386. *The Hydrogenation of Simple Sulphur Compounds. Part III. Reactions of Carbonyl Sulphide and Methylthiol.*

By B. Crawley and R. H. Griffith.

The hydrogenation of carbon oxysulphide (carbonyl sulphide) has been studied between 125° and 200° with nickel subsulphide as the catalyst. From about 150° upwards, the reaction is of the first order with respect to carbon oxysulphide, but at lower temperatures some retardation occurs.

Hydrogenation of methylthiol is also of the first order with respect to the sulphur compound, at 200—300°. These results are compared with those previously obtained for carbon disulphide and sulphur dioxide, and are discussed with reference to data for the adsorption of the reactants on nickel subsulphide.

Part II of this series (this vol., p. 720) dealt with the hydrogenation of carbon disulphide and of sulphur dioxide in the presence of nickel subsulphide. The behaviour of carbon oxysulphide and of methylthiol under similar conditions has now been investigated.

EXPERIMENTAL.

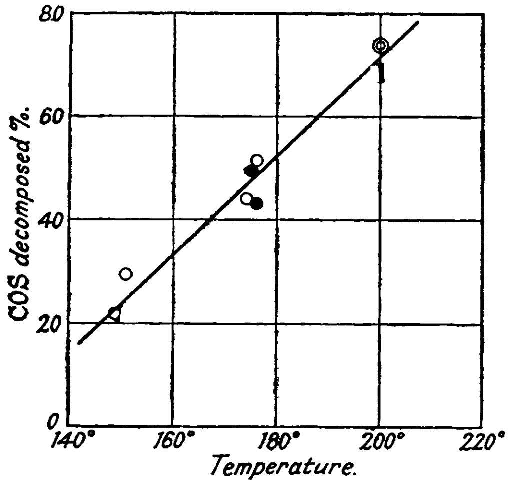
Catalyst pellets occupying 3 c.c. or less were heated as before. The required mixtures of pure dry hydrogen with the sulphur compounds were obtained by passing the gas through a wick carburettor (see following paper) containing liquid carbon oxysulphide or liquid methylthiol cooled to − 78°. Purification of the reactants was carried out by the methods described in Part I (this vol., p. 717). For hydrogenation of carbon oxysulphide, the hydrogen was passed at 236 c.c./min., equal to 0·5 cu. ft./hour; this is half the rate used in the previous experiments with carbon disulphide or sulphur dioxide, but the concentrations of the sulphur compounds were similar, with respect to the actual sulphur content, in all four series of experiments; in order to facilitate comparison, the present results are expressed in mg. per cu. ft. of gas. For hydrogenation of methylthiol the rate of hydrogen passage was 472 c.c./min.

In the preparation of methylthiol by the mild hydrogenation of carbon disulphide, it was found preferable to separate it from hydrogen sulphide by fractionation of the mixed liquids rather than by removal of hydrogen sulphide with a chemical reagent.

Hydrogenation of Carbon Oxysulphide.—The inlet concentration of carbon oxysulphide was determined by combustion of the gas leaving the carburettor, the products being absorbed in hydrogen peroxide solution (20 vols.), and the sulphuric acid formed being titrated with N/50-sodium hydroxide (cf. following paper). The gas leaving the catalyst tube was passed through cadmium acetate solution for determination of hydrogen sulphide, and was then burned as before. The figures thus obtained for total sulphur at inlet and outlet of the reaction tube generally showed a small loss of sulphur, but no trace of methylthiol could be detected in the products.

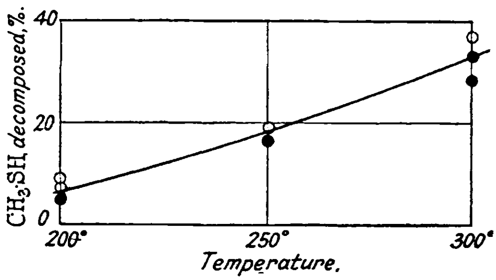
Two sets of experiments were carried out, 3 c.c. of catalyst space being used in one, and about half that quantity in the other, the concentration of carbon oxysulphide being varied from 23 to 47 mg. per cu. ft. The results of the second series are shown in Fig. 1 for two different concentrations of carbon oxysulphide, and the data from the first series appear in the table. It appears from these that, above about 150°, the reaction is of the first order with respect to carbon oxysulphide, but that at lower temperatures some retardation takes place and the reaction approaches zero order.

FIG. 1.



Hydrogenation of carbonyl sulphide.
Black circles : initial COS = 47 *mg./cu. ft.*
Open „ : „ = 23·5 „

FIG. 2.



Hydrogenation of methylthiol.
Black circles : initial CH_3·SH = 25 *mg./cu. ft.*
Open „ : „ = 14 „

As pointed out in relation to previous experiments with nickel subsulphide, it is not possible to investigate the effect of working with an excess of the sulphur compound and a deficiency of hydrogen because under such conditions the composition of the catalyst would not remain unchanged.

The precise cause of the retardation at low temperatures is not clear, but the following figures in conjunction with adsorption data (this vol., p. 717) suggest that it is due to van der Waals adsorption of carbon oxysulphide. When this type of adsorption ceases between 150° and 200°, the reaction takes place by collision of carbon oxysulphide with adsorbed hydrogen, and the reaction becomes of the first order with respect to the sulphur compound.

Hydrogenation of Carbon Oxysulphide.

Catalyst space, **3** c.c.

Temp.	Inlet COS, mg./cu. ft.	Outlet COS, mg./cu. ft.	Conversion of COS, mg./cu. ft.	Conversion of COS, %.	Temp.	Inlet COS, mg./cu. ft.	Outlet COS, mg./cu. ft.	Conversion of COS, mg./cu. ft.	Conversion of COS, %.
150°	43·9	9·4	34·5	78·6	150°	26·8	0	26·8	100
150	43·9	8·1	35·8	81·5	150	26·8	0	26·8	100
144·5	46·1	15·6	30·8	68·4	150	25·9	1·1	24·8	95·8
142	46·1	19·1	27·0	58·6	142	27·2	3·5	23·7	87·1
132·5	46·1	36·0	10·1	21·9	132	27·2	9·9	17·3	63·6
131	46·1	32·5	13·6	29·5	125	27·6	13·5	14·1	51·1
125	46·9	36·6	10·3	22·0	125	27·6	15·5	12·1	43·8
125	46·9	40·1	6·8	14·5					

In comparison with carbon disulphide, carbon oxysulphide reacts almost equally readily with hydrogen when there is a low concentration of sulphur in the system, but more quickly at high concentration on account of the vigorous retardation caused by covering of the catalyst by carbon disulphide. If the two sulphur compounds were in competition, however, there is no doubt that carbon disulphide would suppress the hydrogenation of carbon oxysulphide very appreciably by limiting the space available for adsorption of hydrogen. The experimental investigation of such conditions presents great difficulties in the way of analysis, however, and no attempt has been made to carry it out.

Hydrogenation of Methylthiol.—The inlet concentration of thiol was determined by passing the gas through N/10-silver nitrate solution; after removal of the precipitated silver thiol, the residual silver nitrate was titrated with N/10-potassium thiocyanate solution. Analysis of the reaction products was carried out by washing the gas with 10% cadmium chloride solution containing 1% of free hydrochloric acid in two Arnold bubblers, followed by N/10-silver nitrate solution. Preliminary tests showed that under these conditions only a small proportion of hydrogen sulphide escaped into the silver solution, and no more satisfactory method could be devised. The experimental errors introduced into this series of experiments are accordingly somewhat greater than in working with other sulphur compounds, and the results are subject to corrections of ± 5%.

In Fig. 2 are given the results of tests where the inlet concentration of thiol varied from 14·1 mg./cu. ft. to 25·0 mg./cu. ft. and the catalyst space was 3 c.c. The reaction is seen to be of the first order with respect to methylthiol, and appreciable reaction begins in the temperature range 200—250° where activated adsorption of methylthiol on nickel subsulphide has been found to take place. The fact that carbon disulphide is considerably more easily decomposed by hydrogen than is methylthiol is emphasised by the data for the two reactions, and makes possible the isolation of methylthiol from the products of mild hydrogenation of carbon disulphide.

The whole of the sulphur, in both the hydrogenation reactions described above, is converted into hydrogen sulphide. Although the reactions are both of the first order with respect to the sulphur compounds, the mechanism of the two reactions is essentially different. In view of the data previously published, it is clear that only van der Waals adsorption of carbon oxysulphide takes place on the catalyst. Since this substance also is now shown to retard its own hydrogenation in the temperature range where the adsorption is measurable, it appears to be unlikely that a molecule of carbon oxysulphide held by this type of adsorption can react with an adsorbed hydrogen atom. This view is in agreement with much other evidence concerning the distinction between van der Waals and activated adsorption, and suggests that carbon oxysulphide can react simply by collision with adsorbed hydrogen.

Methylthiol, on the other hand, only reacts when it is held on the surface by activated adsorption, and the slow rate of this step leads to a considerably smaller relative reaction velocity.

FULHAM LABORATORY, THE GAS LIGHT AND COKE CO.,
LONDON, S.W. 6.

[*Received, October 8th*, 1938.]