the viscosity and conductivity should give a constant. It has been found that this relation is only approximately true for the solutions investigated.

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THE ACTION OF VARIOUS ANHYDROUS CHLORIDES ON TELLURIUM AND ON TELLURIUM DIOXIDE.

BY VICTOR LENHER.

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In an earlier paper[1] the action of sulphur monochloride on elementary tellurium has been shown to result in the production of tellurium tetrachloride and sulphur, when the sulphur monochloride is in excess, while Krafft and Steiner,[2] in studying this reaction, observed that when an excess of tellurium is heated with sulphur monochloride, tellurium dichloride results.

Further study on the action of tellurium and the dioxide with active reagents has shown that with many of the anhydrous chlorides, especially with those which are liquid at the ordinary temperature, tellurium tetrachloride is produced. In certain cases the tetrachloride immediately separates from the solution in pure form while with a number of reagents of this character actual union takes place and a crystalline condensation product separates.

Tellurium Dioxide and Sulphur Monochloride.—Tellurium dioxide, when treated with an excess of sulphur monochloride, is transformed into the tetrachloride, sulphur dioxide being formed at the same time, according to the equation:

$$TeO_2 + 2S_2Cl_2 = TeCl_4 + SO_2 + 3S.$$

Analysis, $TeCl_4$: Calculated, Cl, 52.79; Te, 47.21.
Found, Cl, 52.07; Te, 46.65.

When, on the other hand, an excess of tellurium dioxide is heated with sulphur monochloride, the reducing action of this reagent steps in and the result is that the dichloride of tellurium is formed, thus:

$$TeO_2 + S_2Cl_2 = TeCl_2 + S + SO_2.$$

The formation of tellurium tetrachloride by the action of excess of sulphur monochloride on tellurium dioxide takes place readily; the reaction can be materially hastened by warming, and under these conditions, preparation of a large amount of the tetrachloride can be accomplished in a very short time. Extraction of the salt with carbon bisulphide is advisable in order to remove an excess of sulphur.

Behavior of the Oxychlorides of Sulphur toward Tellurium and Tellurium

[1] THIS JOURNAL, **24**, 188.

[2] *Ber.*, **34**, 560.

Dioxide.—With thionyl chloride, either the oxide of tellurium or the metal yields tetrachloride when the anhydrous chloride is in excess and dichloride when the element or oxide is in excess. These reactions are quite similar to the action of sulphur monochloride on the metal or oxide.

Sulphuryl chloride reacts with the element forming tellurium tetrachloride, but when the metal is in excess the dichloride is the resulting product. Tellurium dioxide in contact with sulphuryl chloride acts only very slowly, if at all, in the cold, but when the two are heated together in a sealed tube, crystalline products are formed which, by analysis, appear to be due to the simple solution of the dioxide in the sulphuryl chloride and subsequent recrystallization of condensation products. The end products of the reaction are dependent on the reacting masses and on the pressure at which the reaction is carried out.

Tellurium and Thionyl Chloride, with C. W. Hill.—Tellurium and thionyl chloride, when heated together in a sealed tube for twenty-four hours, yield crystals of the tetrachloride. The supernatant liquid was dark colored and was found to contain tellurium.

Analysis, $TeCl_4$: Calculated, Cl, 52.79; Te, 47.21.
Found, Cl, 52.00; Te, 47.47, 46.60.

In studying the action of thionyl chloride on tellurium it was found most satisfactory to heat the metal in a porcelain boat in a current of the vapor of thionyl chloride, which was produced by boiling thionyl chloride in a distilling bulb. The boat in which the tellurium was contained was placed in a combustion tube connected directly with the distillation bulb, and the combustion tube was drawn out into a series of bulbs. This apparatus was chosen inasmuch as the arrangement allowed the products of the reaction, by carefully regulating the temperature, to be carried from bulb to bulb, and in the first bulbs practically all of the sulphur formed in the reaction was retained, allowing the tellurium tetrachloride to be collected in the bulbs farthest from the boat.

Analysis, $TeCl_4$: Calculated, Cl, 52.79; Te, 47.21.
Found, Cl, 52.80, 52.20; Te, 47.01, 46.95.

The reaction of thionyl chloride on tellurium may be expressed,

$$2SOCl_2 + Te = TeCl_4 + SO_2 + S.$$

Thionyl Chloride and Tellurium Dioxide, with C. W. Hill.—By heating thionyl chloride with tellurium dioxide for twenty-four hours in a sealed tube, long slender crystals of tellurium tetrachloride were obtained. When the tubes in which the reaction was carried out were opened sulphur dioxide was liberated.

Analysis, $TeCl_4$: Calculated, Cl, 52.79; Te, 47.21.
Found, I, Cl, 52.31, 52.71; Te, 47.11, 47.64.
" II, Cl, 52.55, 52.13; Te, 47.55, 47.20.

On heating the dioxide in the vapor of thionyl chloride, tellurium tetrachloride is also readily obtained. Analyses II, above.

Sulphuryl Chloride and Tellurium, with C. W. Hill.—Tellurium and sulphuryl chloride, when heated together in a sealed tube, yield tellurium tetrachloride. On heating tellurium in the vapor of sulphuryl chloride, the metal is first transformed into black dichloride, after which it is further chlorinated to the tetrachloride by the action of excess of the sulphuryl chloride.

Analysis, $TeCl_4$; Calculated, Cl, 52.79; Te, 47.21.
Found, Cl, 52.51, 52.36; Te, 47.14, 47.30.

Sulphuryl Chloride and Tellurium Dioxide, with C. W. Hill.—Tellurium dioxide acts quite differently toward sulphuryl chloride than it does with thionyl chloride or sulphur monochloride. When heated in the vapor of sulphuryl chloride to as high a temperature as it is possible to conduct an experiment in hard glass combustion tubing, there is apparently no action. No volatilization of the tetrachloride occurs, and in our experiments, when a weighed amount of tellurium dioxide was heated in the vapor of sulphuryl chloride to as high a temperature as the glass would permit, the boat and contents weighed precisely the same after this treatment as before. This would indicate that under these conditions the vapor of sulphuryl chloride is without any appreciable action on tellurium dioxide.

When, however, tellurium dioxide and sulphuryl chloride are brought together in a sealed tube and heated, the system undergoes complex changes. When the dioxide was heated in a sealed tube with sulphuryl chloride for twenty-four hours at 165°, a small amount of a crystalline substance was formed, but the larger part of the dioxide remained unchanged. The heating was continued for seventy-two hours when the dioxide completely disappeared, the liquid having assumed a dark yellow color. On allowing the tube to cool, crystals deposited which were entirely unlike tellurium tetrachloride. When the tube was opened so much sulphur dioxide had been formed that the major part of the contents were lost when the pressure was released on opening the tube. The portion saved showed a content of 40.38 per cent. of chlorine.

The experiment was repeated a number of times, the tubes being heated for forty-eight hours to 175°. In each case the tube was strongly cooled before opening and in each tube a crystalline product was obtained.

Analysis showed the crystalline substances formed to vary in composition. Their composition by the analytical data obtained may be indicated as follows:

$3TeO_2, 4SO_2Cl_2$; $5TeO_2, 9SO_2Cl_2$; $TeO_2, 2SO_2Cl_2$; $2TeO_2, 5SO_2Cl_2$.

Sulphuryl chloride appears to have no action on tellurium dioxide at the ordinary temperatures or when the dioxide is heated in the vapor

of sulphuryl chloride, but when the two are heated together to high temperatures in a sealed tube, condensation products of varying composition are obtained.

In each experiment it was found that the excess of sulphuryl chloride contained large quantities of tellurium.

General Remarks.

In studying the action of the chloride of sulphur or the oxychlorides of sulphur it is observed that not infrequently one of the products of the reaction along with tellurium chloride is sulphur dioxide. Frequently in our experiments, in sealed tubes, large volumes of sulphur dioxide escaped on opening the tubes, while in the tube itself pure white tellurium chloride remained. This is an interesting illustration of mass action, as well as of conditions in the system, since sulphur dioxide readily precipitates tellurium from an aqueous or acid solution of the chloride, and the dioxide when heated in a current of sulphur dioxide gas is readily reduced to metal.

While the action of the various chlorides of sulphur on tellurium or on tellurium dioxide goes on readily, a number of other anhydrous chlorides act similarly but not infrequently by-products are formed which contaminate the chloride of tellurium which is produced. For example, *arsenic trichloride* or *antimony trichloride* react with tellurium dioxide, yielding tellurium tetrachloride and arsenic trioxide or antimony trioxide. In these cases it is very difficult to obtain the tellurium chloride in a high degree of purity. *Lead tetrachloride* will convert either the element or the oxide to tellurium tetrachloride. Here again an impure salt is formed and a mixture is obtained from which it is difficult to obtain pure tellurium salt.

Phosphorus trichloride, in contact with the dioxide of tellurium, quickly reduces it to the elementary condition, and when brought in contact with the element in pure condition is without action.

Carbon tetrachloride is without action on tellurium or on tellurium dioxide even when allowed to be in contact with either of them for a great length of time.

Tellurium Dioxide and Antimony Pentachloride.—Antimony pentachloride reacts with tellurium dioxide in the cold, the action of heat materially hastening the reaction, with the formation of the compound $TeCl_4SbCl_5$.

Analysis, $TeCl_4.SbCl_5$: Calculated, Te, 22.49; Sb, 21.16; Cl, 56.35.
Found, Te, 22.02; Sb, 21.74; Cl, ...

The action of antimony pentachloride on tellurium dioxide can be considered as first resulting in tellurium tetrachloride, which immediately unites with an additional molecule of antimony pentachloride, forming the addition product $TeCl_4SbCl_5$:

(*a*) $5TeO_2 + 4SbCl_5 = 5TeCl_4 + 2Sb_2O_5$;

(*b*) $TeCl_4 + SbCl_5 = TeCl_4,SbCl_5$;

or $5TeO_2 + 9SbCl_5 = 5[TeCl_4,SbCl_5] + 2Sb_2O_5$.

The compound $TeCl_4.SbCl_5$ appears in white tabular crystals which are readily decomposed by water.

Phosphorus Oxychloride and Tellurium Dioxide.—When phosphorus oxychloride is brought in contact with tellurium dioxide and the two are allowed to remain together in a warm place, a crystalline mass of large flat monoclinic plates begins to form. The excess of phosphorus oxychloride can be readily removed by means of carbon bisulphide. These crystals are deliquescent and are readily decomposed by water.

Analysis, $TeCl_4.POCl_3$: Calculated, Te, 31.32; P, 7.61; Cl, 61.06.
Found, Te, 30.22; P, 7.90; Cl, 59.13.

While phosphorus oxychloride doubtless first reacts with tellurium dioxide to form tellurium tetrachloride, the tetrachloride, as soon as produced, unites with one molecule of the excess of phosphorus oxychloride forming the addition product. The first reaction could be indicated:

$$3TeO_2 + 4POCl_3 = 3TeCl_4 + 2P_2O_5,$$

and the entire reaction may be expressed:

$$3TeO_2 + 7POCl_3 = 3[TeCl_4.POCl_3] + 2P_2O_5.$$

When the above reaction is carried out with an excess of phosphorus oxychloride, a considerable portion of the reaction product remains in solution in the excess of the reagent.

It thus appears that by the action of the various anhydrous chlorides which have been studied on tellurium or tellurium dioxide, three series of products can form; either tellurium tetrachloride or the dichloride can be produced, or by the use of such compounds as phosphorus oxychloride or antimony pentachloride, double chlorides can be obtained.

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THE HOMOGENEITY OF TELLURIUM.

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When tellurium or its dioxide reacts with a number of the liquid anhydrous chlorides,[1] crystals of tellurium tetrachloride or of a double chloride are formed along with a mother liquor which contains the excess of the reacting anhydrous chloride. This mother liquor contains such by-products of the reaction as may be soluble in it, and has also been found invariably to contain greater or less quantities of tellurium.

When sulphur monochloride is the reacting liquid, the amount of tel-

[1] See preceding paper.