ACTION OF CARBON TETRACHLORIDE VAPOUR ON SULPHIDES

Part I.—Sb_2S_3 and CdS

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In the temperature range 200-500°C, carbon tetrachloride vapour reacts with Sb_2S_3 and CdS according as $2Sb_2S_3 + 3CCl_4 = 4 SbCl_3 + 3CS_2$ and $2 CdS + CCl_4 = 2 CdCl_2 + CS_2$. Formation of metal chlorides were quantitative; but that of CS_2 varied between 80.0–92% in the case of Sb_2S_3 and 84.5–97.9% in the case of CdS depending on temperature. The lower yield was found to be due to a side reaction (involving CS_2) that produces sulphur chlorides at lower temperatures upto 400°C. Above this temperature, the side reaction is minimum and only very small amounts of elementary sulphur were formed. No $CSCl_2$ was traced in the products. Optimum temperature was 450°C for both the reactions.

The usefulness of carbon tetrachloride as a chlorinating agent for inorganic compounds has been realised only recently, although some old references of a qualitative nature are available. Camboulives[1] as far back as 1910 reported the action of carbon tetrachloride on various metal oxides, and indicated the temperatures at which the reaction started with different oxides. The information was of a qualitative nature, but the author suggested the formation of $COCl_2$. The recent trend of reducing metal chlorides by active metals has opened up the feasibility of chlorination of refractory oxides, particularly with carbon tetrachloride. Thus by the action of CCl_4 vapour, niobium and neptunium oxides have been effectively chlorinated;[2,3] recently other oxides such as TiO_2, BeO, ZrO_2 and ThO_2, have also been converted to their corresponding chlorides by the action of CCl_4 at relatively lower temperatures.[4]

The literature relating to the action of CCl_4 vapour on sulphides is still very meagre. Air-CCl_4 mixtures have been used to breakdown several sulphide minerals, the products being absorbed and oxidised in a suitable solvent.[5] Carbon tetrachloride reacts with iron pyrites at 320–400°C giving a mixture of $FeCl_2$, $FeCl_3$, FeS, S, C and $CSCl_2$; but with stibnite (apparently[6] through mistake it was noted as stibine) at 300–320°C the reaction produces $SbCl_3$ and CS_2. Hydrogen sulphide reacts with CCl_4 at red heat to give thiocarbonyl chloride.[7] No information is available regarding the action of any other sulphide with CCl_4.

With gaseous chlorine[8] or even solid anhydrous ferric[9] or cupric[10] chlorides, antimony sulphide has been known to produce antimony trichloride. With CCl_4, although the formation of $SbCl_3$ may be anticipated, the fate of sulphur is not clearly understood and the formation of different carbon-sulphur compounds is probable.

Theoretical considerations suggest the possibilty of formation of CS_2 with a number of metal sulphides at relatively low temperatures, and with H_2S at below 1500°C. This paper reports the results obtained with antimony and cadmium sulphides.

Thermodynamics

The thermodynamic feasibility of the reactions were estimated from the ΔG_T values for the formation of the different compounds calculated from the simple equation, $\Delta G_T = \Delta H_{298} - T\Delta S_{298}$. The values for Sb_2S_3 (s) and $SbCl_3$ (s) were taken from an earlier paper.[10] For the rest of the compounds, ΔH_{298} values were taken from Rossini *et al.*[11] For the different entities, $S°$ was taken from Rossini *et al.*, except for $S_2(g)$ which was from Kubaschewski and Evans,[12] for ease of calculation, the values were rounded off to first decimal place. In the case of $CdCl_2$, the $S°$ values quoted by the above two sources varied somewhat and 30.0 cal °C was chosen as a fair average.

The following data were used for calculation:

Entities	CS_2	CCl_4	CdS	$CdCl_2$
ΔH_{298}	27,550	-25,500	-34,500	-93,000
$S°_{298}$	56.8	74.0	17.0	30.0

The $S°$ for C (graphite), $S_2(g)$, $Cl_2(g)$, and Cd(s) were taken to be 1.36, 54.4, 53.3 and 12.3 cal./°C respectively.

The following expressions were derived.

$$\Delta G_T : CS_2 = 27,550 - 1.04\,T$$
$$\Delta G_T : CCl_4 = -25,500 + 33.96\,T$$
$$\Delta G_T : CdS = -34,500 + 22.50\,T$$
$$\Delta G_T : CdCl_2 = -93,000 + 35.60\,T$$

ΔG for the reaction, $2Sb_2S_3$ (s) $+3CCl_4(g) =$ $4SbCl_3$ (s) $+3CS_2$ (g) can be found to be equal to $(-122, 210-56.40$ T).

°K	298	346	492	903
ΔG	$-139,017$	$-141,724$	$-149,959$	$-173,139$

Similarly for the reaction, $2CdS(s)+CCl_4(g)=$ $2CdCl_2$ (s) $+ CS_2$ (g), the ΔG expression would be given by $(-63,950- 8.80T)$.

°K	298	573	673	773	873
ΔG	$-66,172$	$-68,992$	$-69,872$	$-70,752$	$-71,623$

Thus for both the reactions, the ΔG values are favourable and decrease further with temperature. The temperature dependence of the reaction involving cadmium is relatively smaller. Further if the two reactions are compared with reference to the moles of S_2 or Cl_2 involved, the latter reaction (that involving CdS) will be found to be (thermodynamically) more spontaneous.

Experimental

Materials Used.—B.D.H. grade black antimony trisulphide (98% pure) and cadmium sulphide (99.8% pure), and E. Merck grade sulphur-free carbon tetrachloride were used.

Apparatus and Procedure.—A weighed amount of the chosen sulphide was taken on a porcelain boat and introduced into the reaction tube (Pyrex) placed inside an electrically heated tube furnace (Fig. 1) in such a way that the boat was at the central heating zone. The whole system was thoroughly flushed with dry nitrogen and heated to a steady desired temperature, controlled to within $\pm 5°C$. Carbon tetrachloride vapour was introduced into the reaction tube by bubbling nitrogen through the heated carbon tetrachloride reservoir. This instant was taken as the beginning of the experiment. All connections were through ground glass joints. Relatively less volatile products (mainly $SbCl_3$ and/or traces of sulphur chlorides) condensed in the cooler portion of the reaction tube and the ice-cooled receiving flasks, while the vapours and gases were passed through alcoholic KOH solution to absorb the carbon disulphide. After the reaction was over, the furnace was switched off and the tube flushed with nitrogen till it had cooled. The amount of the antimony trisulphide reacted was determined by weighing the residual sulphide in the boat, which was shown to be free from any contamination.

In the case of CdS, the extent of reaction was determined by analysing the residue in the boat for both $CdCl_2$ and CdS, using standard procedure. $SbCl_3$ produced was determined iodimetrically, and the S_2Cl_2 by hydrolysis and weighing the sulphur liberated; this result could only be semi-quantitative. Carbon disulphide formed was determined by iodimetric titration in alcoholic KOH solutions.[13]

Results and Discussion

The experience in this laboratory[14] has been that the chlorination of refractory metal oxides
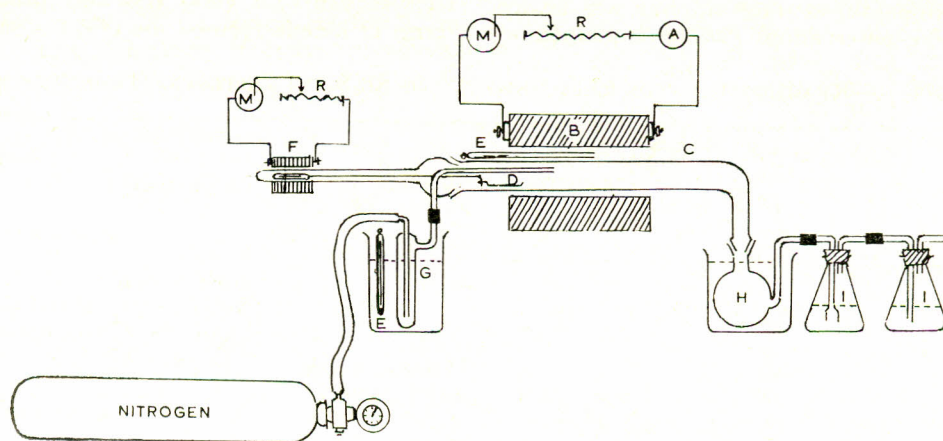
EXPERIMENTAL SET UP FOR THE REACTION OF Sb_2S_3 AND CdS WITH CCl_4 VAPOUR

Fig. 1.—A, ammeter; B, tube furnace; C, reaction tube; D, silica boat; E, thermometer; F, solenoid assembly; G, The CCl_4 bubbler; H, ice-cooled condensing flask; I, CS_2 absorption flask; M, supply main; R, rheostat.

with CCl_4, at the high temperature (600°C) required, takes place through the decomposition of CCl_4 into chlorine, C_2Cl_6, C_2Cl_4 and other compounds. Since the decomposition of CCl_4 is inappreciable below 600°C, and since in the present study Sb_2S_3 and CdS are easily converted into their chlorides at relatively lower temperatures, a different mechanism should be responsible for this reaction.

Results with Sb_2S_3.—The main reaction was $2 Sb_2S_3+3CCl_4=4SbCl_3+3CS_2$. etween 200° and 500°C, $CSCl_2$ was not formed (no evolution of chocolate-brown vapour). In these experiments excess of antimony trisulphide was taken in the reaction boat. The quantity taken in the boat has been referred to as the *input* of Sb_2S_3 (Table 1). There was no reaction at 100°C, and at 200°C the reaction was still not so prominent; but from this temperature onwards the reaction steadily increased, reaching a maximum at 450°C. The smaller extent of reaction (throughput of Sb_2S_3) at 500°C may be due to the incipient sintering or fusion of the Sb_2S_3 near its melting point (ca. 520°C).

At all temperatures, about 97–98% of the Sb_2S_3 (per cent of the input that underwent reaction) converted itself into $SbCl_3$. Since the antimony sulphide used was 98% pure, virtually all the antimony that took part in the reaction was converted into its trichloride. But in so far as the sulphur constituent of the Sb_2S_3 is concerned, the reaction does not seem to be quite as simple. Depending upon the temperature, 80 to 92% of the sulphur in the sulphide that reacted was available as carbon disulphide. Sulphur chloride was definitely present at lower temperatures, while at higher temperatures some sulphur was always found. These observations can be explained by

considering that the primary reaction follows the equation shown above, forming the $SbCl_3$ and CS_2. But the carbon disulphide undergoes a side reaction with chlorine according to the equation, $CS_2+3Cl_2=S_2Cl_2+CCl_4$. This will explain the formation of sulphur chloride at lower temperatures which decomposes at above 400°C to elementary sulphur. Elementary sulphur may also be formed by the following side reactions:

$$2Sb_2S_3+6S_2Cl_2 = 4SbCl_3+9S_2$$
$$2Sb_2S_3+12Cl = 4SbCl_3+3S_2$$

It has not been clearly understood why there should be a lower yield of carbon disulphide at 500°C than at 450°C. But by repeating experiments it has been confirmed that this is so.

Having found 450°C as the optimum temperature for the reaction, the next series of experiments were carried out at this temperature for different periods of time. The rate of feeding of CCl_4 was kept constant throughout the experiment. The reaction proceeded more or less steadily upto 3 hours after which the throughput (i.e. the amount of the Sb_2S_3 reacting) slowed down somewhat and reached an equilibrium value (98.7% in about 5 hours (Table 2). Here again, it was found that steadily from the beginning, the antimony constituent of Sb_2S_3 was converted virtually completely to antimony trichloride. The formation of carbon disulphide was slightly smaller (about 84%) in the first half hour, but later on became steady between 91% and 94%.

Results with CdS.—Although the temperature dependence of the ΔG of the reaction, $2CdS+CCl_4=2CdCl_2+CS_2$, was less pronounced in terms of kinetic factors, the effect of this variable

TABLE 1.—REACTION BETWEEN CCl_4 VAPOUR AND Sb_2S_3 AT DIFFERENT TEMPERATURES.

Temp of reaction (°C)	Sb_2S_3 reacted		$SbCl_3$ formed		CS_2 formed		Remarks
	(g)	% of input	as Sb (g)	as % of Sb reacted	as S (g)	as % of S reacted	
100	nil	—	—	—	—	—	No reaction.
200	0.48	12.0	0.33	95.9	—	—	Much S_2Cl_2 produced; Detn. of CS_2 difficult.
300	1.81	45.3	1.26	97.1	0.41	80.0	Traces of S_2Cl_2 etc.
400	2.58	64.5	1.80	97.3	0.63	86.3	,, ,,
450	2.84	71.0	1.98	97.3	0.72	89.6	No $S_2 Cl_2$; some sulphur.
450	2.88	72.0	2.01	97.3	0.75	92.0	,,
500	2.53	63.3	1.77	98.1	0.61	85.2	,,
500	2.61	65.3	1.82	97.3	0.63	85.3	,,

Sb_2S_3 taken (input) $=4.00\pm0.01$ g.; CCl_4 passed $=3.19$ g (2 ml);
Duration of CCl_4 feeding $=2$ hr 15 min ± 5 min.

(temperature) was studied in this case also. The results are presented in Table 3. The reaction was comparable to that with antimony trisulphide. The chlorination became significant only above 200°C, and reached a maximum (conversion 70%) at 450°C, and again tending to decrease slightly beyond this temperature. In the case of Sb_2S_3, the slower reaction at 500°C was explained as being due to the fusion of the sulphide itself; this could not be possible for CdS (m.p. 1750°C). It was noted, however, that the solid residue on the silica boat after completion of reaction at 500°C consisted of a greyish black mass, composed of $CdCl_2$ and a black variety of CdS which did not easily dissolve in acidic solution. The products at lower temperature consisted of the yellow CdS easily soluble in acids. On heating yellow CdS alone in nitrogen atmosphere between 450°C and 600°C, there was no change of colour; but in the presence of even traces of the chloride the CdS changed to the black variety at or above 500°C.

This suggests that the lower yield at 500°C was due to the formation of a black variety of CdS which was apparently less reactive. The percentage of cadmium recovered as cadmium chloride was the same at all temperatures and more or less quantitative. The formation of carbon disulphide also had a similar trend as that for the reaction with Sb_2S_3, although the decrease in the yield at 500°C was relatively less pronounced. The results indicate that the same mechanism is operative here also for the reaction involving the sulphur constituent of the cadmium sulphide.

After determining that the optimum temperature in the case of CdS was also 450°C, the progress of reaction with time was studied at this temperature (Table 4). The reaction proceeds quite rapidly from the beginning and continues for 2 hours when the sulphide in the boat was almost exhausted (compare with Sb_2S_3 in Fig. 2). The speed of this reaction was relatively more rapid.

TABLE 2.—PROGRESS OF REACTION BETWEEN CCl_4 VAPOUR AND Sb_2S_3 WITH TIME AT 450°C.

Duration of expt. (hr)	Sb_2S_3 reacted		$SbCl_3$ formed		CS_2 formed	
	(g)	% of input	as Sb (g)	as % of Sb reacted	as S (g)	as % of S reacted
0.5	0.80	20.0	0.55	95.9	0.19	83.9
1.0	1.30	32.5	0.91	97.6	0.32	87.0
1.5	2.09	52.3	1.44	96.1	0.54	91.3
2.25	2.88	72.0	2.01	97.4	0.75	92.0
3.0	3.46	86.5	2.43	98.0	0.92	93.9
4.0	3.88	97.0	2.67	96.0	1.01	92.0
5.0	3.95	98.8	2.74	96.8	1.00	89.4

Sb_2S_3 (input)$=4.00\pm0.01$ g; CCl_4 passed$=1.37$ g per hour.

TABLE 3.—REACTION BETWEEN CCl_4 VAPOUR AND CdS AT DIFFERENT TEMPERATURES.

Temp. of reaction	CdS taken (g)	CdS reacted		$CdCl_2$ formed		CS_2 formed		Remarks
		(g)	% of input	as Cd (g)	as % of Cd reacted	as (g) S	as % of S reacted	
100	3.02	nil	—	—	—	—	—	No reaction
200	3.05	0.45	14.8	0.34	97.1	—	—	Detn. of CS_2 difficult.
300	3.07	1.44	46.9	1.10	98.2	0.27	84.5	Some S produced.
400	3.03	1.98	65.4	1.51	98.0	0.43	97.9	Very little S;
450	3.04	2.08	68.4	1.59	98.7	0.45	97.5	No S_2Cl_2
450	3.04	2.13	70.1	1.62	97.8	0.46	97.3	,,
500	3.03	1.76	58.1	1.35	98.6	0.38	97.3	,,
500	3.05	1.71	56.1	1.31	98.5	0.36	94.9	,,

CCl_4 passed$=3.19$ g; duration of CCl_4 feeding$=2.0$ hr±5 min.

Table 4.—Progress of Reaction between CCl_4 Vapour and CdS at 450°C.

Duration of expt. (hr)	CdS taken (g)	CdS reacted		CdCl₂ formed		CS₂ formed	
		(g)	% of input	as Cd (g)	as % of Cd reacted	as S (g)	as % of S reacted
0.5	3.06	1.50	49.0	1.15	98.5	0.32	96.1
1.0	3.04	2.08	68.4	1.60	98.9	0.45	97.5
1.5	3.02	2.42	80.1	1.86	98.8	0.52	96.8
2.0	3.03	2.97	98.0	2.28	98.7	0.64	97.1
3.0	3.01	2.99	99.3	2.29	98.4	0.65	98.0

CCl_4 passed $= 1.60$ g/hr.

Fig. 2.—Progress of reaction of Sb_2S_3 and CdS with CCl_4 vapour with time.
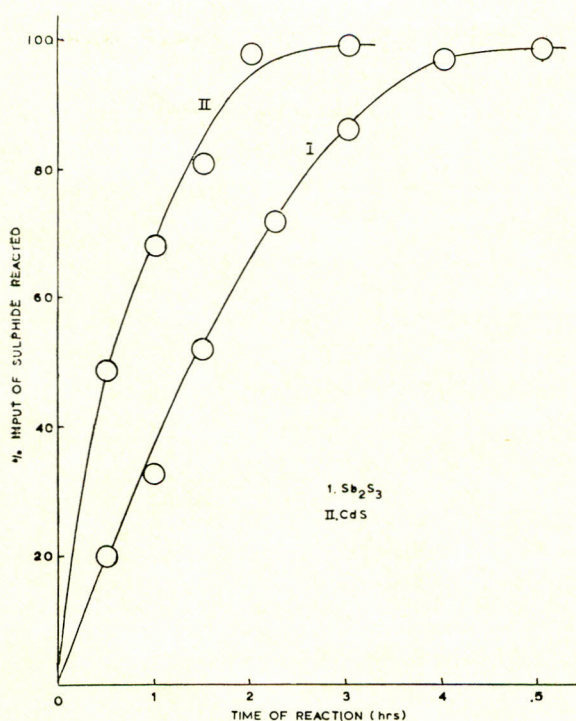

Fig. 3.—Variation of chlorination efficiency of the reactions of Sb_2S_3 and CdS with CCl_4 vapour with temperature.

The recovery of $CdCl_2$ and CS_2 was better, thus indicating that the side reactions were probably less effective.

Comparison of the Two Reactions.—The reactivity of the two sulphides has been compared by plotting the number of moles of the sulphides reacting per mole of CCl_4 flowing in 2 hours against the temperature (Fig. 3). Though the curve for CdS occupying the upper position apparently indicates that this sulphide is more reactive towards CCl_4, a more logical comparison should have a reference to the reactions postulated.
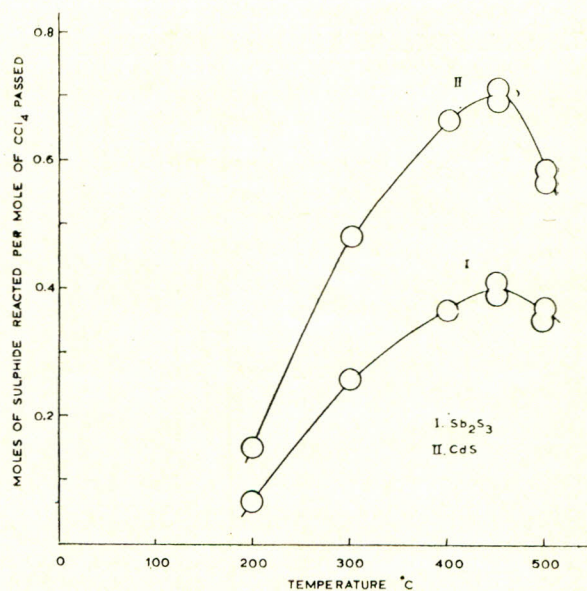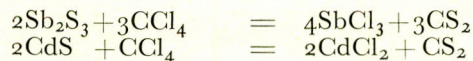
$$2Sb_2S_3 + 3CCl_4 = 4SbCl_3 + 3CS_2$$
$$2CdS + CCl_4 = 2CdCl_2 + CS_2$$

For convenience, let 450°C, the temperature of maximum reactivity for both, be taken for comparison. From the equation it will be seen that for each mole of CCl_4 fed in, a maximum of 0.66 mole of Sb_2S_3 may react; actually about 0.40 mole reacted—thus showing a *chlorination efficiency* of about 60%. In view of the flow system and the nature of the reaction, this should be considered as rather good. The corresponding values for CdS are a theoretical maximum of 2.0 mole per mole of CCl_4 fed in, and a *chlorination efficiency* of about 35%. Thus examining critically the Sb_2S_3 may be taken to be about twice as reactive, which is in accord with the energetics of the reactions.

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