JOURNAL

OF

THE CHEMICAL SOCIETY.

I.—*The Action of Ammonia on Sulphochloride of Phosphorus.*

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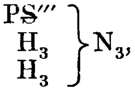
DURING the continuation of the researches referred to in a previous paper * we have examined the action of ammonia on sulphochloride of phosphorus. Schiff † had previously stated that there results a white mass which is decomposed very quickly by cold water, and evolves sulphuretted hydrogen when treated with hot water. He supposed it to contain, in addition to chloride of ammonium, sulphosphotriamide,  $\left.\begin{matrix}PS'''\\H_3\\H_3\end{matrix}\right\}N_3$, but he gives no analyses. He states also that, when heated without access of air, this white mass gives off ammonia, while there remains a white substance difficult to decompose.

We found that when dry ammoniacal gas was passed into a flask containing pure sulphochloride of phosphorus, at the ordinary temperature, four equivalents were the most that it would absorb. At 0°C. the same amount was absorbed, though more slowly, and when heated to almost the point of decomposition, it absorbed no more. The following were the results of experiment:—

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* Chem. Soc. J. [2], ii, 225.

† Ann. Ch. Pharm., ci., 303.

3·713 grms. PCl_3S	absorbed	1·485 grm.	NH_3	=	39·9 p.c.
5·327 „	„	2·180	„	=	40·9 „
4·142 „	„	1·685	„	=	40·7 „
3·160 „	„	1·282	„	=	40·6 „

Now 4 equivalents of ammonia would cause an increase in weight of 40·3 per cent.

The result is a white substance, caked together, dissolving entirely in water, except perhaps a trace of the sulphochloride, and yielding then an acid solution. The solution gives no indication of phosphoric acid when tested with ammonia and sulphate of magnesium, nor does it contain any trace of sulphuretted hydrogen. When rendered neutral, it gives precipitates with several metallic salts.

With sulphate of copper it gives a yellowish-white flocculent precipitate, insoluble in dilute hydrochloric acid or ammonia, soluble in cyanide of potassium; it becomes brown on drying: when heated *per se* in a tube, it gives off ammonia and sulphide of ammonium.

With sulphate of zinc, it gives also a white flocculent precipitate readily soluble in dilute acids and ammonia; it suffers the same decomposition when heated *per se.*

With chloride of cadmium it gives a similar precipitate.

With chloride of lead, a white precipitate was obtained, soluble in dilute nitric acid. The precipitate when boiled with water slowly turned black.

With sulphate of nickel, a greenish-white precipitate was produced, readily soluble in dilute acids and ammonia. The ammoniacal solution when boiled deposited sulphide of nickel.

With chloride of cobalt, it gave an exactly similar precipitate of a bluish-white colour.

A solution of protochloride of tin produced a bulky white precipitate, readily soluble in dilute hydrochloric acid.

Nitrate of silver gives a white precipitate mixed with chloride of silver. This precipitate is insoluble in dilute nitric acid and in ammonia; the presence of an excess of nitrate of silver causes it to turn black.

No precipitates were obtained with solutions of chloride of barium, chloride of calcium, sulphate of magnesium, ferric chloride or sulphate of aluminum.

With chloride of mercury it gave a bulky white precipitate, but this soon changed to a yellow one, which was found to be nothing else than the compound of sulphide and chloride of mercury, $Hg_2S.HgCl$. It forms no black sulphide of mercury, even if the sulphur acid in solution be in large excess. The solution from this yellow precipitate gives no precipitate with ammonia and sulphate of magnesium, and probably contains an amidated acid; but we have not yet submitted it to a complete examination.

The copper, cadmium, and zinc salts were well washed, dried, and analysed. The process adopted was as follows:—To determine the metal, sulphur, and phosphorus, the salt was oxidized with fuming nitric acid till completely dissolved, and the sulphuric acid formed was precipitated by chloride of barium; after separating the excess of barium, the metal was precipitated by sulphuretted hydrogen or sulphide of ammonium, and the phosphoric acid in the filtrate was determined in the usual manner as magnesium-salt. To determine the nitrogen, the salt was digested with hydrochloric acid for some time till completely decomposed, the copper or cadmium precipitated by sulphuretted hydrogen, and the nitrogen determined as ammonio-platinum-salt in the filtrate. The cadmium was weighed as sulphide, but the sulphides of copper and zinc were re-dissolved, and weighed as oxides.

Copper-salt.

I. ·4205 grm. gave ·675 grm. Ba_2SO_4, ·1195 grm. Cu_2O, and 322 grm. $Mg_4P_2O_7$.

II. ·2455 grm. gave ·0695 grm. Cu_2O and ·7515 grm. $PtCl_2,NH_4Cl$.

III. ·297 grm. gave ·0835 grm. Cu_2O and ·915 grm. $PtCl_2.NH_4Cl$.

IV. ·549 grm. ignited with oxide of copper gave ·1475 grm. H_2O.

These numbers reckoned to 100 parts give:—

	I.	II.	III.	IV.
Phosphorus	21·38	—	—	—
Nitrogen	—	19·19	19·31	—
Hydrogen	—	—	—	2·98
Copper	22·67	22·59	22·49	—
Sulphur	22·02	—	—	—

This agrees with the composition PN_2H_4CuSO, which we may term the thiophosphodiamate of copper.

	Calculated.		Mean of analyses.
Phosphorus	31	21·74	21·38
Nitrogen	28	19·64	19·25
Hydrogen........	4	2·80	2·98
Copper	31·6	22·16	22·58
Sulphur	32	22·44	22·02
Oxygen..........	16	11·22	11·79 (by loss)
	142·6	100·00	100·00

Cadmium-salt.

I. ·2795 grm. gave ·1195 grm. Cd_2S, and ·7655 grm. $PtCl_2.NH_4Cl$.

II. ·338 grm. gave ·144 grm. Cd_2S, ·488 grm. Ba_2SO_4, and ·2295 grm. $Mg_4P_2O_7$.

III. ·265 grm. gave 114 grm. Cd_2S, and ·725 grm. $PtCl_2.NH_4Cl$.

IV. ·405 grm. ignited with oxide of copper gave ·0855 grm. H_2O.

Or in 100 parts :—

	I.	II.	III.	IV.
Phosphorus....	—	18·96	—	—
Nitrogen......	17·18	—	17·15	—
Hydrogen	—	—	—	2·34
Cadmium	33·25	33·13	33·46	—
Sulphur	—	19·78	—	—

This agrees equally with the formula PN_2H_4CdSO, thio-phosphodiamate of cadmium.

	Calculated.		Mean of analyses.
Phosphorus	31	18·57	18·96
Nitrogen..........	28	16·76	17·16
Hydrogen	4	2·40	2·34
Cadmium	56	33·53	33·28
Sulphur	32	19·16	19·78
Oxygen	16	9·58 (by loss)	8·48
	167	100·00	100·00

Zinc-salt.

I. ·607 grm. gave ·9705 grm. Ba_2SO_4, ·169 grm. Zn_2O, and ·4745 grm. $Mg_4P_2O_7$.

II. ·1775 grm. gave ·546 grm. $PtCl_2.NH_4Cl$.

These determinations agree with the formula PN_2H_4ZnSO.

	Calculated.		I.	II.
Phosphorus	31	21·60	21·82	—
Nitrogen	28	19·52	—	19·29
Hydrogen......	4	2·78	—	—
Zinc	32·5	22·65	22·28	—
Sulphur........	32	22·30	21·94	—
Oxygen........	16	11·15	—	—
	143·5	100·00		

Two attempts were made to obtain the acid itself in a fit state for analysis. The mixed thio-phosphodiamate and chloride of silver was treated with hydrochloric acid, and the thio-phosphodiamate of copper was treated with sulphuretted hydrogen, and in each case the filtered solution was allowed to evaporate over sulphuric acid. The solutions, which were very feebly acid to test-paper, continued to deposit sulphur for some days, when they appeared to contain the ammonium-salt of some amidated phosphoric acid. That the acid can exist for awhile in a free state is evident from the mode of preparation.

A portion of sulphochloride of phosphorus, instead of being treated with gaseous ammonia, was thrown into the strongest aqueous solution of that gas. A clear solution resulted, which, when neutralised, gave a copper-salt similar to that previously examined, but on analysis it yielded 27·7 per cent. of copper and 12·2 per cent. of nitrogen. Thinking it might be a mixture of thio-phosphodiamate of copper with a salt containing a smaller amount of amidogen, we varied the mode of preparation. The very strong aqueous ammonia was mixed with about an equal bulk of water, and the sulphochloride was thrown into it and shaken well with it. It slowly disappeared, and the neutralised solution gave the following reactions:—

With sulphate of copper, a yellowish-white precipitate insoluble in dilute hydrochloric acid or ammonia; it becomes dark-brown while drying.

With solution of chloride of lead a white precipitate is produced, soluble in dilute nitric acid; it becomes pale-yellow when dry.

Chloride of cadmium produces a bulky white precipitate, soluble in excess of either precipitant, in dilute acids, and ammonia; when dry it was pale-yellow.

Sulphate of zinc produced a white precipitate which resembled the cadmium-salt in every particular.

A solution of protochloride of tin and potassium, produced a bulky white precipitate, soluble in hydrochloric acid.

No precipitates were obtained with solutions of nickel, cobalt, iron, aluminum, barium, calcium, or magnesium.

With chloride of mercury, it gave the yellow mercuric sulpho-chloride, and if the sulphur-acid was in excess, the black sulphide. This affords a reaction capable of distinguishing the present from the preceding acid.

The cadmium and lead salts were submitted to analysis :—

Cadmium-salt.

I.—·479 grm. gave ·309 Cd_2S, and ·477 grm. $PtCl_2NH_4Cl$.

II.—·4055 grm. gave ·2605 Cd_2S, ·435 grm. Ba_2SO_4, and ·201 grm. $Mg_4P_2O_7$.

III.—·957 grm. ignited with oxide of copper, gave ·0845 grm. H_2O.

These numbers reckoned to 100 parts give :—

	I.	II.	III.
Phosphorus......	—	13·84	—
Nitrogen........	6·24	—	—
Hydrogen	—	—	·98
Cadmium	50·17	49·96	—
Sulphur	—	14·50	—

This agrees almost exactly with what would be required by the formula $PNH_2Cd_2SO_2$, or thio-phosphamate of cadmium.

	Calculated.		Mean of analyses.
Phosphorus	31	13·90	13·84
Nitrogen	14	6·28	6·24
Hydrogen......	2	·90	·98
Cadmium......	112	50·22	50·07
Sulphur	32	14·35	14·50
Oxygen........	32	14·35	14·37 (by loss)
	223	100·00	100·00

Lead-salt.

I.—·412 grm. gave ·392 grm. Pb_2SO_4, and ·2825 grm. $PtCl_2NH_4Cl$.

II.—·248 grm. decomposed by fuming nitric acid, gave a white powder of sulphate of lead, which was collected after the excess of nitric acid had been in a great measure driven off, and was washed with alcohol. It weighed ·236 grm. The solution yielded only the faintest traces of either lead or sulphuric acid.

III.—·2845 grm. gave ·271 grm. Pb_2SO_4 and ·097 grm. $Mg_4P_2O_7$.

IV.—·8765 grm. ignited with oxide of copper, gave ·054 grm. H_2O.

Or in 100 parts :—

	I.	II.	III.	IV.
Phosphorus	—	—	9·52	—
Nitrogen	4·30	—	—	—
Hydrogen......	—	—	—	·68
Lead..........	65·00	65·01	65·02	—
Sulphur	—	10·05	—	—

This also coincides with what should be given by thio-phosphamate of lead, $PNH_2Pb_2SO_2$.

	Calculated.		Mean of analyses.
Phosphorus	31	9·75	9·52
Nitrogen	14	4·40	4·30
Hydrogen......	2	·62	·68
Lead..........	207	65·09	65·01
Sulphur	32	10·07	10·05
Oxygen........	32	10·07	10·44 (by loss)
	318	100·00	100·00

The two acids described above may be viewed as amidated sulphoxiphosphoric acids. Wurtz has shown that when sulphochloride of phosphorus is treated with an aqueous solution of potash or soda, there is produced a salt of a tribasic acid analogous to phosphoric acid, but containing one atom of oxygen replaced by sulphur. This acid seems even to be produced, though not so well by water alone. Now, when ammonia acts on the sulphochloride at the same time as water does, the acid produced contains NH_2 in place of HO, and is bibasic. It might be called sulphoxiphosphamic acid; but in order somewhat to curtail the name we have preferred to call it thio-phosphamic acid. If, however, the aqueous ammonia is very strong indeed, or if the ammonia act on the sulphochloride of phosphorus first and water act afterwards, the acid produced contains two atoms of NH_2 in place of two of HO, and is monobasic. It is sulphoxiphosphodiamic or thio phosphodiamic acid. The scheme of decomposition in the three cases is as follows :—

$PCl_3\text{Ꞩ} + 3H_2\Theta = 3HCl + PH_3\text{Ꞩ}\Theta_3$ thio-phosphoric acid

$PCl_3\text{Ꞩ} + NH_3 + 2H_2\Theta = 3HCl + P(NH_2)H_2\text{Ꞩ}\Theta_2$ thio-phosphamic acid

$PCl_3\text{Ꞩ} + 2NH_3 + H_2\Theta = 3HCl + P(NH_2)_2H\text{Ꞩ}\Theta$ thio-phosphodiamic acid.

But in practice of course, a large amount of ammonia is required, as ammoniacal salts and not free acids are produced; and in the production of thio-phosphodiamic acid there is an intermediate stage.

When sulphochloride of phosphorus is brought in contact with aqueous ammonia, 6 equivalents of ammonia take part in the reaction, thus :—

$$PCl_3\text{Ꞩ} + 6NH_3 + 2H_2\Theta = 3NH_4Cl + PNH_2(NH_4)_2\text{Ꞩ}\Theta_2;$$

or, if the ammonia be more concentrated, it seems probable we may have the reaction more or less according to the scheme :—

$$PCl_3\text{Ꞩ} + 6NH_3 + H_2\Theta = 3NH_4Cl + P(NH_2)_2NH_4\text{Ꞩ}\Theta.$$

When sulpho-chloride of phosphorus is brought in contact with dry ammonia, it is difficult to suppose that the four atoms of the gas act in any other way than by removing two atoms of chlorine and leaving two atoms of amidogen in their place, according to the equation:—

$$PCl_3\text{Ꞩ} + 4NH_3 = 2NH_4Cl + P(NH_2)_2Cl\text{Ꞩ}.$$

This latter compound we have not succeeded in separating from the chloride of ammonium that accompanies it; but supposing it to exist as a distinct substance, the formation of thio-phosphodiamic acid from it by means of water is of the simplest character, namely, the replacement of the chlorine by $H\Theta$, thus :—

$$P(NH_2)_2Cl\text{Ꞩ} + H_2\Theta = HCl + P(NH_2)_2H\text{Ꞩ}\Theta.$$
