combination with the manganese, and the reaction might be regarded in a sense as one of nitridation. Before this matter can be decided one way or the other, it will be necessary to perform a series of quantitative experiments upon the decomposition of the potassium trinitride, and upon the behavior of the substance toward manganese dioxide, in which the deportment of the nitrogen is studied gasometrically. The author is now engaged in this investigation and hopes to be able to present a definit solution of the problem in the near future.

Preliminary experiments have been performed in connection with the action of potassium trinitride and certain other trinitrides at high temperatures upon a number of other substances. When potassium trinitride is heated in air for a few moments with chromic oxide, for example, a considerable quantity of potassium chromate is obtained.

Summary.

In the preliminary experiments described in the preceding paragraphs, it has been shown that:

(1) Mixtures of potassium trinitride and manganese dioxide containing one, two, three and five molecules of the trinitride respectively to one of the dioxide yield when heated with free access of air considerable amounts of potassium manganate.

(2) The reaction apparently takes place in several stages. First, decomposition of the trinitride with liberation of metallic potassium; second, action of the potassium upon the manganese dioxide; third, oxidation of the product by means of atmospheric oxygen to potassium manganate. The precise nature of the reaction can not, however, be stated with certainty until the completion of a series of gasometric determinations which are now in progress.

The work was undertaken at the suggestion of Professor A. W. Browne, and has been carried out under his supervision.

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THE ACTION OF THIONYL CHLORIDE ON METALS AND METALLOIDS.

BY H. B. NORTH AND A. M. HAGEMAN.

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Although thionyl chloride has long been employed as a reagent in organic chemistry, its reaction on metals and metalloids has been but little studied. Apparently the first research along this line was carried out in 1883 by Heumann and Köchlin[1] who investigated the action of thionyl chloride on antimony. During the following year the reaction with selenium was studied by Prinz,[2] and this work was repeated by Lenher and North[3] in

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[1] *Ber.*, 16, 1625 (1883).

[2] *Ann.*, 223, 355 (1884).

[3] THIS JOURNAL, 29, 33 (1907).

1907. The reaction with tellurium was studied by Lenher and Hill[1] in 1908 and again in 1910 by Bela von Horvath.[2] The reaction with mercury was investigated by North[3] in 1910.

In the majority of the above enumerated researches, the reactions were carried out in sealed glass tubes at temperatures varying from 100–250° and in each case the product formed was a chloride. The action of thionyl chloride on metals and metalloids is, in general, a simple chlorination and proceeds according to the following equation, in which "M" represents a divalent metal:

$$3M + 4SOCl_2 = 3MCl_2 + 2SO_2 + S_2Cl_2.$$

When an excess of metal is employed the above equation does not represent the entire reaction, as no sulfur monochloride is formed. In such cases, the reaction appears to proceed according to the equation:

$$3M + 2SOCl_2 = 2MCl_2 + MS + SO_2.$$

With but one exception, the experiments described in this paper were carried out in sealed glass tubes and the metals employed were in the form of powder. The temperature varied from 150–200° as indicated in the descriptions of the various experiments.

Iron.—About 1 gram of iron was sealed in a glass tube with a large excess of the reagent. At the ordinary temperature there was no apparent reaction. The tubes were then heated at 150° for about thirty hours. Reaction appeared to be complete and the tubes contained well defined hexagonal plates, green by reflected light and red by transmitted light. The supernatant liquid was clear but slightly colored. Upon opening the tubes, considerable sulfur dioxide was evolved and the odor of sulfur monochloride was very noticeable. Analysis showed the crystals to be anhydrous ferric chloride, $FeCl_3$. Reaction evidently took place according to the following equation:

$$2Fe + 4SOCl_2 = 2FeCl_3 + 2SO_2 + S_2Cl_2.$$

From the size of the crystals, it is evident that ferric chloride is quite soluble in thionyl chloride at higher temperatures. The ferric chloride crystals agree perfectly with those obtained by one of the authors[4] from the action of sulfuryl chloride on iron.

Other tubes were prepared in which an excess of iron was used and these were heated for a time at 150°. When the reaction was complete, the tubes were found to contain ferrous chloride, ferrous sulfide and sulfur dioxide, hence the reaction took place according to the following equation:

$$3Fe + 2SOCl_2 = 2FeCl_2 + FeS + SO_2.$$

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[1] THIS JOURNAL, **30**, 738 (1908).

[2] *Z. anorg. Chem.*, **70**, 408 (1911).

[3] THIS JOURNAL, **32**, 184 (1910).

[4] *Bull. soc. chim.*, [4] **9**, 646 (1911).

Bismuth.—Thionyl chloride was found to be entirely without effect on bismuth at the ordinary temperature. Even when heated at 150° the reaction proceeded only very slowly. When the temperature was raised to 200°, however, the metal gradually disappeared with the formation of many small white crystals. These crystals analyzed to bismuth trichloride, $BiCl_3$, hence the reaction undoubtedly proceeded according to the equation

$$2Bi + 4SOCl_2 = 2BiCl_3 + S_2Cl_2 + 2SO_2,$$

for, as in the case with iron, considerable sulfur dioxide and sulfur monochloride were formed.

Other tubes were prepared using a large excess of thionyl chloride, and these were heated at 200° for many days. The products formed were always the same, the bismuth appearing as the trichloride.

Gold.—Gold, in the form of thin foil, was found to be entirely unattacked by thionyl chloride in the cold. Sealed tubes containing the two were heated at 150° for a number of days and still reaction did not take place. The temperature was then raised to 200° and the heating continued for ten days, at the end of which period the tubes still contained the gold foil though the liquid had become distinctly colored. After heating at 200° for several days longer, the tube contained, besides the gold and the liquid, a few small red crystals which were undoubtedly $AuCl_3$.

Tin.—The reaction between thionyl chloride and tin was found to proceed at the ordinary temperature with the formation of a mass of yellowish white crystals. This was found to be true even though a large excess of reagent was employed. When an excess of tin was used, the same yellowish white crystals were formed and remained, together with the excess of tin, even after the tube had been heated at 150° for several hours.

Analysis showed these crystals to be stannous chloride, hence the authors are of the opinion that the reaction proceeded according to the following equation:

$$3Sn + 2SOCl_2 = 2SnCl_2 + SnS + SO_2.$$

Stannous sulfide was always found to be present with the excess of tin.

When the tubes containing an excess of reagent were heated for a time at 150°, reaction was found to proceed further. The yellowish crystals first formed soon disappeared leaving a clear but somewhat yellowish liquid. It was at once thought that the dichloride had been oxidized to the tetrachloride, but inasmuch as the latter compound is a liquid and remained mixed with the excess of thionyl chloride, proof was rendered somewhat difficult. Sulfur dioxide and sulfur monochloride were also formed in this reaction.

Inasmuch as thionyl chloride distils at 78° and tin tetrachloride at

114°, an attempt was made to separate them by fractional distillation. A residue was thus obtained by one fractionation which did not boil at 105°, but which gave a strong test for chlorine. Most of the residue was dissolved in water containing hydrochloric acid and tests were made for tin. This solution gave no test with mercuric chloride solution, but with hydrogen sulfide a heavy yellow precipitate of tin disulfide was formed, proving conclusively that the residue contained considerable tin and that it was in the tetravalent form. Tin tetrachloride had undoubtedly been formed, reaction proceeding according to the equation

$$3SnCl_2 + 4SOCl_2 = 3SnCl_4 + 2SO_2 + S_2Cl_2,$$

or if the entire reaction with the metal is represented,

$$3Sn + 8SOCl_2 = 3SnCl_4 + 4SO_2 + 2S_2Cl_2.$$

Antimony.—As stated at the beginning of this paper, the action of thionyl chloride on antimony has been studied by Heumann and Köchlin. According to them, the reaction proceeds as follows:

$$3Sb_2 + 6SOCl_2 = 4SbCl_3 + Sb_2S_3 + 3SO_2.$$

The authors have repeated this work and have found the above equation to be correct when an excess of antimony is used. Furthermore, they have found that the reaction takes place with considerable violence even at ordinary temperatures. However, when sealed tub escontaining antimony and a large excess of thionyl chloride were heated, the white crystals which were at first formed gradually disappeared and the tubes contained only a clear though somewhat colored liquid. Evidently the trichloride had been oxidized to the pentachloride, according to the equation

$$3SbCl_3 + 4SOCl_2 = 3SbCl_5 + S_2Cl_2 + 2SO_2,$$

or the following, if the entire reaction on the metal is represented:

$$6Sb + 20SOCl_2 = 6SbCl_5 + 5S_2Cl_2 + 10SO_2$$

To bring about a complete separation of the antimony pentachloride from the sulfur monochloride and excess of thionyl chloride has been impossible on account of the small quantities of material used. The authors have, however, brought about a partial separation by distilling off as much of the liquid as possible up to a temperature somewhat close to the boiling point of the antimony compound. The residue left from this separation was tested and found to contain much chlorine and pentavalent antimony, hence it has been concluded that antimony pentachloride was the product of the reaction.

Arsenic.—Arsenic dissolved to a clear solution when heated with thionyl chloride in a sealed tube at about 150°. An excess of thionyl chloride was also tried, and the tube was heated for many hours with no further apparent result. The tube gave sulfur dioxide and sulfur monochloride when opened. The liquid was fractionated once and the residue which did not boil at 125° was found to give a strong test for chlorine and also for trivalent arsenic. On account of this the authors are of the opinion that arsenic chloride was formed, the reaction proceeding as follows:

$$2As + 4SOCl_2 = 2AsCl_3 + S_2Cl_2 + 2SO_2.$$

Zinc.—Thionyl chloride appeared to have no action on zinc, either in the cold or after heating for several days at temperatures from 150–200°.

Cadmium.—Like zinc, cadmium is entirely unacted upon by thionyl chloride either hot or cold.

Magnesium.—A thoroughly cleaned piece of magnesium ribbon was treated with thionyl chloride, but no reaction was found to take place even though the tubes containing the material were heated for many hours at 200°.

Lead, Chromium, Nickel.—These metals were likewise found to be entirely unattacked by the reagent at 200°.

A comparison of some of the above described thionyl chloride reactions with the corresponding sulfuryl chloride reactions is interesting. Iron, as mentioned heretofore, reacts as easily with one as with the other, and the product formed, anhydrous ferric chloride, is the same in both cases when an excess of reagent is used. Again, zinc and cadmium, which are not attacked by sulfuryl chloride, have been shown likewise to be unattacked by thionyl chloride. With gold, a marked difference is seen. The reaction between gold and sulfuryl chloride proceeds quite readily with the formation of large, red crystals of anhydrous gold chloride, whereas with thionyl chloride, very little reaction was found to take place, even though the tubes were heated for days at 200°.

It is interesting to note that magnesium, zinc and cadmium are not attacked by thionyl chloride whereas mercury, which is also a member of this group of elements, has been previously shown[1] to react readily with the formation of mercurous and mercuric chloride, depending upon the amount of reagent used.

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THE DETERMINATION OF IODINE IN THE PRESENCE OF OTHER HALOGENS AND ORGANIC MATTER.

BY E. C. KENDALL.

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During an investigation of the iodine bearing compound of the thyroid gland a method for the determination of small amounts of iodine in organic

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[1] THIS JOURNAL, 32, 184 (1910).