate of reaction would be controlled by the rate of reduction of NiS to Ni_3S_2. The maximum initial rate of formation of hydrogen sulphide from NiS can be calculated from the data of Part I as about 3 mg. per min. per g. of sulphide at 250°, whereas the rate of catalytic production of hydrogen sulphide from carbon disulphide at 250° was found to be only a few mg. per hour per g. of catalyst.

The results now described suggest that the reaction of carbon disulphide with hydrogen occurs in steps, leading to the formation of methylthiol as one of the intermediate products. The adsorption of both reagents is necessary for the primary reaction to take place, and the adsorption of the disulphide is so much more pronounced that it easily leads to complete covering of the catalyst surface and consequent retardation. In the further decomposition of the thiol formed, this substance also is adsorbed, but the kinetics of this reaction have not yet been investigated. Experiments with a smaller quantity of catalyst in the range 250—300° showed that the retarding effect of carbon disulphide persisted at the higher temperatures.

FIG. 2.



Hydrogenation of SO_2 *on* Ni_3S_2 *catalyst.*

A. *Inlet* S = 8·7 *mg./c. ft.*
B. ,, 21·5 ,,

Hydrogenation of Sulphur Dioxide.—The catalyst was prepared and heated as before, and hydrogen (dried and oxygen free) was supplied at 1 c. ft. per hour. The required concentration of dry sulphur dioxide was obtained by mixing with the main stream a small measured portion (5—10 c.c./min.) of another stream containing 300 c.c./min. of hydrogen and 5—10 c.c./min. of the dioxide. This procedure was adopted to avoid the measurement of very small rates of flow of the latter gas. The content of dioxide at the inlet to the reaction tube was checked at frequent intervals.

The outlet gas was led into excess of N/10-iodine solution, and the amounts of sulphur dioxide and hydrogen sulphide were determined by titration with thiosulphate and with alkali. No trace of sulphur was observed to separate at any stage of the investigation.

In Fig. 2 are shown the results at temperatures between 100° and 300°. It is clear that the reaction is of first order with respect to sulphur dioxide, with very slight but definite retardation at the higher concentration. This conclusion also agrees with the observations of adsorption of sulphur dioxide on the catalyst described in Part I, where the amount taken up was shown to be very much larger than the volume of hydrogen adsorbed, but somewhat smaller than was the case with carbon disulphide.

From the foregoing results it appears that excessive adsorption of one reactant on a catalyst is generally an undesirable condition, and an improved catalyst would be one on which relatively less extensive adsorption of such a reagent took place.

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