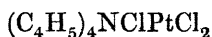


XXIX.—*Note of the Action of Chloride of Ethyl upon Ammonia.*

BY CHARLES EDWARD GROVES.

It has often struck me as remarkable, that while the deportment of ammonia with the bromide and iodide of ethyl had been so carefully studied, the action of this substance upon the chloride of ethyl should scarcely have been noticed. Although the difficulty of manipulating so volatile a substance as chloride of ethyl promised but little advantage in the practical preparation of the ethyl bases; it appeared nevertheless desirable to examine the reaction, in order to complete the history of the formation of these substances. When chloride of ethyl sealed up in stout glass tubes with about three times its bulk of alcoholic ammonia—formed by nearly saturating alcohol with dry ammonia—was digested for six or seven hours at the temperature of 100° C., a large quantity of a white crystalline substance was deposited in the tubes, apparently consisting of chloride of ammonium. The tubes were then opened and the contents thrown on a filter, the white crystalline powder washed with absolute alcohol, and the filtrate evaporated to dryness on the water-bath, to expel alcohol and excess of ammonia. The residue was then dissolved in water, filtered, and submitted in a retort to the action of an excess of oxide of silver, in order to set free the bases formed during the reaction. On heating the mixture, the whole of the volatile bases passed over. The residue in the retort, consisting of oxide and chloride of silver, together with the hydrated oxide of a non-volatile ammonium-base, was thrown on a filter and washed with water until the washings were no longer alkaline. The filtrate neutralized with hydrochloric acid, evaporated to a small bulk on the water-bath, and filtered, yields with bichloride of platinum, a yellow crystalline precipitate, which was washed with a small quantity of cold water and recrystallized from boiling water.

0.185 grammes of substance yielded 0.0545 grammes of platinum; this shows a percentage of platinum equivalent to 29.4 per cent. The formula—

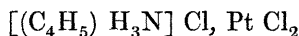


requires 29.44 per cent. of platinum. The non-volatile base produced in the reaction between chloride of ethyl and ammonia, is

therefore, as might have been expected, the hydrated oxide of tetrethylammonium. The alkaline distillate, containing the volatile portion of the bases was neutralized with hydrochloric acid, evaporated to a small bulk on the water-bath, and precipitated with an insufficient quantity of bichloride of platinum. The precipitate, consisting of thin crystalline hexagonal plates, was recrystallized from a small quantity of water, to which it was found convenient to add a few drops of alcohol, the salt being rather insoluble in dilute alcohol.

0.235 grammes of substance gave 0.092 of platinum.

The formula—



requires 39.29 per cent. of platinum and the analysis gave 39.15 per cent.

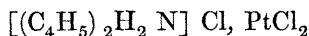
This result shows the existence of ethylamine among the volatile products of the action of chloride of ethyl upon ammonia.

By successive partial precipitations and recrystallizations, a considerable quantity more of the platinum-salt of ethylamine was separated; until at last a very small quantity of another and more soluble salt was deposited from the mother-liquors. After a single recrystallization, which was all that was possible, owing to the amount being so small, it was dried and analysed; and although some crystals of the ethylamine platinum-salt could be discerned by the microscope, it gave results which approximated closely with the theoretical percentage of the diethylamine platinum-salt.

0.170 of substance gave 0.062 of platinum;

this gives a percentage of 36.47 of platinum.

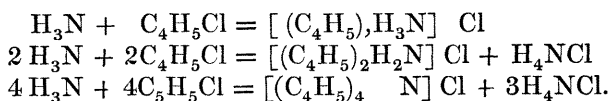
The formula—



requires 35.35 per cent of platinum. The above platinum determination might also represent a mixture of the salt of ethylamine and triethylamine; but the compound analysed, although more soluble in water than the ethylamine-salt, was not nearly so soluble as the salt of triethylamine; moreover the latter substance is easily recognised by its crystalline form. In addition to the salts above mentioned, a small quantity of triethylamine was, in all probability, present among the products of the reaction of

chloride of ethyl upon ammonia; but owing to the small proportion in which it existed, and the known solubility of its platinum-compound, I have not been able to establish its formation by experiment.

The following equations represent the action of chloride of ethyl upon ammonia:—



The experiments which I have described show a marked difference in the action of the chloride when compared with that of the bromide and iodide of ethyl. The chloride of ethyl produces almost exclusively the chloride of ethylammonium, together with small quantities of the chlorides of diethylammonium and tetrethylammonium. The bromide of ethyl, according to the experiments of Dr. Hofmann, gives chiefly the bromide of ethylammonium, but also very appreciable quantities of the bromides of diethyl- and triethylammonium, with but a small proportion of the tetrethylammonium-compound; and lastly, the iodide produces the three volatile bases in about equal proportions, but generally very appreciable quantities of the tetrethyl-ammonium-compound.

The above experiments were performed in the Laboratory of Dr. Hofmann.

---