

ACTION OF AMMONIUM HYDRATE ON THE HALOGEN
SALTS OF LEAD.

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In Watt's Dictionary (III. 556) we find the statement that by decomposing lead chloride with ammonia a hydrated oxychloride $Pb_4Cl_2O_3 \cdot H_2O$ is obtained. As certain observed facts seemed to disagree with this, a set of experiments were undertaken to determine what oxychloride or oxychlorides were formed by this action of ammonium hydrate and the conditions of formation.

The lead chloride for these experiments was gotten by precipitating pure lead nitrate with hydrochloric acid. The precipitate was thoroughly washed and dried. To about 7 grains of this chloride 140 c. c. of ammonia solution was added, the mixture being heated then some six hours upon a sand bath. The residue was washed, dried and analyzed with the following results :

I. .6200 grams of substance gave .3585 grams AgCl. p. c.
Cl.=14.20.

The water was determined and Cl. calculated on a dry basis=14.68.

II. .5003 grams of substance gave .2950 grams AgCl. p. c.
Cl.=14.57.

No water in the specimen.

III. .5650 grams of substance gave .3265 grams AgCl. p. c.
Cl.=14.29.

Calculated water-free=14.54.

IV. 1.3345 grams of substance gave 1.5340 grams $PbSO_4$. p. c.
Pb. 78.52.

Water-free=81.14.

V. H_2O in air dried substance=3.33 p. c.

		I.	II.	III.	IV.	V.
Pb_2	Calculated, p. c.	82.56				81.14
O	" "	3.31	" "			
Cl_2	" "	14.13	" "	14.68	14.57	14.54
H_2O	" "	3.46	" "			3.33

Again, between ten and eleven grams of the chloride was heated with 175 c. c. ammonia solution for twelve hours on a water-bath, then washed and dried as before.

I. .145 grams of substance gave .0525 grams AgCl. p. c.
Cl.=8.61.

Water-free=8.70.

II. .4935 grams of substance gave .1490 grams AgCl. p. c.
Cl.=7.48.

Water-free=7.56.

III. .5035 grams of substance gave .1594 grams AgCl. p. c.
Cl.=7.81.

Water-free=7.89.

IV. 1.5353 grams of substance gave 1.9420 grams PbSO₄ p. c.
Pb=86.31.

Water-free=87.26.

	I.	II.	III.	IV.
Pb ₄ Calculated, p. c.	87.53.			87.26
Found, p. c.				
Cl ₂ " " 7.48	" 8.70	7.56	7.89	
O ₃ " " 4.99				

These two experiments, then, would point to the formation of two entirely different bodies, the first having the formula PbCl₂. PbO. H₂O., the second the formula PbCl₂. 3PbO. H₂O.

The most plausible explanation of this difference of action seemed to be that in the case of the substance heated upon the sand-bath the mixture was kept boiling briskly at the higher temperature, the loss of ammonia was consequently more rapid, and, for a portion of the time, whatever oxychloride had been formed was subjected to the action of a boiling solution of ammonium chloride.

To test the correctness of these results two equal amounts of the chloride (about five grams) were taken, ammonia solution added and the two then heated, one upon the sand-bath and the other upon the water-bath. As the one on the sand-bath was kept at a brisk boil, evaporation was faster and more of the ammonia had to be added to replace that which was thus lost. Hence to the chloride upon the sand-bath 145 c. c. were added, whereas 65 c. c. sufficed for that heated on the water-bath. The object was to keep the ammonia solution strong enough to give always a decided smell of ammonia. Once or twice, however, that upon the sand bath became very weak.

The residue from the sand-bath mixture was washed. The substance was creamy yellow and was unchanged by heating up to 200° C.

I. .5060 grams of substance gave .2745 grams AgCl. p. c.
Cl.=13.41. Water-free = 13.89.

II. 1.2700 grams of substance gave 1.4730 grams PbSO_4 p. c.
 Pb = 78.45. Water-free = 81.26.

	I.	II.
Pb calculated p. c.	82.56	found p. c.
Cl_2 " " 14.13	" "	13.89
O " " 3.31	" "	

The formula then is $\text{PbCl}_2 \cdot \text{PbO}$.

The residue from the water-bath was much yellower and became a deep yellow on heating. The analysis gave the following results :

I. .520 grams of substance gave .1370 grams AgCl p. c.
 Cl. = 6.51. Water-free = 7.28.

This corresponds with the per centage of chlorine calculated for the tribasic chloride $\text{PbCl}_2 \cdot 3\text{PbO}$.

For the experiments with the iodide conducted by Mr. Borden, lead iodide was prepared by precipitating pure lead nitrate with pure potassium iodide and thoroughly washing and drying the precipitate. In the first set of experiments three portions were taken. One was heated on the sand-bath ten hours, the second a similar time on the water-bath, the third was covered with ammonia solution and set aside for three days at a temperature of $15-20^\circ \text{C}$. In the first two instances no precautions were taken to keep a strong solution of ammonia over the iodide. In the analyses, lead alone was determined as pointing with sufficient accuracy to the nature of the body formed. Corrections were made for the percentage of water retained in the powders analyzed. Generally two simultaneous lead determinations were made of each substance. The means of concordant analyses are given :

1. Substance heated on water-bath gave ... 62.50 p. c. Pb.
2. Substance heated on sand-bath gave 60.11 p. c. Pb.
3. Substance standing in the cold gave 58.82 p. c. Pb.

Calculated for $\text{PbI}_2 \cdot \text{PbO}$, p. c. Pb = 60.51. Calculated for $\text{PbI}_2 \cdot 2\text{PbO}$, p. c. Pb. = 68.45.

From this it would seem that the ammonia which was only moderately heated had the greatest effect; that which was not heated at all had the least.

In the second set of experiments the heating lasted only seven hours (the mixture stood three days before heating) but care was taken to insure a strong solution of ammonia always covering the iodide. The results were as follows:

1. Substance heated on water-bath gave...64.13 p. c. Pb.
2. Substance heated on sand-bath gave....63.25 " "

Another set heated ten hours without previous standing were analyzed:

1. Substance heated on water-bath gave...61.60 p. c. Pb.
2. Substance heated on sand-bath gave... 60.37 " "

From these results it is seen that the longer ammonia is allowed to act upon the iodide, the more iodine is removed, and hence the more oxide of lead formed. To test this, two portions were taken and the ammonia allowed to act on one for 38 hours (heating it on the water-bath); on the second 68 hours. The analyses were as follows:

1. Substance heated 38 hours gave.....74.10 p. c. Pb.
2. Substance heated 68 hours gave.....78.94 " "

Calculated for PbI_2 , $3PbO$, 73.26 p. c. Pb; for PbI_2 , $4PbO$, 76.38 p. c. Pb.; for PbI_2 , $5PbO$, 79.31 p. c. Pb.

These experiments then would lead to the following conclusions:

1. By the action of ammonia in the cold the monobasic oxyiodide of lead is formed.

2. By heating the solution we get oxyiodides, the basicity of which is determined by the length of heating. If, by the more active boiling upon the sand-bath, the ammonia solution becomes weak, then the tendency is to form the monobasic oxyiodide. The oxide of lead previously formed reacts upon the ammonium iodide, forming lead iodide and setting free ammonia.

In the case of the action of ammonia on lead chloride as examined by Mr. Wood, it seems that the oxychloride formed is not dependent upon the time of heating, but a definite oxychloride is formed whether heated six, ten or fifteen hours, provided the chloride is kept covered with an excess of ammonia. If, by active boiling on the sand-bath, the ammonia solution becomes too much weakened, then a definite oxychloride is formed, independent of the number of hours the solution is heated. Some of Mr. Wood's experiments were repeated to test these conclusions.

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