

XXIV.—*On the Action of Normal and Acid Salts upon Ammonium Salts, especially upon Ammonic Chloride.*

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H. ROSE* investigated in 1847 the action of sal-ammoniac at a high temperature upon different metallic oxides and salts, and found that, for the most part, chlorides of the respective metals were formed, some of which, *e.g.*, the chlorides of ammonium, iron, &c., were readily volatilised. Rose observed also that basic oxides of the formula $M''O$, such as CoO , NiO , MnO , FeO , likewise oxides of the formulæ $M_2''O$, such as Cu_2O , decompose ammonic chloride, when heated in an aqueous solution, with evolution of ammonia gas and formation of fixed metallic chlorides, whereas not one of the sesquioxides has this power.

These reactions are of great use in qualitative and quantitative analysis. Rose found that borax is not changed when ignited with ammonic chloride, that sodic phosphate is converted into sodic chloride and a little phosphorous chloride, whilst calcic phosphate is not affected, and that alkaline chromates leave chromic oxide and alkaline chlorides; but he appears to have omitted to study the changes which are produced when various salts are heated in aqueous solution with ammonium salts, more especially with the chloride.

Bolley† observed in 1848 that free ammonia is evolved on mixing solutions of borax and ammonic chloride in the proportions of one molecule of the former to one of the latter; the solution when slowly evaporated, deposited crystals requiring five or six parts of water for their solution, and exhibiting the composition $B_5O_{11}NaO_2 + 10H_2O$. The solution of this salt had no action, either upon litmus or upon turmeric paper, and on the addition of *dilute* sulphuric or nitric acid, gave a white precipitate of boric acid. Bolley found that an excess

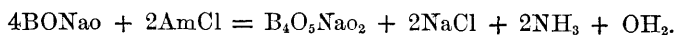
* Pogg. Ann., lxxiii, 582.

† Ann. Ch. Pharm., lxxviii, 122.

of ammoniac chloride converts the borax entirely into common salt and boric acid; he based upon this observation some interesting speculations regarding the presence of boric acid in fumaroles, and suggested that native boric acid may probably have been produced by the action of ammoniac chloride upon minerals containing this acid.

I have observed that various other salts containing fixed bases when brought together, in the dry state, or in aqueous solution, with ammoniac chloride, likewise decompose the latter, with formation of fixed metallic chlorides and evolution of gaseous ammonia, and have thought it of sufficient interest to determine quantitatively the amount of ammonia so evolved. This was done by heating in a retort weighed quantities of sal-ammoniac and salts to be operated upon, and collecting the ammonia by passing it through a solution of semi-normal sulphuric acid. I found that various other salts, besides borax, evolve ammonia most readily, but that the decomposition is more or less sluggish, according to the nature of the salts employed, the reaction being based upon the formation of acid salts from various normal saline compounds, part of the base being removed as chloride, thus giving rise to the evolution of ammonia. I examined, among other salts, the action of sal-ammoniac upon normal potassic chromate, phosphates, microcosmic salt, or hydro-ammoniac sodic phosphate (this latter, being prepared by mixing the common sodic phosphate with ammoniac chloride, is known to evolve ammonia when heated in aqueous solutions) upon trisodic and common or hydro-disodic phosphate, upon dipotassic tartrate, dipotassic succinate, trisodic citrate, &c., &c., and I have determined *quantitatively* the amount of ammonia evolved from aqueous solutions of the sodic metaborate and common borax, as well as from normal potassic chromate and acid sodic phosphate.

On mixing weighed quantities of carefully prepared sodic metaborate (obtained by igniting borax with sodic nitrate till the whole of the nitrate was decomposed) with weighed quantities of sal-ammoniac in the proportion of four molecules of sodic metaborate to two of ammoniac chloride, ammonia was evolved most copiously, and the whole decomposed very rapidly and completely, leaving only the biborate and sodic chloride, according to the equation—



2·466 grms. of sodic metaborate, mixed with 1 grm. of ammoniac chloride, and dissolved in about 2 ounces of water, evolved, when submitted to distillation, ammonia equal to 99·51 per cent. of the ammoniac chloride employed.

3·57 grms. of commercial borax mixed with ·500 grm. of ammoniac chloride, and dissolved in about 2 ounces of water, gave on distil-

lation, 100·04 per cent. of the ammoniac chloride employed. The decomposition may be expressed by the equation —



This sodic tetra-metaborate is the salt prepared and described by Bolley.

I studied these reactions again, because the changes produced by normal potassic chromate upon ammoniac salts, which I was then examining, were not so sharp and concise as might have been expected, and also in the hope of providing a substitute for the slaked lime or caustic soda usually employed for liberating ammonia from various ammoniacal salts, the temperature at which the gas comes off being so much less.

Normal and acid borates may be employed with advantage for setting free ammonia from its salts, and the reaction is both neat and perfect, no frothing taking place. The expectation of being able to evolve ammonia from ammoniac salts in presence of nitrogenous bodies, such as urea, without the latter undergoing partial decomposition, was not realized, for on boiling a solution of urea (2 molecules) with sodic metaborate (4 molecules), 10·88 per cent. of ammonia were evolved, the total possible amount being 56·66 per cent.

Tri-sodic, as well as hydro-disodic phosphate, readily decompose ammoniac salts :—

3·551 grms. of crystallised trisodic phosphate, when mixed with ·5 grm. of ammoniac chloride and distilled from an aqueous solution, gave off ammonia gas equal to 100·04 per cent. of the ammoniac chloride employed. 3·345 grms. of common sodic phosphate distilled from an aqueous solution with ·5 grm. of ammoniac chloride, yielded ammonia corresponding only to 75·69 per cent. of ammoniac chloride employed.

This latter experiment, when viewed in connection with the known fact that a solution of microcosmic salt is capable of yielding ammonia when boiled in aqueous solutions, probably giving rise to the formation of dihydro-sodic phosphate, appears to show that the tendency to form acid salts, which in the borates is so pronounced, as to yield (according to Bolley) boric acid, by the continuous action of sal-ammoniac upon a solution of borax, does not hold good in the case of phosphates.

Normal alkaline, as well as other soluble and insoluble metallic chromates, evolve ammonia when distilled in aqueous solution with ammoniac salts. This reaction attracted my attention, more especially; metallic chlorides are formed, and an acid chromate or bichromate is left, according to the equation :—



On dissolving equivalent quantities of the two salts, submitting the mixture to long continued ebullition, and absorbing the evolved ammonia gas in a standard solution of sulphuric acid, I was never able to obtain the theoretical amount of ammonia corresponding to the quantity of ammoniac chloride employed.

1·859 grm. of pure dipotassic chromate were mixed in an aqueous solution with 0·5 grm. of ammoniac chloride, and boiled in a retort during several hours, as long as any ammonia was evolved. The yield of ammonia corresponded to 81·6 per cent. of the ammoniac chloride employed.

Digestion in sealed tubes had no better effect:—

1·817 grm. of dipotassic chromate digested in a sealed glass tube at 100° C., yielded on distillation ammonia equal to 84·53 per cent. of the ammoniac chloride employed.

Slight excess of one or the other salt did not appear to affect the reaction in any marked manner.

2 grms., *i.e.*, excess of dipotassic chromate, digested with ·5 grm. of ammoniac chloride in a sealed tube for about an hour at 100° C., yielded on distillation ammonia corresponding to 81·32 per cent. of ammoniac chloride.

1·859 grm. of dipotassic chromate, when heated in a sealed tube with ·7 grm. (or excess) of ammoniac chloride, yielded ammonia corresponding to 81·6 per cent. of ammoniac chloride.

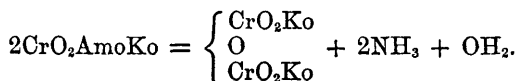
I was able to trace the reaction somewhat more fully by distilling on a larger scale theoretical quantities of the two salts. I employed 65 grms. of dipotassic chromate and 17·87 grms. of ammoniac chloride, distilled as long as any ammonia came off, and collected the gas so evolved in dilute hydrochloric acid, from which the crystalline salt was obtained by evaporation. The contents of the retort were then turned out into an evaporating dish, and the solution concentrated till dipotassic dichromate crystallised out. The crop of crystals so obtained was recrystallised, and then submitted to analysis. The salt gave in two experiments 36·05 and 36·10 per cent. of chromium. The theoretical percentage of chromium in bichromate being 35·59.

On evaporating the mother-liquor further down, ammonia gas was *again evolved most copiously*, and a further impure crop of crystals of dipotassic dichromate obtained. The mother-liquor contained the potassic chloride, a quantity of which I purified by crystallisation, and by removing the last traces of chromate by means of baric chloride.

It is evident, therefore, that the presence of a large excess of dipotassic dichromate prevents the complete decomposition of the ammoniac chloride.

The action appears to be purely molecular, for on nearly neutralising some dipotassic dichromate with ammonia, and boiling the solution,

ammonia gas was evolved in abundance; but on the addition of a large excess of a solution of dichromate and again boiling, only the merest trace of ammonia was perceptible. It appears to be probable that ammonio-potassic chromate can exist in the presence of much acid chromate, and that, on the removal of a portion of dichromate, the normal ammonio-potassic chromate breaks up according to the equation:—



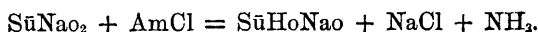
Dr. Frankland has used for some time past excess of phosphoric acid, in order to prevent the loss of ammonia when evaporating polluted waters, sewage-waters, &c., before submitting the residues so obtained to organic analysis. Phosphoric acid was found to prevent the loss in proportion to the quantity of free acid present. May not this be explained from the analogous action of the acid chromate just described, by the formation of acid phosphates which fix ammonia and prevent the decomposition of ammoniac salts?

I have only been able to make one experiment, which, however, tends to show the correctness of this view: for on distilling an aqueous solution of 3.551 grms. of trisodic phosphate (which, as we have seen, evolves the whole of the ammonia from the ammonium salt), together with .5 grm. of ammoniac chloride, and adding excess of the dihydrosodic phosphate (3 grms.), 23.5 per cent. of the ammoniac chloride was decomposed.

The experiments I made with ammoniac sulphate in place of ammoniac chloride, had to be rejected, as it was found that the neutral sulphate evolves ammonia when boiled by itself in an aqueous solution, probably owing to the formation of an acid sulphate.

It deserves to be mentioned that this action upon ammoniac chloride is not confined to normal alkaline chromates, but that insoluble chromates, such as baric or plumbic chromate, likewise evolve ammonia when boiled with ammoniac chloride, with formation of acid chromates, and that ignited plumbic chromate appears to evolve ammonia more copiously than precipitated chromate.

In conclusion I would mention that ammonia is given off when normal sodic succinate is heated in an aqueous solution with ammoniac chloride. The reaction may be expressed by the equation:—



The same holds good for normal potassic tartrate and normal citrate.

790 WILLIAMS ON BURNT IRON AND BURNT STEEL.

I am much indebted to Mr. Valentin for the assistance and advice he gave me whilst conducting these experiments.
