SELENIUM NITRIDE

By Victor Lenher and E. Wolesensky Received November 24, 1906.

When ammonia gas is brought in contact with selenyl chloride in the cold, the reaction, according to Michaelis¹ proceeds as follows,

$$6SeOCl_2 + 16NH_3 = 3SeO_2 + 3Se + 4N + 12NH_4Cl.$$

Michaelis in studying this reaction, brought ammonia gas directly in contact with selenyl chloride. At low temperatures only slight action was noted while at higher temperatures, the reaction proceeds with evolution of heat.

In studying the behavior of ammonia gas when conducted into a solution of selenyl chloride in either benzene or toluene, the reaction under these conditions was found to be of a different character than that indicated by the equation of Michaelis, one of the principal products being the nitride of selenium.

When dry ammonia gas is conducted into a strong solution of selenyl chloride in benzene or toluene, considerable heat is evolved and a brick-red precipitate forms, which when treated with cold water leaves a bright red residue. This residue when dissolved in nitric acid shows complete absence of chlorine but a large percentage of selenium.

Quantitative data obtained on the precipitate obtained before treatment with water seem to indicate that it consists of ammonium chloride, selenium, selenium dioxide and a small amount of selenium nitride.

By using a more dilute solution of selenyl chloride (2 to 4 per cent.) in benzene, the reaction is materially moderated and a buff colored precipitate appears, which on drying becomes orange-red. This material when washed with cold water to remove the ammonium salts and then extracted with potassium cyanide to remove the free selenium left a brick-red nitride, which proved to be a highly explosive body. Analyses showed,

	I	II	Calculated for SeN
Se	84.7	84.7	84.8
N	15.5	16.3	15,2

Espenscheid² obtained this compound by conducting dry ammonia gas diluted with hydrogen over selenium tetrachloride cooled by a freezing mixture, and obtained a brown mass which when treated with water and extracted with carbon bisulphide or potassium cyanide left an orange-red powder of SeN, which exploded violently when struck or when brought in contact with chlorine or hydrochloric

¹ Jeanische Z. 6, 91.

² Ann. Chem. 114, 101.

acid either in the gaseous form or in concentrated solution. When heated to 150° it began to darken and exploded at 200°. On the other hand, the nitride obtained by the action of ammonia on selenyl chloride dissolved in benzene begins to darken at a comparatively low temperature and explodes at 130°. When the substance has been carefully purified and is thoroughly dry a slight shock will cause it to detonate violently.

Verneuil' in a manner differing but slightly from that of Espenscheid, obtained a similar substance but to which he ascribed the formula Se₃N.

The result of the interaction between ammonia and selenyl chloride in benzene solution evidently depends on the temperature and the concentration of the reacting substances. When the temperature is not too high and the solution is dilute, a highly explosive compound of selenium and nitrogen is formed which has the composition SeN. If, however, a solution of considerable strength be employed, the temperature of the reaction causes the separation of a large quantity of free selenium.

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HYDRONITRIC ACID. VI.

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Anhydrous Hydronitric Acid.

Anhydrous hydronitric acid was first prepared by Curtius and Radenhausen² in 1891. They describe the acid as a colorless, mobile liquid which boils at 37°, and which explodes with great violence when brought into contact with a hot substance. They add that it sometimes explodes spontaneously even at room temperature. They decided to discontinue their investigations because of the explosive character of the compound (Herr Radenhausen was quite seriously injured by one explosion), and they urgently warned others against making further experiments with the anhydrous acid.

It seemed probable, however, that with suitable precautions the operator might be protected from serious injury, and consequently the study of the anhydrous acid was taken up in this laboratory. The devices that were employed to guard against accident are described below; but it may here be stated that, although several violent explosions of the acid occurred during the progress of the investigation, Miss Isham suffered no injury whatever in any case.

¹ Bull. soc. chim., 238, 548.

² J. pr. Chem., 43, 207.