LVIII.—*The Action of Potassium on Tetraalkylammonium Iodides.*

By C. M. THOMPSON and J. TUDOR CUNDALL.

ACCORDING to Weyl (*Watts's Dictionary*, 5, 329), when potassium in solution in anhydrous liquefied ammonia acts on ammonium chloride, ammonium in the free state is produced, and dissolves in the ammonia, forming a blue solution. This statement lacks confirmation, and has been contradicted by Seeley (*Chem. News*, 23, 169).

It seemed possible that more decisive results might be obtained by using some tetraalkylammonium-compound instead of ammonium chloride, since just as the tetraalkylammonium hydrates are easily obtainable whilst ammonium hydrate is not, so the free tetraalkylammonium might be more stable than ammonium, and in any case the products of the reaction would be more easily separated and examined.

We experimented first with tetramethylammonium iodide. Some of this substance was inclosed with excess of metallic potassium in one limb of a sealed V-tube about 1 to 1½ cm. in diameter, the other limb

of which contained ammoniated silver chloride. In preparing this latter compound care was taken to exclude water as completely as possible. Nevertheless we found that some was present, and in order to dry the ammonia before condensation a quantity of sodium chips were placed between plugs of glass-wool immediately over the silver-compound.

- aaa.* Plugs of glass wool.
- b.* Bent-up capillary tube.
- A.* Ammoniated silver chloride.
- B.* Sodium chips.
- C.* Potassium and organic iodide.

The tubes were left sealed up for two or three days before distilling over the ammonia, so as to allow time for the sodium to remove the traces of water.

The potassium was placed in a separate small tube, so that its solution in the ammonia did not at once come in contact with the iodide. On spilling some of the blue solution on the iodide, no apparent change could be observed when the above precautions as to the removal of water were taken, although in previous experiments when traces of water were present rapid decolorisation with evolution of gas took place.

After the potassium solution and the iodide has been mixed, the tube was left at the ordinary temperature for some hours, in which time the ammonia was almost entirely reabsorbed by the silver chloride. On opening the tube, the pressure observed was not very great, and the odour of trimethylamine could be detected notwithstanding the strong smell of ammonia.

The residue in the tube was treated with alcohol, which would convert the excess of potassium and any trimethylammonium which might have been formed into alcoholates. The greater part of the tetramethylammonium iodide was left undissolved and quite unchanged by this treatment although excess of potassium was present. It was collected on a filter, and in one case weighed 3.3 grams, 5 grams having been originally employed.

The strongly alkaline filtrate was neutralised with hydriodic acid and evaporated. In the solid residue, we could detect nothing but potassium iodide. A portion of the gas contained in the tube was collected after passing through dilute hydrochloric acid. The results got on explosion with excess of oxygen and absorption of carbon dioxide by potash indicated that it consisted of a mixture of hydrogen, ethane, and nitrogen.

The ammoniated silver chloride left in the tube was heated, and the gas evolved absorbed by dilute hydrochloric acid. This solution was mixed with the hydrochloric acid solution got in purifying the gas and the whole evaporated to dryness. The solid was extracted with alcohol, the solution evaporated, and the residue converted into platinumchloride.

The quantity of salt obtained from one tube was too small to divide into fractions. It contained 42.6 per cent. platinum, whilst ammonium platinumchloride contains 44 per cent., showing that trimethylamine is probably present.

Whilst, therefore, the greater portion of the tetramethylammonium iodide remains unchanged, a part is acted on by the potassium, giving potassium iodide, ethane, and trimethylamine. Tetramethylammonium, if formed at all, is, under the conditions of the experiment, unstable.

As the results got with tetramethylammonium iodide were unsatisfactory, we performed another series of experiments with phenyltrimethylammonium iodide. This substance was easily prepared by bringing together dimethylaniline and methyl iodide in molecular proportion, and was purified by crystallising from water, heating with aqueous sodium hydrate to decompose hydriodides, washing well with alcohol, and finally crystallising from alcohol. Since the iodide is insoluble in ether, it might be better after washing out the sodium hydrate to wash thoroughly with ether. That the substance which we employed was pure was shown by the fact that it was odourless and that the aqueous solution gave no turbidity on warming with sodium hydrate.

5 grams of the carefully dried iodide were treated with excess of potassium in a sealed tube as before. On allowing the potassium solution to come in contact with the iodide, the blue colour was at once changed to brown. After the action was complete the tube contained two liquids, one brown and wetting the glass, the other showing a red metallic lustre like that of copper, and running about in globules like mercury. The latter liquid is exactly like a strong solution of potassium in ammonia as described by Seeley and repeatedly obtained by us.

The tubes had to be left for some time before the ammonia was

reabsorbed, for the brown liquid checked its evaporation. On opening they showed only a slight pressure, and the escaping gas smelt strongly of trimethylamine.

A portion of the gas was washed with dilute sulphuric acid, transferred to a eudiometer, and exploded with excess of oxygen. Addition of potash then caused only a slight diminution of volume. Calculating on the assumption that the whole of the carbon dioxide is derived from ethane, the rest of the gas consisting of hydrogen and nitrogen, we found the percentage of ethane in one case to be 8.15, in another 13.2. Since the total quantity of gas, free from ammonia, which could be got from one tube containing 5 grams of iodide did not exceed 100 c.c., the quantity of hydrocarbons formed in the reaction is exceedingly small, and may be the result of some secondary reaction.

The end of the tube was cut off, and the residual products of the reaction were extracted with dry ether. On evaporating the ether a liquid was left which boiled at 187—188° (uncorr.), and on heating with benzotrichloride and zinc chloride gave malachite-green. It was therefore dimethylaniline. In one case, from 5 grams phenyltrimethylammonium iodide we obtained 1.1 gram, though some was undoubtedly lost during the evaporation of the ether.

The residue, after extracting with ether, was treated with cold absolute alcohol. A crystalline substance was left which was found to be pure potassium iodide. The alcoholic solution was neutralised with sulphuric acid, and the potassium sulphate, which was free from organic matter, was filtered off and the filtrate evaporated. It gave a residue which consisted of unchanged phenyltrimethylammonium iodide mixed with a small quantity of resinous substance soluble in ether.

By heating the silver compound contained in the tube, a gas was given off which was absorbed by dilute hydrochloric acid. The solution got in this way from one tube containing 5 grams of the iodide was evaporated and the residue extracted with alcohol. The aqueous solution of the salts soluble in alcohol was precipitated by platinum chloride in five fractions. The first three on analysis gave numbers showing that they consisted of ammonium platinochloride. The fourth and fifth contained 37.2 and 37.9 per cent. of platinum respectively, the calculated percentage for $(\text{NMe}_3)_2\text{H}_2\text{PtCl}_6$ being 37.0. Whilst these fractions were being heated, a strong smell of trimethylamine was observed, so that there can be no doubt as to the nature of the substance. The two fractions weighed 0.778 gram, containing 0.173 gram trimethylamine, so that the latter is formed in considerable quantity if we take into account the facts that some of the phenyltrimethylammonium iodide is not acted on, and that its molecular weight is very high.

The following products of the reaction were therefore recognised with certainty :—Potassium iodide, dimethylaniline, and trimethylamine; whilst ethane or other hydrocarbon was not identified and cannot have been present in any considerable amount.

If phenyltrimethylammonium were formed and afterwards decomposed, in all probability dimethylaniline and ethane would be produced. The maximum quantity of ethane which could have been formed from 5 grams iodide (13 c.c.) weighs about 0·017 gram, while the amount calculated from the equation—

weighs 0·28 gram, or assuming that one quarter of the iodide remains unchanged 0·21 gram. The formation of trimethylamine also shows that the above equation does not represent the main reaction, and on the whole it appears to us improbable that phenyltrimethylammonium is formed at all.

University College, Cardiff.