

ACTION OF CARBON TETRACHLORIDE VAPOUR ON SULPHIDES

Part III.—Hydrogen Sulphide

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Reaction between hydrogen sulphide and carbon tetrachloride vapour is unsatisfactory at low temperatures. At high temperatures two reactions take place; (i) $2\text{H}_2\text{S} + \text{CCl}_4 = \text{CS}_2 + 4\text{HCl}$, and (ii) $\text{H}_2\text{S} + \text{Cl}_2 = 2\text{HCl} + \frac{1}{2}\text{S}_2$. The latter reaction is believed to be through the decomposition of carbon tetrachloride into other compounds and chlorine. The reaction is also dependent on the rate of flow of H_2S (even if the carbon tetrachloride vapour was in excess) and can be considerably improved by using suitable catalysts.

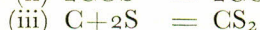
At 870°C in the absence of any catalyst about 40% of the H_2S escaped unreacted, with only 22% of it being converted to CS_2 and about 29% of free sulphur. With asbestos powder as the catalyst the formation of sulphur can be very much suppressed as well as the proportion of unreacted H_2S and consequently the total conversion to CS_2 was 71.5% (together with 12% of sulphur). Compared to this with active charcoal as catalyst, CS_2 yield was 57.6% with 20% unreacted H_2S . About 15% of the sulphur is believed to remain adsorbed on the catalyst.

The reaction in presence of asbestos is believed to have commercial possibilities for production of CS_2 .

Carbon disulphide is an important industrial solvent. Its main use is in the manufacture of rayon and cellophane. It is also used as solvent in a large number of other industries and recently in the cold vulcanization of rubber.

On a large scale, carbon disulphide is still mostly produced by heating sulphur and wood charcoal. During the Second World War, the requirement of elementary sulphur for this process posed a serious handicap due to the world shortage of brimstone. As a consequence, several alternate reactions were studied and suggested for large scale production of carbon disulphide. The utilization of by-product sulphur dioxide and hydrogen sulphide also attracted attention; and carbon-sulphur dioxide and carbon-hydrogen sulphide reactions were most widely studied for the production of carbon disulphide.

The carbon-sulphur dioxide reaction was first studied by Rassow and Hoffmann¹ but they got a low yield between 800 and 900°C . Later, Siller² worked out a three-step process as follows:



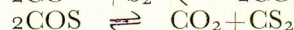
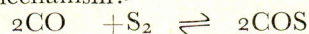
and claimed an overall yield of 85%.

The carbon-hydrogen sulphide reaction was studied by Owen *et al.*³ between 700 to 1300°C who obtained a maximum yield of 70% carbon disulphide depending on the quality of the charcoal used. They also explored the possibility of the exothermic production of carbon disulphide through the introduction of a little oxygen into the system.⁴

Use of hydrocarbon gases (particularly methane) with hydrogen sulphide for the production of carbon disulphide have been claimed in two patents^{5,6} and also systematically studied by Waterman and Vlodrop.⁷ The overall endothermic reaction could be carried out between 1080 to 1280°C with a conversion of 50 to 70% of H_2S .

In the above reactions, it was found that the yield and the reaction mechanism is affected by the nature of the carbon used. A number of other reactions have also been studied in which the sulphur component remained the same but the carbon was replaced by hydrocarbon. Thus Thacker and Miller⁸ studied the reaction between CH_4 and S (vapour) at up to 700°C and by using various catalysts obtained a conversion up to 90%.

The reaction between CO and sulphur was believed to take place through the following mechanism:⁹

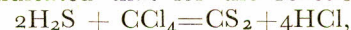


It was later found¹⁰ that best results were obtained when CO was bubbled through molten sulphur containing suspended silica powder.

A number of sulphides have been chlorinated in this laboratory with gaseous chlorine and it was found that under optimum condition metal chlorides and elementary sulphur were obtained.¹¹ In continuation of this work, it was recently observed^{12,13} that some metal sulphides could be successfully chlorinated with carbon tetrachloride to obtain carbon disulphide in relatively high yields. The reactions followed the general equation:



Therefore, the reaction between hydrogen sulphide and carbon tetrachloride, which may have industrial importance, was explored. Thermodynamic calculations presented in the next section indicated that for the reaction:

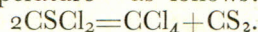


$$\Delta G_T = -25,750 - 63.04T.$$

The reaction was thus considered favourable but dependent greatly on temperature.

Very little information is available on the above reaction. An old reference is available in which the reaction was claimed to be useful for the production of thiocarbonyl chloride. Thiocarbonyl

chloride was also reported to decompose apparently at high temperature¹⁴ as follows:



It was therefore the purpose of the present investigation to study the reaction between hydrogen sulphide and carbon tetrachloride in detail and set up conditions for the high yields of CS_2 .

A brief communication on the results obtained have already been made.¹⁵

Thermodynamics

The Thermodynamic Feasibility of the Reaction.— $2\text{H}_2\text{S} + \text{CCl}_4 = 4\text{HCl} + \text{CS}_2$, was estimated from the ΔG_T values for the formation of the different compounds calculated from the simple relation $\Delta G_T = \Delta H_T - T\Delta S$, where ΔG_T is the change in free energy, ΔH_T the change in enthalpy, T the absolute temperature and ΔS the change in entropy. The values of ΔH_{298} and entropies for the components were collected from standard sources.^{16,17}

The following data were used for the calculation:

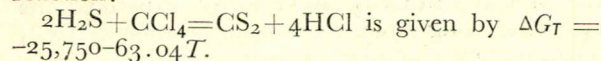
Entities	$\text{CS}_2(\text{g})$	$\text{CCl}_4(\text{g})$	$\text{H}_2\text{S}(\text{g})$	$\text{HCl}(\text{g})$
ΔH_{298}° (cal)	27,550	-25,500	-4,800	-22,100
S_{298}° (cal/°C)	56.8	74.0	49.2	44.65

The S° for C (graphite), $\text{S}_2(\text{g})$, $\text{Cl}_2(\text{g})$, $\text{H}_2(\text{g})$ were taken to be 1.36, 54.4, 53.3 and 31.2 cal/°C respectively.

The following expressions were derived:

$$\begin{aligned}\Delta G_T : \text{CS}_2 &= -3,450 - 1.04T \\ \Delta G_T : \text{CCl}_4 &= -25,500 - 34.0T \\ \Delta G_T : 2\text{H}_2\text{S} &= -40,600 - 18.6T \\ \Delta G_T : 4\text{HCl} &= -88,400 - 9.40T\end{aligned}$$

Therefore the ΔG expression for the complete reaction:



Experimental

Reagents and Materials Used.—Hydrogen sulphide was prepared by the action of dilute sulphuric acid on iron sulphide in a Kipp's apparatus. The gas was purified by passing first through water, then through a saturated solution of $\text{Ba}(\text{OH})_2$ in water. Drying was accomplished by passing the gas through fused CaCl_2 . E. Merck's pure (sulphur-free) CCl_4 was used for the reaction. E. Merck grade ultracarbon (5 g) BDH brand active charcoal (5 g) and asbestos powder (3g) were respectively used as catalysts in the various sets of experiments carried out. A 15% solution of KOH in absolute alcohol was used for absorbing the reaction products (gases) and unconverted gases. The KOH was of E. Merck while the absolute alcohol was of local origin. The alcohol was distilled twice (over CaO) to ensure high purity.

Experimental Procedure and Analytical Technique.—The reaction was carried out in a flow system.

A mixture of CCl_4 vapour and H_2S gas in desired proportion was introduced into a silica reaction tube heated in an electric tube furnace, having provisions for control and measurement of temperature. A suitable catalyst was used which was loosely packed inside the central zone of the reaction tube and the latter placed in such a position in the furnace that the catalyst could be in the zone of uniform temperature. Before the commencement of each experiment, the furnace was switched on and raised to the desired temperature of reaction and kept constant at that temperature.

The reaction products were HCl, CS_2 , unconverted H_2S and sometimes elementary sulphur. These were absorbed in 15% alcoholic KOH solution. The CS_2 reacted to form alkali xanthate, H_2S formed K_2S and/or KHS while HCl reacted to form KCl. Separation of the sulphide sulphur from the xanthate was done by treating the alcoholic KOH with ammoniacal ZnCl_2 solution,¹⁸ which precipitated the sulphide as ZnS leaving the xanthate in solution. After separation of ZnS , the xanthate was analysed by an iodometric method¹⁹ to determine the CS_2 . The ZnS was dried, transferred to an evolution flask and decomposed by moderately hot 1:1 HCl. The evolved H_2S was determined in an inert atmosphere (in this case CO_2 atmosphere) by absorption in a known volume of standard $\text{N}/10$ iodine solution.²⁰ This gave the amount of unreacted H_2S escaping during the reaction.

Results and Discussion

The theoretical calculation of the energetics of the reaction, $2\text{H}_2\text{S} + \text{CCl}_4 = \text{CS}_2 + 4\text{HCl}$, showed that although the reaction was thermodynamically feasible even at ordinary temperature, the overall ΔS function was considerably high indicating that the forward reaction would be more favourable at high temperatures. And since the reaction is also in the vapour phase some catalysts were expected to enhance the reaction rate. The fact was borne out by several preliminary reactions.

In the course of the preliminary experiments without using any catalyst it was found that reaction between H_2S and CCl_4 was unsatisfactory even in the neighbourhood of 900°C . A considerable amount of the H_2S escaped unreacted and formation of CS_2 was low and accompanied by the simultaneous formation of free sulphur. The latter reaction is believed to take place through the decomposition of CCl_4 to chlorine, followed by the action of Cl_2 on the H_2S .²¹ This indicated the use of some catalyst. In all the experiments the rate of feeding of CCl_4 vapour was attempted to be kept constant and it was noted that the variation of H_2S rate had remarkable

influence on the reaction. Therefore the experiments were arranged, in different sets, first on the reactivity of some of the catalysts, and subsequently with two of the catalysts, namely active carbon and asbestos powder. The effect of the other variables were studied with these two catalysts.

Reactions with Different Catalysts

Active carbon had been successfully employed in the chlorination of oxides²² and hydrocarbons²³ and also in the reaction between H₂S and olefins.²⁴ Again an aluminosilicate catalyst²⁵ had been used for the reaction between H₂S and hydrocarbons to give CS₂. Since silica gel is known to be attacked by CCl₄,²⁶ use of asbestos (a complex silicate) was found successful for the present reaction.

A comparative study of the efficiency of the different catalysts was carried out at 870°C with the rate of feeding of the reactants remaining the same, and the results are presented in Table 1. It will be noted that in all cases the CCl₄ vapour was considerably in excess but still, in absence of any catalyst, 40% of the H₂S passed over unreacted whereas with ultracarbon the portion of unreacted H₂S surprisingly increased further. Therefore, this was not considered helpful for this reaction. With active charcoal and still more with asbestos powder the reactivity of H₂S increased. With asbestos powder only 12.5% H₂S escaped unreacted, in a single pass over. This should be considered quite favourable.

It will be seen that in the reaction without catalyst the percentage of CS₂ formed was only 22.1%. This is due to the direct reaction, 2H₂S + CCl₄ = CS₂ + 4HCl; but simultaneously 29% of free sulphur was also formed. This can be explained to be due to the reaction between H₂S and Cl₂²¹ (H₂S + Cl₂ = 2HCl + $\frac{1}{2}$ S₂). The latter is known to be formed through the decomposition of CCl₄. In this reaction only a little over 90% of the H₂S could be accounted for. During collection of the elementary sulphur deposited in the exit end of the reaction tube and adapter, there was minor loss. Therefore it can be said that CS₂ and elementary sulphur were the only

products. But this reaction is considered unsatisfactory for getting high yield of CS₂.

The relatively lower yield of CS₂ was believed to be due to the decomposition of excess CCl₄. It was considered that the situation could be improved if some material be present that would adsorb H₂S and thus accelerate its reaction directly with CCl₄. Activated carbon was an obvious choice and responded fairly successfully. The unreacted H₂S with this catalyst fell down to 20.5% whereas the yield of CS₂ was 57.6% (Table 1). This was wonderful but interestingly only traces of free sulphur was found at the exit end of the reaction tube and the adapter. Taking 95% accountability of the H₂S throughput, we had a deficiency of about 15% H₂S. This is believed to be chemisorbed in the charcoal body whose possibility has been suggested by Emmett.²⁷

The reaction with ultracarbon was surprisingly different. It did not seem to have any adsorption effect on H₂S. It, however, atopped the decomposition of CCl₄ because no free sulphur was formed. Further examination of this catalyst was abandoned as it failed to give a good yield of CS₂.

It has earlier been mentioned that an aluminosilicate catalyst²⁵ was found satisfactory for the reaction of H₂S with hydrocarbons giving CS₂. In analogy to that, asbestos was used in the present study with successful results. It will be seen that asbestos not only suppressed the decomposition of CCl₄ (thereby decreasing the yield of elementary sulphur to only 12%), but also accelerated the direct reaction between H₂S and CCl₄ giving a yield of 71.5% CS₂. While the enhancement of the reaction of H₂S with CCl₄ can be easily explained, its rule of slowing down the decomposition of CCl₄ opens up new channels for further studies.

Effect of Rate of Flow of H₂S

In the exploratory experiments it was found that the rate of flow of H₂S had a direct influence on the yield of CS₂. This effect was therefore studied with two catalysts, namely, active charcoal and asbestos powder. Other variables such as the reaction temperature (870 ± 10°C), duration of

TABLE I.—REACTION BETWEEN H₂S AND CCl₄ VAPOURS IN PRESENCE OF DIFFERENT CATALYSTS.

H₂S flow rate = 6.4 m-mole/hr (approx); reaction temperature = 870 ± 10°C;
duration of reaction = 2 hr 20 min; temperature of CCl₄ bath = 83–85°C.

Catalyst used	Total CCl ₄ Throughput (m-mole)	Total H ₂ S throughput (m-mole)	Unreacted H ₂ S		CS ₂ formed		% free sulphur formed
			(m-mole)	% throughput	(mg-atom S)	% H ₂ S throughput	
None	22.3	15.2	6.0	39.1	3.4	22.1	29.0
Active charcoal	22.2	15.1	3.1	20.5	8.7	57.6	Very little, not determined
Ultracarbon	24.2	15.4	8.4	54.0	6.4	41.4	Very little, not determined.
Asbestos powder	28.2	14.4	1.8	12.5	10.3	71.5	12.0

experiment ($2 \text{ hr} \pm 10 \text{ min}$) and throughput of CCl_4 (as far as possible) were kept the same for each experiment of a set. Results are presented in Table 2.

As is expected, with both the catalysts the yield of CS_2 was dependent on the rate of flow of H_2S although to different degrees. With active charcoal, with a flow rate of 4.4 mg mol/hr of H_2S the yield of CS_2 was only 30.9% . With increase of the flow to 6.3 m-mole/hr it went to a maximum yield of 58.0% ; but with further increase in the flow rate the yield dropped sharply as can be seen from the relevant curve in Fig. 1. In the first case, availability of H_2S was relatively low but CCl_4 did not take part in the direct reaction but rather preferred to decompose yielding Cl_2 which reacted with the H_2S and produced sulphur. This will be clear by noting (from $\%$ CS_2 formed and unreacted H_2S) that about 35% of the sulphur introduced as H_2S remained adsorbed on the charcoal. The sharp fall in the yield indicates that active charcoal was not particularly effective in enhancing the direct reaction between H_2S and CCl_4 . In the other three experiments with active charcoal, CS_2 and unreacted H_2S accounted for was about 80% of the H_2S throughput, thereby confirming that about 15% of the H_2S remains adsorbed.

With asbestos powder, the nature of variation is similar but the total conversion to CS_2 was relatively much higher as can be seen on a comparative basis from Fig. 1. A maximum yield of 72.2% was obtained with a flow rate of 6.4 mg-mol/hr . But with further increase in the rate, the CS_2 yield decreased but to a much lesser extent. The total accountability of sulphur was about 95% in all cases. And except for the first reaction in which the H_2S throughput was low, the lowering of yield of the CS_2 was accompanied by corresponding increase in the unreacted H_2S . The extent of free sulphur varied between 11 to 12% . It was thus considered that asbestos powder was a much better catalyst for the formation of CS_2 and probably good enough for industrial exploitation.

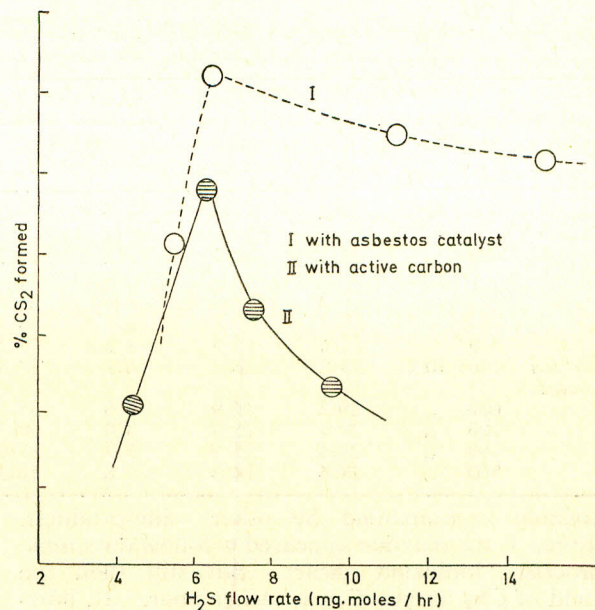


Fig. 1.—Reaction between H_2S and CCl_4 vapour at different H_2S flow rate.

Effect of Temperature

The effect of temperature on the reaction was studied in presence of active charcoal and asbestos powder respectively. Relevant data are given in Table 3.

Experiments carried out with active charcoal between 400° to about 900°C showed that reactions are slow and complicated by other side reactions at up to 700°C . This tends to interfere with analytical procedure thus giving slightly erroneous results. Only above 700°C , CS_2 and free sulphur, if any, were the only products. Here again, the activity of catalyst towards production of CS_2 sharply increased from 39.6% (for 780°C) to 57.6% (for 870°C). The question of chemisorption of 15% or a little more of the sulphur with high temperature reactions with active charcoal can also be confirmed.

With asbestos powder, at temperatures up to 600°C the reaction is not straightforward and is

TABLE 2.—REACTION BETWEEN H_2S AND CCl_4 VAPOURS AT DIFFERENT H_2S FLOW RATES.

Duration of reaction= $2 \text{ hr} \pm 10 \text{ min}$; reaction temperature= $870 \pm 10^\circ\text{C}$; temperature of CCl_4 bath= $83\text{--}85^\circ\text{C}$.

Catalyst used	Total CCl_4 throughput (m-mole)	H_2S flow rate (m-mole/hr)	Unreacted H_2S		CS_2 formed		% free sulphur formed
			(m-mole)	% throughput	(mg-atom S)	% of H_2S throughput	
Active charcoal	22.2	4.4	2.8	31.7	2.7	30.9	Small amounts of free sulphur deposited in all cases but was not determined.
	22.2	6.3	2.6	22.4	6.7	58.0	
	22.5	7.5	5.9	39.2	6.5	43.0	
	26.3	9.5	8.7	45.8	6.3	33.1	
Asbestos powder	28.2	5.5	3.0	26.0	5.9	51.3	16.0
	28.2	6.4	1.3	10.6	9.4	72.2	11.0
	28.4	11.2	3.8	16.8	14.3	64.7	12.0
	30.3	14.5	5.7	19.6	17.9	61.8	12.0

TABLE 3.—REACTION BETWEEN H₂S AND CCl₄ VAPOURS AT DIFFERENT TEMPERATURES.
Duration of reaction = 2 hr 30 min; H₂S flow rate = 6.4 m-mole/hr (approx); temperature of CCl₄ bath = 83–85°C.

Catalyst used	Reaction temp °C	Total CCl ₄ through-put (m-mole)	Total H ₂ S through-put (m-mole)	Unreacted H ₂ S		CS ₂ formed		Free sulphur formed	Remarks
				(m-mole)	% throughput	(mg-atom S)	% H ₂ S throughput		
Active charcoa	400±10°C	28.2	16.3	2.6	16.3	6.5	39.9	Nil	Chocolate brown vapours observed; CSCI ₂ possibly formed.
	600 "	29.3	17.1	3.2	18.7	5.4	31.5	Nil	
	700 "	28.2	16.7	3.6	21.5	4.4	26.1	Nil	
	780 "	29.3	15.9	3.8	24.2	6.4	39.6	Negligible	
	870 "	27.6	15.5	3.2	20.7	8.9	57.6	Very little	
Asbestos powder	400±10°C	28.2	16.2	6.1	37.6	7.6	47.1	11.0	Chocolate brown CSCI ₂ possibly formed
	600 "	28.2	15.9	5.6	35.3	6.8	42.3	16.0	
	700 "	28.4	15.9	8.0	50.3	4.5	28.0	15.0	
	780 "	28.4	15.5	5.7	37.0	7.4	47.5	12.0	
	870 "	28.4	14.4	1.8	12.5	10.3	71.5	12.0	

possibly accompanied by other side-products. By 700°C the reaction appeared to follow the simple processes indicated earlier. But still then the yield of CS₂ at 700°C was rather poor. It, however, sharply increased with increase of temperature and went to a maximum of 71.5% for 870°C. In most of these latter experiments the accountability of sulphur was in the neighbourhood of 95%.

It should be noted that the experiment with asbestos powder at 870°C as presented in Table 3 and that in Table 2 were carried out under similar conditions (as far as it was possible with experimental controls) and the results given in the two tables are those actually found in the two experiments. Slight variation will be noted in some of the results. The same is also true for active charcoal, and are to be taken to be due to slight change in the variables.

At the end of reaction, particularly at high temperatures, the white asbestos powder was found to be blackish presumably due to some carbon deposits. This lends support to the idea of decomposition of CCl₄ giving Cl₂ to react with H₂S producing elementary sulphur.

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