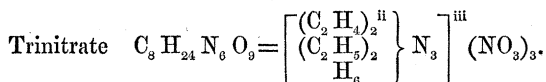
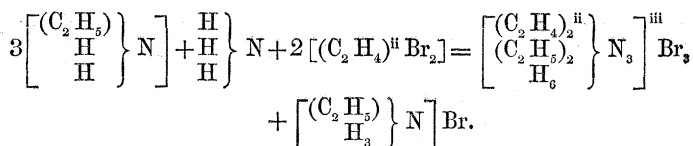


solution on cooling in large rectangular tables presenting the aspect of nitrate of silver. The combustion of this salt has led to the formula



The formation of the diethylated diethylenetriamine is readily intelligible. I have satisfied myself that the origin of this body was always due to the presence of minute quantities of ammonia which had not been entirely removed from the ethylamine employed in the reaction.

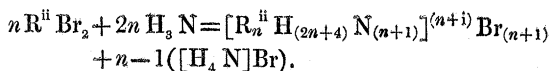


The formation of diethylene-diethyltriamine furnishes an elegant illustration of the simple mechanism involved in the construction of the polyatomic bases.

# VII. "Notes of Researches on the Poly-Ammonias."—No. XVIII.

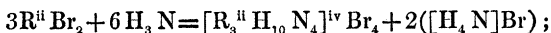
Tetrammonium-Compounds. By A. W. HOFMANN, LL.D.,  
F.R.S. Received July 29, 1861.

In several previous communications I have submitted to the Royal Society a sketch of the triatomic bases which are generated by the assimilation of three molecules of ammonia linked together by the intervention of diatomic molecules. In the same sketch I endeavoured to trace the general principle upon which the bases of higher atomicity are formed. I pointed out that the accumulation of ammonia-molecules is determined by the number of diatomic radicals which are fixed; that, for the production of an  $(n+i)$ -atomic ammonia, at least  $n$  diatomic radicals are required; and lastly, that the number of molecules of diatomic bromides and the quantity of ammonia involved in these accumulative processes are given in the general equation

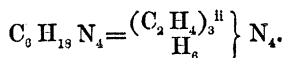


I moreover showed how this equation applies to the first terms of the series of diammonium- as well as triammonium-salts.

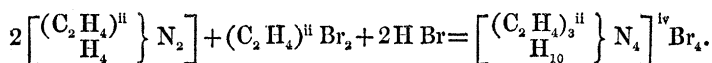
In following up the natural development of these ideas, I had to search for the tetrammonium-compounds. For if  $n=3$ , the above equation reduces itself to



and the simplest tetramine of the ethylene-series—the triethylene-tetramine—is represented by the formula



I have vainly searched for this compound among the difficultly volatile bases resulting from the action of dibromide of ethylene upon ammonia, which distil after the triammonias have passed. But it is obvious that so complex a compound must have a very high boiling-point, and thus be liable to decomposition by distillation. To avoid this decomposition, the product of the action of dibromide of ethylene upon ammonia was treated with an excess of oxide of silver; the liberated bases were then submitted to a long-continued current of steam, by which all the volatile matter was carried over. A considerable proportion of non-volatile bases remained behind, the mixed character of which was easily proved by progressive precipitation by dichloride of platinum. The analysis of these platinum-salts has convinced me that this liquid indeed contains the tetramine in question, mixed, however, with other compounds of very similar properties; so that my endeavours to obtain it in a state of purity have failed. I have, however, succeeded in preparing the pure compound by a somewhat different process, viz. by submitting ethylene-diamine, instead of ammonia, to the action of dibromide of ethylene. The formation of the tetrammonium-compound in this reaction is represented by the equation



The hydrobromic acid which figures in this equation arises from another phase of the reaction, which I have not yet completely studied.

Triethylene-tetramine is a powerfully alkaline liquid which is separated from the bromide by means of oxide of silver. It dries up to a syrup, which shows no tendency to crystallize. Its composition

was fixed by the analysis of the pale-yellow, amorphous, almost insoluble platinum-salt, which was found to contain



Although less intricate than the result of the reaction between ammonia and dibromide of ethylene, the products obtained under similar circumstances from ethylene-diamine present still considerable complexity; and the impossibility of separating the tetramines by distillation, together with their rapidly diminishing faculty of yielding crystalline compounds, render the investigation of these substances rather difficult, more particularly since time, temperature, and even relative proportion of the reacting compounds are apt to vary the nature of the products formed.

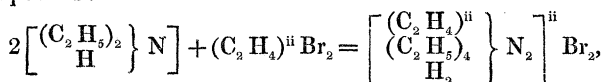
A simplification of these difficulties appeared to present itself by adopting the method which had so greatly facilitated the study of the bases of lower atomicity, viz. by examining the deportment of some of the ethylated monamines under the influence of dibromide of ethylene.

As a chemical theory expands and becomes more and more consolidated, the interest attached to the individual compounds used as scaffolding in raising the structure becomes less and less, diminishing in fact in the inverse ratio of the number of the compounds which the theory suggests. It thus became a matter of comparative indifference, in what series and by what materials the construction of the group of tetrammonium-compounds was attempted. Ethylamine and diethylamine appeared to recommend themselves by their accessibility. Owing to the greater simplicity of the reaction, I will first mention the results elicited in studying the deportment of the diethylated monamine.

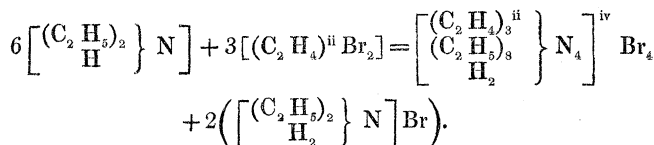
#### *Action of Dibromide of Ethylene upon Diethylamine.*

The reaction is rapidly accomplished, both in the absence and presence of alcohol. On opening the tubes after several hours' digestion at 100°, the liquid is found to be acid; the powerful evolution of bromide of vinyl, which is invariably observed, at once points out the existence, among the products of the reaction, of considerable quantities of bromide of diethylammonium. In addition to this bromide, the reaction of dibromide of ethylene upon diethylamine furnishes

only two other bromides, viz. the dibromide of ethylene-tetrethylidiammonium and, lastly, the tetrabromide of triethylene-octethyltetrammonium. The following equations represent the formation of these compounds:—

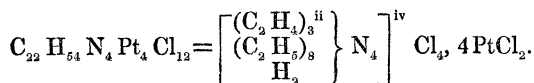


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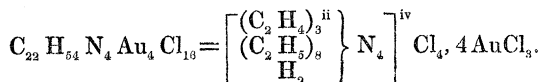


The separation of these three salts presents no difficulties. Liberated by oxide of silver and submitted to a protracted current of steam, the mixture of bases separates on the one hand into diethylamine and ethylene-tetrethylidiamine, which pass over with the steam, and hydrate of triethylene-octethyltetrammonium, which remains behind.

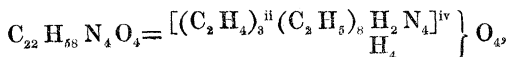
The octethylated tetrammonium-compounds are remarkable for their definite characters: they are still crystalline,—a circumstance which has facilitated their study in no common degree. The composition of the series was fixed by the analysis of the platinum-salt, of the gold-salt, and of the tetr iodide. The platinum-salt is almost insoluble in water. Precipitated from a dilute and gently warmed solution, it is obtained in small crystalline plates containing



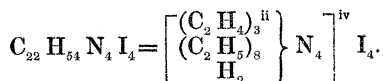
This substance has served in the preparation of the other salts. Treated with sulphuretted hydrogen, the platinum-salt is converted into the difficultly crystallizable chloride, which yields with trichloride of gold a crystalline gold-salt of the composition



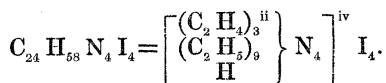
The chloride, submitted to the action of oxide of silver, furnishes the powerfully alkaline free base



which has all the characters of the non-volatile monammonium-, diammonium-, and triammonium-bases which I have previously described. Treated with hydriodic acid, it is converted into the tetriodide, which is very soluble in water, but which may be obtained from alcohol in white exceedingly soluble crystals, of the composition



It deserves to be noticed that the tetrammonium-compound, which I have endeavoured to sketch, does not contain more than three molecules of ethylene—that it is, in fact (if we disregard the accidental circumstance of its octethylated condition), the simplest tetrammonium-compound which could possibly be formed, three molecules of ethylene being, as is evident from a glance at the general equation given at the commencement of this note, the smallest number of diatomic molecules by which a tetrammonium-compound may acquire the necessary stability. I have submitted the free octethylated base to the action of iodide of ethyl. This treatment gives rise to a beautifully crystallized iodide less soluble in alcohol, which contains—

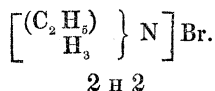


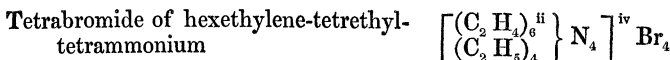
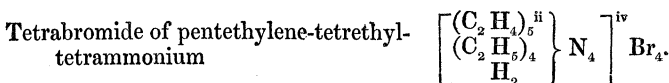
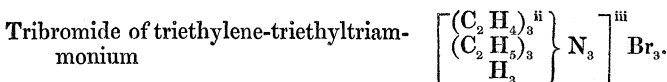
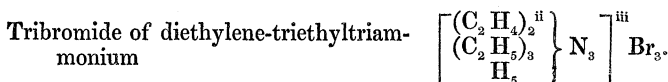
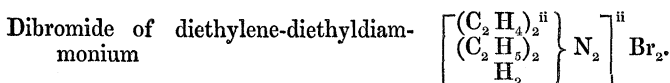
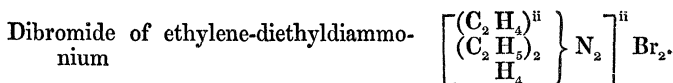
I have not carried the ethylation any further.

#### *Action of Dibromide of Ethylene upon Ethylamine.*

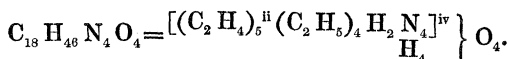
The reaction between these two bodies, as might have been expected from the number of unreplaced hydrogen-equivalents in ethylamine, is far more complex than the process previously examined. The action is rapidly accomplished at 100°; and it deserves to be noticed that very little bromide of vinyl is formed in this operation, only traces of gas being evolved on opening the digestion-tubes. The crystalline mass which remains on evaporating the product of the reaction to dryness, is a mixture of six, and occasionally of seven bromides, viz.

Bromide of ethylammonium

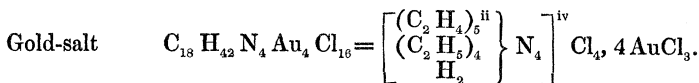
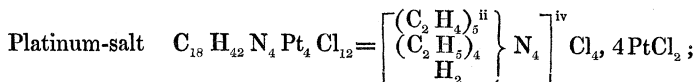




The ammonias corresponding to the first five of these bromides are known by former researches. They are all volatile; there was therefore no difficulty in separating them from the mixture. Liberated by means of oxide of silver and submitted to the action of steam, they were carried over, leaving behind a powerfully alkaline liquid, which in most cases was found to consist exclusively of the hydrate of pentethylene-tetrethyltetrammonium,

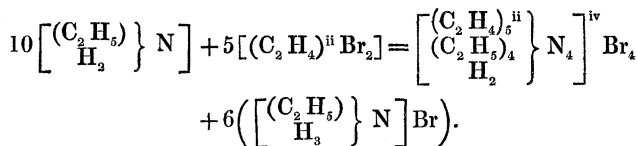


The simple salts of this tetrammonium are extremely soluble, and crystallize with the greatest difficulty; I have therefore established the composition of the series by the analysis of the difficultly soluble platinum-salt and gold-salt. They are obtained in the form of yellow, amorphous or very indistinctly crystalline precipitates, containing,

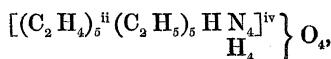


The formation of the pentethylenated tetrammonium is represented

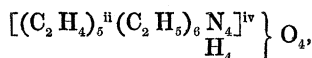
by the following equation :—



The pentethylene-tetrethylated tetrammonium contains still 2 equivalents of replaceable hydrogen. By the action of iodide of ethyl they may, although with difficulty, be removed and replaced by ethyl. I have thus obtained successively the pentethylene-pentethylethylated and, lastly, the pentethylene-hexethylethylated tetrammonium,—

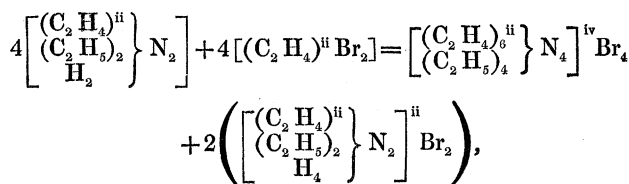


and

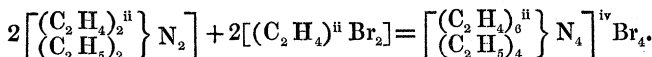


the composition of which was established by the analysis of the platinum- and the gold-salts.

I have mentioned above, that the action of dibromide of ethylene upon ethylamine produces occasionally also the hexethylene-tetrethyl-tetrammonium. This substance may be obtained in a state of purity by the action of dibromide of ethylene upon ethylene-diethyldiamine and diethylene-diethyldiamine,



and



The composition of the hexethylene-tetrethylated tetrammonium was likewise established by the analysis of the platinum-salt and gold-salt.

The analysis of these salts completes my researches on the tetrammonium compounds. In a further paper I propose to examine the ammonias of higher atomicity.