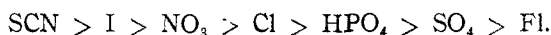


the colloidal solution. Electrostatic repulsion keeps the particles apart if the charge is high, while with a small or no charge the Brownian movement agglutinates the particles into greater masses, thus causing precipitation. This explanation was first given by Hardy and has often been confirmed. As the chemical composition and the concentration of the solution affects the charge, according to my experiments, it is possible to explain the precipitating action of salts. If the change of the charge brought about by increasing the concentration is such that the charge becomes smaller, precipitation may occur. Pauli,¹ in his investigation on the precipitating action of salts on egg albumin, finds that with salts of the same bases the precipitating power increases according to the anion in the following series:



As seen from the data on page 350, salts of these anions create negative e. m. f. on toluidine, if a potassium thiocyanate solution is kept constant on the one pole; the magnitude of the e. m. f. increases in the same series. One should conclude, according to the theory proposed, that the colloidal albumin particle has a high positive charge. This is the case in an acid solution where, as a rule, the action of anions is clearly manifested.

A series of cations, according to precipitating strength, which is in accordance with the above experiments, has also been found.

[The experiments described in this paper were performed in the writer's private laboratory at Berlin, Germany, during summer 1912.]

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THE ACTION OF THIONYL CHLORIDE ON THE OXIDES OF METALS AND METALLOIDS.

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The action of thionyl chloride on oxides of metals and metalloids has been studied but little. The first research of this nature appears to have been made by Lenher and North,² who investigated the reaction of thionyl chloride on selenium dioxide in 1907. This work was followed in 1908 by a study of the reaction on tellurium dioxide by Lenher and Hill.³ In 1910 North⁴ investigated the reaction of thionyl chloride on both the red and yellow varieties of mercuric oxide.

In each of the above-mentioned investigations reaction was found to proceed readily at elevated temperatures, with the formation of the

¹ *Hofmeister's Beiträge*, 3, 225.

² *THIS JOURNAL*, 29, 33 (1907).

³ *Ibid.*, 30, 738 (1908).

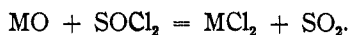
⁴ *Ibid.*, 32, 184 (1910).

chloride of the metal and the corresponding production of sulfur dioxide. The reactions were carried out in sealed glass tubes.

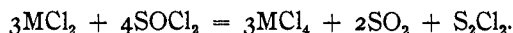
In 1911 Darzens and Bourion¹ investigated the reaction of thionyl chloride on a number of oxides, chiefly those of rare earths. They found that with ThO_2 , La_2O_3 , Sm_2O_3 , ZrO_2 , and Cr_2O_3 the corresponding chlorides were formed, while V_2O_5 yielded the oxychloride VOCl_3 , and WO_3 gave a mixture of the two oxychlorides, WO_2Cl_2 and WOCl_4 . TiO_2 gave a peculiar compound which they supposed to be a sulfochloride, and Gd_2O_3 gave a mixture of chloride and oxychloride.

It is very probable that Darzens and Bourion made no examination of the by-products formed, inasmuch as no mention was made of them and equations were not given for the reactions.

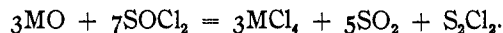
In general, the action of thionyl chloride on an oxide of a metal results in the formation of a chloride of the metal and the liberation of sulfur dioxide. This reaction can be represented by the following general equation in which "M" represents a divalent metal:



There are cases, however, for which this type equation does not hold. For example, with a metal having two series of salts, the lower oxide, when treated with a decided excess of the reagent, gives rise to the higher chloride, hence the reagent appears to act first as a chlorinating agent and then as an oxidizing agent. If "M" in the above equation represents a metal which is tetravalent as well as divalent, the reaction first proceeds as above with the formation of the dichloride; and this compound is then oxidized to the tetrachloride according to the equation



By combining the two equations we obtain the following:



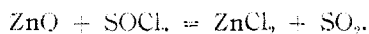
In such an oxidizing reaction, the by-products are always sulfur dioxide and sulfur monochloride.

All of the reactions to be described in this paper were carried out in sealed glass tubes and with one or two exceptions, a temperature of 150–200° was employed. In each experiment about 1 gram of the oxide, carefully dried, was treated with an excess of the reagent. All of the oxides were as pure as could be obtained.

Zinc Oxide.—Zinc oxide and thionyl chloride were heated together in sealed glass tubes for several hours at 150° without any apparent change in appearance. However, when the tubes were opened considerable pressure due to sulfur dioxide was noted. The white powder was well washed with carbon disulfide, dried and weighed. It was then dissolved in water containing a few drops of nitric acid. Determination of

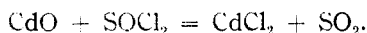
¹ *Compt. rend.*, 153, 270 (1911).

chlorine and zinc proved the compound to be anhydrous zinc chloride, ZnCl_2 , hence the reaction undoubtedly proceeded according to the equation:



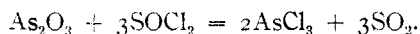
Judging from the fine state of division, it is probable that anhydrous zinc chloride is only slightly soluble in thionyl chloride.

Cadmium Oxide.—Thionyl chloride was found to have no action on cadmium chloride in the cold but when heated at 200° in sealed glass tubes the brown color of the oxide gradually disappeared with the simultaneous production of a white, non-crystallin compound. This proved upon analysis to be cadmium chloride, CdCl_2 , hence the reaction proceeds according to the equation:



It is evident that cadmium chloride, like zinc chloride, is at best only slightly soluble in thionyl chloride and liquid sulfur dioxide.

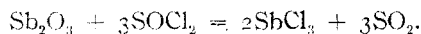
Arsenic Trioxide.—In the case of arsenic trioxide the reaction proceeds in the cold and the oxide gradually goes into solution. It was naturally thought that the reaction follows the equation:



Inasmuch as arsenic trichloride is a liquid and remains mixed with the excess of thionyl chloride and liquid sulfur dioxide, a quantitative separation is difficult. Furthermore, although arsenic trichloride boils at 130° and thionyl chloride at 78° , separation by fractional distillation is difficult owing to the small quantities of material used. A single fractionation was made, however, the portion boiling below 128° being rejected and that boiling between 128° and 132° being retained. The latter was examined qualitatively and was found to contain arsenic in the trivalent form in addition to considerable chlorine. From this it was assumed that the above equation is correct and that arsenic trichloride was formed.

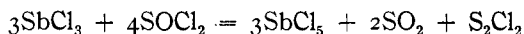
Other experiments were performed in which a decided excess of thionyl chloride was employed at a temperature of 200° , but these, upon examination in the manner described above, gave the same tests, hence they undoubtedly contained the same compound.

Antimony Trioxide.—Antimony trioxide was found to react immediately with thionyl chloride at the ordinary temperature with the liberation of considerable heat. The oxide dissolved completely in the reagent but upon cooling white crystals of antimony trichloride separated. The reaction proceeds according to the equation:

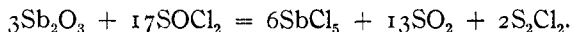


Other experiments were made in which a large excess of thionyl chloride was used and the tubes were sealed and heated at 150° for several hours. Upon cooling, no crystallin deposit was formed, hence it was supposed

that the excess of thionyl chloride had oxidized the antimony trichloride to pentachloride according to the equation:



or, representing the entire reaction by a single equation:

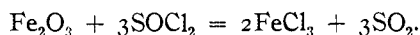


The liquid contents of the tubes were examined carefully and were found to contain pentavalent antimony, sulfur dioxide and sulfur monochloride, hence the authors are confident that the reaction proceeds according to the equations given above. No attempt was made to separate the products quantitatively.

Bismuth Trioxide.—Bismuth trioxide, in contrast to arsenic and antimony trioxides, was unattacked by the reagent at the ordinary temperature, but after heating for several hours at 150–200° the formation of small, white crystals was noted. These crystals analyzed to BiCl_3 ; hence, reaction proceeds according to the equation:



Ferric Oxide.—Although ferric oxide is not at all attacked by thionyl chloride at the ordinary temperature, when heated at 150° the reaction proceeds readily with the formation of anhydrous ferric chloride in large, green, hexagonal plates, which by transmitted light are red in color. The reaction evidently proceeds as follows:

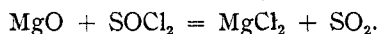


Judging from the size of the crystals, it is evident that anhydrous ferric chloride is exceedingly soluble in thionyl chloride at elevated temperatures. In all respects the crystals appear to be identical with those obtained by the action of thionyl chloride¹ and sulfuryl chloride² on metallic iron.

Glucinum Oxide.—Glucinum oxide was found to be unattacked by thionyl chloride even after tubes containing the oxide and reagent had been heated at 200° for 30 hours.

Calcium Oxide and Strontium Oxide.—Neither calcium nor strontium oxide were found to be attacked by thionyl chloride at temperatures up to 200°.

Magnesium Oxide.—Magnesium oxide, which had been strongly ignited and cooled over sulfuric acid, was heated with thionyl chloride for 24 hours at a temperature of 150–200°. The white powder, which to all appearances had not changed, was well washed with carbon disulfide, dried and weighed. Analysis showed it to be MgCl_2 ; hence, reaction evidently proceeds according to the equation:



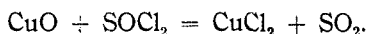
¹ North and Hageman, THIS JOURNAL, 34, 890 (1912).

² North, Bull. soc. chim., [4] 9, 646 (1911).

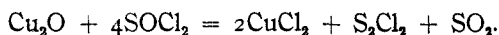
Two other samples of magnesium oxide, which were tested without previous blasting, were found to react readily at slightly elevated temperatures, due, undoubtedly, to the presence of considerable magnesium hydroxide.

Silver Oxide.—Silver oxide was found to be unattacked by the reagent in the cold, and even after heating for several hours at 150° reaction had apparently not taken place, inasmuch as the brown powder appeared to be unchanged. The tubes were opened, the brown powder was well washed with carbon disulfide, dried and examined qualitatively. It was found to contain a trace of silver chloride. It is possible that the reaction proceeded to a slight extent and that the silver chloride formed, due to its insolubility in the reagent, served to protect the remainder of the oxide.

Cupric Oxide.—Cupric oxide was not attacked by the reagent at the ordinary temperature, but after the tubes containing the two were heated at a temperature of 200° for several hours, they were found to contain a brownish green, noncrystallin powder. This substance was washed, dried and analyzed and was found to be anhydrous cupric chloride, CuCl_2 ; hence, the reaction took place according to the equation:



Cuprous Oxide.—Cuprous oxide, like the higher compound, was found to react with thionyl chloride at about 200° and the product formed was cupric chloride, CuCl_2 . Inasmuch as the reaction is one of oxidation as well as chlorination, it was thought that it proceeds according to the equation:



When the tubes were opened they were found to contain sulfur dioxide and sulfur monochloride in addition to the excess of the reagent; hence, the equation above is undoubtedly correct.

Aluminum Oxide, Chromic Oxide, and Tin Dioxide.—These compounds were entirely unattacked by thionyl chloride, even after being heated with the reagent at 200° for hours. This is not surprising, however, inasmuch as these compounds are little attacked by reagents in general, especially after having been highly heated.

As mentioned at the beginning of this paper, Darzens and Bourion state that chromic oxide is changed to the chloride by thionyl chloride at elevated temperatures, though they make no mention of the temperature employed. It is possible that the oxide used by Darzens and Bourion may have been made at a correspondingly low temperature, or it may possibly have contained a trace of moisture. The authors of this article have been absolutely unable to bring about even the slightest reaction between chromic oxide and thionyl chloride at temperatures up to 200°.