Reaction between Vanadium Trichloride Oxide and Hydrogen Sulfide

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The details of the reaction between vanadium trichloride oxide and hydrogen sulfide were examined at 20 and 60 °C. The main products by the reaction were vanadium dichloride oxide, sulfur, and hydrogen chloride. In addition to these products, small amounts of vanadium trichloride, vanadium tetrachloride, disulfur dichloride, and sulfur dioxide were formed. The formations of the above-mentioned reaction products can be explained as follows: The first stage is the reaction between vanadium trichloride oxide and hydrogen sulfide, $2VOCl_3(l)+H_2S(g)\rightarrow 2VOCl_2(s)+S(s)+2HCl(g)$. Then the resulting sulfur reacts with the unreacted vanadium trichloride oxide, $2VOCl_3(l)+2S(s)\rightarrow 2VOCl_2(s)+S_2Cl_2(l)$. The resulting disulfur dichloride subsequently reacts with the unreacted vanadium trichloride oxide, $2VOCl_3(l)+S_2Cl_2(l)\rightarrow 2VCl_4(l)+S(s)+SO_2(g)$. The resulting vanadium tetrachloride reacts with the sulfur formed during the reaction, $2VCl_4(l)+2S(s)\rightarrow 2VCl_3(s)+S_2Cl_2(l)$, and also reacts with hydrogen sulfide, $2VCl_4(l)+H_2S(g)\rightarrow 2VCl_3(s)+S(s)+2HCl(g)$.

As regards the reaction between vanadium trichloride oxide ($VOCl_3$) and hydrogen sulfide, Ehrlich and Siebert[1] have briefly reported that $VOCl_3$ reacts with hydrogen sulfide to form vanadium dichloride oxide ($VOCl_2$), sulfur, and hydrogen chloride. Also, there have been patents which report that the precipitate formed by the reaction between the $VOCl_3$ dissolved in titanium tetrachloride and hydrogen sulfide consists of vanadium sulfide,[2] and that the precipitate contains vanadium chiefly in the forms of vanadium trichloride (VCl_3) and $VOCl_2$.[3]

In this study, the details of the reaction between $VOCl_3$ and hydrogen sulfide were examined.

Experimental

Materials. The sample of $VOCl_3$ used was prepared by the chlorination of divadium pentaoxide, which had been obtained by the thermal decomposition of guaranteed reagent ammonium metavanadate, in the presence of carbon at 300 °C.[4] Disulfur dichloride(S_2Cl_2) was prepared by the chlorination of guaranteed reagent sulfur.[5] Vanadium tetrachloride(VCl_4) was prepared by the chlorination of high purity vanadium(V 99.8% up) at 500 °C.[6]

Experimental Procedures. The apparatus used for this experiment consisted of a Pyrex reaction vessel of 21 mm inner diameter and 70 mm height with a water-cooled condenser which was connected to a gas absorption unit. 8—9 g of $VOCl_3$ was poured into the reaction vessel and held at 20 or 60 °C in an argon atmosphere. Then pre-dried hydrogen sulfide was introduced into the reaction vessel at a flow-rate of 10 ml/min for a specified period with stirring.

The gaseous hydrogen chloride which formed was absorbed in water. The unreacted $VOCl_3$ containing the liquid product was separated from the solid product by distillation under reduced pressure at room temperature. The solid, liquid, and gaseous products were examined by chemical analysis and X-ray diffractometry.

The possible reactions which were considered to occur on the basis of the above-mentioned experiments, $VOCl_3+S$, $VOCl_3+S_2Cl_2$, VCl_4+S, and VCl_4+H_2S, were examined in the manner described above.

Throughout this work, all the chlorides and chloride oxides were handled in an argon atmosphere or in vacuo to prevent any contamination with moisture.

Analytical. X-Ray analysis of the solid product was performed using Ni filtered Cu radiation. The part of the diffractometer containing the sample was designed to be maintained in a dry nitrogen atmosphere, in order to prevent contamination of the sample with moisture during the irradiation.

Chemical analysis of the sample was performed as follows: The sample was hydrolyzed with dilute nitric acid and filtered. The vanadium content in the filtrate was determined by chelatometric titration,[7] while the chlorine and sulfur contents in the filtrate were gravimetrically determined as AgCl and $BaSO_4$, respectively. The filtered residue, solid sulfur, was dissolved in acetone and determined by titration with 0.05 N sodium cyanate solution.[8]

The gaseous hydrogen chloride which formed was determined gravimetrically as AgCl. The gaseous sulfur dioxide which formed was determined by iodometry after being absorbed in an iodine–potassium iodide solution.

Results and Discussion

Reaction Products for $VOCl_3$ and Hydrogen Sulfide. The reaction between $VOCl_3$ and hydrogen sulfide was examined with special attention given to the reaction product which formed. The variations of the amount of the solid product formed by the reaction between $VOCl_3$ and hydrogen sulfide with the reaction time

Table 1. Experimental results for the reaction between $VOCl_3$ and H_2S

Temp (°C)	$VOCl_3$ used (g)	Product: Solid: Amount (g)	Solid: $VOCl_2$ (%)	Solid: VCl_3 (%)	Solid: S (%)	Liquid: VCl_4 (g)	Liquid: S_2Cl_2 (g)	Gas HCl (g)	Note
20	8.62	5.98	84	6	10	0.05	0.00_8	1.36	Unreacted $VOCl_3$ 1.74 g
60	8.50	6.31	82	8	10	0.04	0.00_5	1.41	Unreacted $VOCl_3$ 1.18 g

were examined at 20 and 60 °C. Using these preliminary experimental results, the reaction products obtained by passing hydrogen sulfide through $VOCl_3$ for 4 h at 20 °C and 3 h at 60 °C were examined. The amounts of the solid products obtained at 20 and 60 °C are shown in Table 1.

The X-ray diffraction diagrams of the solid products obtained at 20 and 60 °C showed them to be a mixture of $VOCl_2$,[9] VCl_3,[10] and sulfur(orthorhombic),[11] as shown in Fig. 1. Chemical analysis gave V 33.0, Cl 47.2, S 10.0% for the product obtained at 20 °C, and V 32.9, Cl 47.6, S 10.0% for the product obtained at 60 °C. The percentages of $VOCl_2$, VCl_3, and S in the solid products, which were calculated from the chemical analysis (Cl base), are shown in Table 1. From these results, it was observed that the constituents of the solid products were almost the same regardless of the reaction temperature.

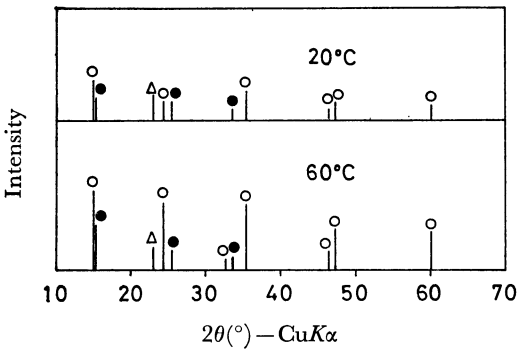

Fig. 1. X-Ray diffraction diagrams of the solid products obtained by the reaction between $VOCl_3$ and H_2S.
○: $VOCl_2$, ●: VCl_3, △: S.

Chemical analysis of the $VOCl_3$ containing the liquid product obtained at 20 and 60 °C gave V 29.1, Cl 61.5, S 0.2%. In the course of the chemical analysis of the sample, a liberation of sulfur was observed on dissolving the sample in dilute nitric acid. This indicated that the $VOCl_3$ contained S_2Cl_2[12] as a reaction product. The atomic ratio of the V content to the Cl content obtained by subtracting the Cl content corresponding to the S_2Cl_2 from the total Cl content was calculated to be 1: 3.0_3. This ratio is lower than the calculated value, 1: 3.00, for $VOCl_3$. The only vanadium chloride in the liquid state at room temperature is VCl_4, except for $VOCl_3$ itself. From these reasons, it was considered that VCl_4 was formed in addition to S_2Cl_2. The amounts of VCl_4, S_2Cl_2, and unreacted $VOCl_3$ are shown in Table 1.

The amounts of gaseous hydrogen chloride which formed during the reaction are also shown in Table 1. In addition, it was observed that a small amount of sulfur was deposited inside the glass line outside the reaction vessel. This fact indicated that sulfur dioxide was formed and reacted with hydrogen sulfide to form sulfur according to the reaction, $SO_2+2H_2S\rightarrow 3S+2H_2O$.[12]

The calculations to obtain the moles of the above-mentioned reaction products, based on the amounts shown in Table 1, showed that $VOCl_2$, sulfur, and hydrogen chloride were the main products and that the molar ratio of $VOCl_2$: S: HCl was approximately 2: 1: 2. From this result, the main reaction which occurred by passing hydrogen sulfide through $VOCl_3$ was found to be the following:

$$2VOCl_3(l) + H_2S(g) \longrightarrow 2VOCl_2(s) + S(s) + 2HCl(g). \quad (1)$$

The formations of small amounts of VCl_4, sulfur dioxide, and S_2Cl_2 were observed as mentioned above. Considering this observation and the description[13] that $VOCl_3$ reacts with sulfur to form VCl_4, SO_2, and $VOCl_2$, it seemed to be probable that the formations of VCl_4, SO_2, and S_2Cl_2 were due to the following reactions, which occurred during the reaction between the unreacted $VOCl_3$ and the sulfur which had formed:

$$2VOCl_3(l) + 2S(s) \longrightarrow 2VOCl_2(s) + S_2Cl_2(l),$$

$$2VOCl_3(l) + S_2Cl_2(l) \longrightarrow 2VCl_4(l) + S(s) + SO_2(g).$$

In addition to the above-mentioned reaction products, VCl_3 was also formed. The formation of VCl_3 was considered to be due to the reactions between the VCl_4 and the sulfur to form VCl_3 and S_2Cl_2, and between the VCl_4 and hydrogen sulfide to form VCl_3, sulfur, and hydrogen chloride.[1]

Side Reactions during the Reaction between $VOCl_3$ and Hydrogen Sulfide. In order to confirm the side reactions which were considered to occur during the reaction between $VOCl_3$ and hydrogen sulfide, experiments on these reactions: $VOCl_3+S$, $VOCl_3+S_2Cl_2$, VCl_4+S, and VCl_4+H_2S, were carried out at 20 °C for 4 h and at 60 °C for 3 h. Solid products were determined by X-ray diffractometry and chemical analysis. Liquid products were determined by chemical analysis in the same manner as described in the previous paragraph.

Experimental conditions and results for the reaction between $VOCl_3$ and sulfur are shown in Table 2.

Table 2. Experimental results for the reaction between $VOCl_3$ and S

Temp (°C)	$VOCl_3$ used (g)	S used (g)	Product: Solid $VOCl_2$ (g)	Product: Liquid S_2Cl_2 (g)	Product: Liquid VCl_4 (g)	Product: Gas SO_2 (g)
20	8.13	1.14	0.06	0.03_1	0.01	0.00_2
60	7.86	1.32	0.07	0.03_7	0.01	0.00_2

From the experimental results described later, the formations of small amounts of VCl_4 and sulfur dioxide may be due to the reaction between the unreacted $VOCl_3$ and the S_2Cl_2 which formed during the reaction. From these results, $VOCl_3$ would seem to react gradually with sulfur to form $VOCl_2$ and S_2Cl_2, as follows:

$$2VOCl_3(l) + 2S(s) \longrightarrow 2VOCl_2(s) + S_2Cl_2(l). \quad (2)$$

The experimental results for the reaction between $VOCl_3$ and S_2Cl_2 are shown in Table 3.

From these results, $VOCl_3$ reacts gradually with S_2Cl_2 to form VCl_4, sulfur, and sulfur dioxide, as

TABLE 3. EXPERIMENTAL RESULTS FOR THE REACTION BETWEEN $VOCl_3$ AND S_2Cl_2

Temp (°C)	$VOCl_3$ used (g)	S_2Cl_2 used (g)	Product: Solid S (g)	Product: Liquid VCl_4 (g)	Product: Gas SO_2 (g)
20	8.43	3.24	0.00_7	0.08	0.01_2
60	8.67	3.13	0.01_0	0.12	0.01_7

follows:

$$2VOCl_3(l) + S_2Cl_2(l) \longrightarrow 2VCl_4(l) + S(s) + SO_2(g). \quad (3)$$

It was also found that the formation of a small amount of sulfur dioxide during the reaction between $VOCl_3$ and hydrogen sulfide, described in the previous paragraph, was due to the reaction between $VOCl_3$ and S_2Cl_2.

Experimental results for the reactions between VCl_4 and sulfur and between VCl_4 and hydrogen sulfide are shown in Tables 4 and 5, respectively.

TABLE 4. EXPERIMENTAL RESULTS FOR THE REACTION BETWEEN VCl_4 AND S

Temp (°C)	VCl_4 used (g)	S used (g)	Product: Solid VCl_3 (g)	Product: Liquid S_2Cl_2 (g)
20	7.78	1.29	5.37	2.30_9
60	7.79	1.30	5.64	2.42_3

TABLE 5. EXPERIMENTAL RESULTS FOR THE REACTION BETWEEN VCl_4 AND H_2S

Temp (°C)	VCl_4 used (g)	Product: Solid VCl_3 (g)	Product: Solid S (g)	Product: Liquid S_2Cl_2 (g)	Product: Gas HCl (g)
20	7.97	5.45	0.41_1	0.21_5	1.15
60	7.86	5.90	0.42_3	0.24_4	1.23

The results shown in Table 4 confirm that the reaction between VCl_4 and sulfur proceeds at an appreciable rate to form VCl_3 and S_2Cl_2, as follows:

$$2VCl_4(l) + 2S(s) \longrightarrow 2VCl_3(l) + S_2Cl_2(l). \quad (4)$$

From the result of the reaction between VCl_4 and sulfur, the small amount of S_2Cl_2 formed during the reaction between VCl_4 and hydrogen sulfide may be due to the reaction between the unreacted VCl_4 and the sulfur which formed. These results confirm that the reaction between VCl_4 and hydrogen sulfide proceeds at an appreciable rate to form VCl_3, sulfur, and hydrogen chloride, as follows:

$$2VCl_4(l) + H_2S(g) \longrightarrow 2VCl_3(s) + S(s) + 2HCl(g). \quad (5)$$

As described in the previous paragraph, $VOCl_2$, sulfur, and hydrogen chloride were formed as the main products by the reaction between $VOCl_3$ and hydrogen sulfide. In addition to these products, small amounts of VCl_3, VCl_4, S_2Cl_2, and sulfur dioxide were formed.

From the above-mentioned experimental results, the formations of the reaction products mentioned above can be explained as follows: The first stage is the reaction between $VOCl_3$ and hydrogen sulfide to form $VOCl_2$, sulfur, and hydrogen chloride according to Reaction 1. Then the resulting sulfur reacts with the unreacted $VOCl_3$ to form $VOCl_2$ and S_2Cl_2 according to Reaction 2. The resulting S_2Cl_2 subsequently reacts with the unreacted $VOCl_3$ to form VCl_4, sulfur, and sulfur dioxide according to Reaction 3. The resulting VCl_4 reacts with the sulfur formed during the reaction to form VCl_3 and S_2Cl_2 according to Reaction 4, and also reacts with hydrogen sulfide to form VCl_3, sulfur, and hydrogen chloride according to Reaction 5.

Consequently, the amonts of VCl_4, VCl_3, S_2Cl_2, and sulfur dioxide are small. Also, since Reactions 4 and 5 proceed at appreciable rates, the amount of VCl_4 is smaller than that of VCl_3.

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