XIV. *Researches into the Molecular Constitution of the Organic Bases.*

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(*Second Memoir.*) *Communicated by Sir* JAMES CLARK, *Bart., F.R.S.*

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ABOUT twelve months ago I had the honour of presenting to the Royal Society an account of a series of researches into the molecular constitution of the *volatile* organic bases*: at present I beg to submit to the consideration of the Society the history of a new group of alkaloids, which, although intimately connected with the former by their origin, differ from them altogether by their properties, and especially in *not being volatile*.

The members of this new group of alkaloids are so numerous, their deportment is so singular, and their derivatives ramify in so many directions, that I have not as yet been able to complete the study of these substances in all their bearings; nor is it my intention to go fully into the chemistry of the subject in the present communication, my object being merely to establish the existence of these bodies, and to give a general outline of their connection with the *volatile* bases, and of their most prominent chemical and physical properties, reserving a detailed description of their salts and derivatives to a future memoir.

In the paper above referred to, I advanced the position that the majority of the volatile organic bases might be represented by the general expression

$$\left.\begin{array}{l} X \\ Y \\ Z \end{array}\right\} N,$$

a formula which coincides with that of ammonia, if $X=Y=Z=H$. I proved by experiment that the terms X, Y and Z may represent, not only hydrogen, but a variety of hydrocarbons, especially the so-called alcohol-radicals ($C_n\ H_{(n+1)}$), and endeavoured, on the ground of these experiments, to classify the volatile organic bases according to the amount of basic† hydrogen retained in the several alkaloids. I thus arrived at three groups of bases, for which, in accordance with traditional names, I proposed the terms amidogen-bases, imidogen-bases and nitrile-bases.

The ideas enunciated regarding the constitution of the volatile organic bases, were, it is true, to a certain extent, the result of theoretical speculation; but they were so

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* Philosophical Transactions, Part I. 1850, p. 93.

† Ibid. p. 111.

perfectly in accordance with all the observations recorded, and had been submitted to the test of experiment in so many directions, that no doubt was left in my mind regarding their correctness. Still, the former inquiry had elicited several facts which I was unable to explain by the view which I had taken. These facts I have since endeavoured to elucidate by additional experiments; the results detailed in the following pages, I am happy to say, are in perfect accordance with my former observations, the extension of which has led me, at the same time, to a still more general conception of the question.

After having succeeded in replacing, step by step, one, two or three equivalents of hydrogen in ammonia by a corresponding number of compound atoms, the question arose whether the agent by which these changes were affected would exert a still farther influence upon the last product of the reaction. In order to decide this question by experiment, I submitted two nitrile-bases, diethylaniline and triethylamine, to a prolonged action of bromide of ethyl. These experiments, of which a full account is given in my preceding memoir (pages 106 and 122), did not lead to perfectly decisive results. It was evident that in these cases a reaction ensued; even on using both the base under examination, and the bromide in the absolutely dry state, a gradual change was observed to take place, a small but unmistakeable quantity of hydrobromates being invariably formed. No doubt, however, could be entertained as to this reaction being altogether different from the preceding stages of the process, for instance, the conversion of ammonia into ethylamine, of ethylamine to diethylamine, &c.; it was proved, moreover, by careful and frequently-repeated experiment, that this process, whatever its nature might be, in no case gave rise to the formation of any other *volatile* bases containing a larger number of replacing radicals than the nitrile-base submitted to investigation.

I have been again studying these reactions during the past year on a much larger scale, whereby the experiments were greatly facilitated; and here I gladly avail myself of an opportunity of expressing my sincere thanks to the Royal Society for the kind and encouraging interest they have taken in this inquiry, the new results of which are mainly attributable to their liberal and munificent support.

ACTION OF BROMIDE AND IODIDE OF ETHYL UPON TRIETHYLAMINE.

In the paper repeatedly referred to, I have stated that a mixture of an aqueous solution of triethylamine and bromide of ethyl, sealed up in a tube, solidified after several hours' ebullition, and that the crystals consisted chiefly of the fibrous hydrobromate of triethylamine, with which however a certain quantity of white opake granular crystals invariably was mixed. I have endeavoured to increase the quantity of the latter by using both the bromide of ethyl and the triethylamine in the anhydrous state. But by thus changing the conditions of the formation, the progress of the reaction is retarded in the most remarkable manner, days elapsing before the conversion is completed. While engaged in these experiments, I found that the result intended may be obtained almost instantaneously by substituting the iodide for the bromide of ethyl; and as this observation was immediately followed by a perfect elucidation of the whole question, I have scarcely returned again to the use of the bromide.

On adding perfectly anhydrous iodide of ethyl to triethylamine dried over hydrate of potassa, the mixture becomes slightly turbid, heat being evolved at the same time. At the common temperature the action goes on very gradually, and after the lapse of several days, the mixture is converted into a solid mass. On the other hand, if the mixture be exposed for a minute or two to the temperature of boiling water, a very powerful reaction ensues; the liquid remains, even after the removal of the source of heat, for some time in a state of lively ebullition, and solidifies after cooling, into a hard mass of crystals, which is snow-white or of a yellowish tint, according as either the triethylamine or the iodide of ethyl has been in excess. To avoid losing iodide of ethyl, and especially triethylamine, which is the result of a long series of troublesome and expensive processes, I have usually performed the reaction in strong glass tubes of between three and four feet in length, which were sealed before the blowpipe after the substances had been introduced.

The crystalline mass produced in this reaction readily dissolves even in cold water. If the iodide was in excess this substance separates in heavy oily globules, which may be readily separated and recovered by distillation, and the solution is inodorous, and either neutral or very slightly acid; in the latter case it has always a marked yellowish tint. On the other hand, if the base was in excess, the solution of the crystals was colourless and alkaline; the alkaline reaction disappears however on ebullition, triethylamine being disengaged. The crystals are likewise soluble in alcohol, but almost insoluble in ether.

The purification of the crystals is not attended with any difficulties; it is in fact sufficient to dissolve them in cold water and to allow the solution to evaporate spontaneously, when beautiful well-defined white crystals of considerable size are deposited, which may be easily separated by mechanical means, from small quantities of a reddish iodine-compound, which is sometimes formed by the action of the air. This latter substance is formed in much larger quantity at higher temperatures, wherefore it is advisable to avoid the use of boiling water in the purification.

The crystals are anhydrous; when exposed to the temperature of boiling water they exhibit no change in weight. When submitted to analysis they gave the following results:—

I. 0·4385 grm. of substance gave 0·6015 grm. of carbonic acid and 0·3040 grm. of water.

II. 0·5538 grm. of substance gave 0·5050 grm. of iodide of silver.

III. 0·5205 grm. of substance gave 0·4752 grm. of iodide of silver.

IV. 0·5000 grm. of substance gave 0·4552 grm. of iodide of silver.

These numbers lead to the following percentage composition:—

	I.	II.	III.	IV.
Carbon	37·41	——	——	——
Hydrogen	7·71	——	——	——
Iodine	——	49·29	49·35	49·21

The simplest formula into which these results may be translated is

$$C_{16}\,H_{20}\,N\,I,$$

the theoretical values of which I subjoin for comparison with the experimental numbers.

	Theory.		Mean of Experiments.
16 equivs. of Carbon . . .	96·0	37·34	37·41
20 equivs. of Hydrogen . .	20·0	7·78	7·71
1 equiv. of Nitrogen . . .	14·0	5·45	——
1 equiv. of Iodine	127·1	49·43	49·28
1 equiv. of Iodine-compound	257·1	100·00	

Hence it would appear that the formation of the white crystals simply depends upon a direct combination of triethylamine with iodide of ethyl, for—

$$\underbrace{C_{12}\,H_{15}\,N}_{\text{Triethylamine.}}+\underbrace{C_4\,H_5\,I}_{\text{Iodide of Ethyl.}}=\underbrace{C_{16}\,H_{20}\,N\,I.}_{\text{New crystalline compound.}}$$

In perfect accordance with this formation is the change which the iodine-compound undergoes when subjected to the action of heat; when rapidly heated the crystals fuse and are decomposed, the products being triethylamine and iodide of ethyl, which form two layers in the receiver, but rapidly unite again to the original compound. In fact this recombination takes place to a considerable extent in the neck of the retort; so that when first I became acquainted with this substance, I was for some time under the impression that the iodine-compound might be volatilized without decomposition.

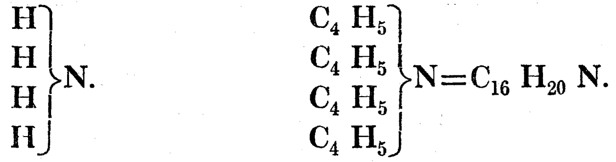
I confess I had not anticipated the possibility of the existence of a compound having the above composition; it appeared at the first glance in direct opposition to the theoretical view repeatedly referred to. For if it was possible to decompose the new iodide by potassa just as the preceding iodides, obtained respectively by the action of bromide (or iodide) of ethyl upon ammonia, ethylamine and diethylamine, if it was possible to separate from this substance a new volatile base analogous to the preceding ethylated alkaloids, there was no reason why the process of ethylation should cease with the fourth equivalent of ethyl. On the contrary, it then appeared more than probable, that the formations of ethylamine, diethylamine and triethylamine, far from being due to a successive replacement of the various equivalents of hydrogen in ammonia, were rather to be considered as special instances of a far more general tendency of carbon and hydrogen to accumulate in organic substances.

The eagerness with which I submitted this question to the test of experiment may be readily imagined. On adding potassa to a solution of the iodine-compound in water, the liquid solidified at once into a crystalline mass, which I took of course for the base existing in the iodide; analysis however soon showed that the substance thus precipitated is nothing but the iodide itself, which is less soluble in an alkaline solution than in pure water. In fact, Analysis IV. was made with a specimen which had thus been treated with potassa. The iodide was now distilled with a very concentrated solution of potassa for several hours; but during this time nothing but pure water passed over; the solution in the retort solidified on cooling to crystals of the unchanged iodide. When the solution of the iodide in potassa had become very concentrated, it separated into two layers, an aqueous one and an oily one, which floated on the surface. But even now no decomposition had been induced, the oily stratum solidifying on cooling into a crystalline cake of iodide perfectly unaltered. It was only when the liquid was evaporated to dryness that a change took place; but then the change was no longer due to the action of the potassa, but to the influence of heat, and in no way differed from the decomposition which the crystals undergo when heated alone.

The deportment with potassa of the new iodine-compound altogether precludes the idea of considering it as an analogue of the hydriodides of ethylamine, diethylamine, and triethylamine, all of which are readily decomposed under the influence of the alkalies.

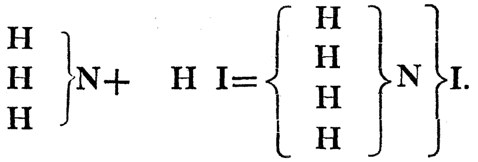
However, the iodine, though it cannot be eliminated from the crystals by the alkalies, may be separated with the greatest facility by silver-salts; in fact, the nitrate, the sulphate, the oxide of silver, behave with the iodine-compound exactly as with iodide of potassium or sodium. On adding nitrate of silver to a solution of the iodide, iodide of silver is at once precipitated and a nitrate remains in solution, which on evaporation crystallizes in deliquescent needles. With sulphate of silver, a perfectly similar change takes place, an analogous sulphate remaining in solution. During these interchanges the liquids remain perfectly neutral. If the solution of the iodide be digested with freshly precipitated protoxide of silver, the solution at once assumes a powerfully alkaline reaction, iodide of silver being formed: the same effect is produced by the action of caustic baryta upon the sulphate, sulphate of baryta being precipitated. These reactions, when viewed collectively, exhibit a striking analogy between the new iodide and the metallic iodides, especially those of the alkali-metals. In fact the molecular group combined with iodine, in the compound under examination, behaves like sodium or potassium; it is a true organic metal in all its bearings. For this metal I propose, on the ground of its formation and composition, the name Tetrethylammonium (τέτρα), which implies that it is built up by the intimate union of nitrogen with four equivalents of the hypothetical hydrocarbon called ethyl, and that it may be viewed as ammonium, in which the whole of the hydrogen is replaced by an equivalent proportion of the above hydrocarbon.

Ammonium. Tetrethylammonium.

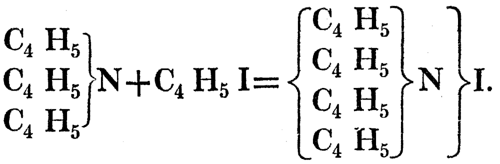


$$\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}N. \qquad \left.\begin{matrix}C_4\,H_5\\C_4\,H_5\\C_4\,H_5\\C_4\,H_5\end{matrix}\right\}N=C_{16}\,H_{20}\,N.$$

The new crystalline compound, according to this mode of viewing it, must be considered as iodide of tetrethylammonium, and its formation takes place in consequence of a transposition of the elements, which is perfectly analogous to that assumed by the followers of the ammonium-theory, in the formation of iodide of ammonium from ammonia and hydriodic acid.



$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N+\;H\,I=\left\{\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}N\right\}I.$$



$$\left.\begin{matrix}C_4\,H_5\\C_4\,H_5\\C_4\,H_5\end{matrix}\right\}N+C_4\,H_5\,I=\left\{\left.\begin{matrix}C_4\,H_5\\C_4\,H_5\\C_4\,H_5\\C_4\,H_5\end{matrix}\right\}N\right\}I.$$

I will not enter here into the merits of the ammonium-theory; the question whether this mode of representing the constitution of the ammonia-salts be correct or not, may be left out of consideration for the present. The view I have taken of the new compound, and which I readily admit must stand and fall with the ammonium-theory, has the great advantage of closely assimilating these substances to the compounds of mineral chemistry, whereby the nomenclature is essentially facilitated.

I will now proceed to give a sketch of the tetrethylammonium-compounds, as far as this is necessary, in order to convey a clear perception of the character and the peculiarities of this group of bodies. I reserve a detailed account of the derivatives of this group to a special memoir, in which I intend to give moreover a fuller description of diethylamine and triethylamine, which were only briefly noticed in my former paper.

Among the various substances derived from the new iodide, the corresponding oxide, the compound corresponding to oxide of ammonium, attracted my attention in a pre-eminent degree.

Oxide of Tetrethylammonium.

I have already briefly stated how this substance is prepared; on decomposing the iodide with an excess of sulphate of silver, a sulphate is obtained, from which sulphuric acid and excess of silver may be separated by baryta. This was in fact the first process by which I separated the base; it is, however, difficult to obtain the solution in this manner free from either baryta or sulphuric acid; nor have I ever used this process again, after I had found that digestion with freshly precipitated protoxide of silver produces at once the same effect. The oxide is added in small proportions to the solution of the iodide, which is gently heated; it is immediately converted into yellow iodide of silver, which assumes a white colour on stirring, as long as any undecomposed iodide is in solution. Gradually the yellow colour becomes permanent, and the decomposition is complete as soon as an excess of unchanged oxide becomes perceptible by its colour.

On filtering off the silver-precipitate, a clear and colourless liquid is obtained, which contains the isolated base in solution. It is of a powerfully alkaline reaction, which manifests itself, not only in its deportment with vegetable colours, but also in its possessing the pungent bitterness of quinine; the solution, when strongly concentrated, not only burns the tongue, but it acts upon the epidermis, which it destroys like caustic potassa or soda. On rubbing a solution of the oxide between the fingers, the well-known sensation produced by the fixed alkalies under the same circumstances is felt, and we perceive moreover the same peculiar odour.

Oxide of tetrethylammonium saponifies the fats as readily as potassa. The experiment was made with cocoa-nut oil, which after half an hour's ebullition with the new alkali was converted into a beautiful soft soap, having the appearance of an ordinary potassa-soap. This soap washes very well.

I have traced the analogy of the new body with potassa in many other directions. Chemists recollect the remarkable effect produced by ebullition with potassa in certain nitrogenous substances. It was by this process that Dr. FOWNES, the discoverer of this reaction, converted furfuramide into the isomeric alkaloid, *furfurine*. I found that boiling with oxide of tetrethylammonium effects this molecular change as rapidly as potassa.

Like potassa it decomposes oxalic ether into oxalic acid and alcohol, and evolves ammonia from ammonia-salts, even in the cold. It may be substituted for potassa in TROMMER's well-known sugar-test. Copper-solutions, mixed with either cane- or grape-sugar, yield on addition of oxide of tetrethylammonium, a light-blue precipitate of the hydrate of the protoxide, which redissolves in an excess of the base, forming a deep blue solution, with a shade of green; on ebullition the cane-sugar solution deposits a greenish precipitate, which is only slowly and always very incompletely converted into suboxide of copper. In the presence of grape-sugar the reduction ensues instantaneously on application of heat.

The reactions of the new base with metallic oxides assimilate this compound as nearly as possible to the fixed caustic alkalies. The following table exhibits the reactions of this body.

Barium-salts	White precipitate of the hydrate of the earth, insoluble in an excess of the base.
Strontium-salts . . .	White precipitate of the hydrate of the earth, insoluble in an excess of the base.

Calcium-salts	White precipitate of the hydrate of the earth, insoluble in an excess of the base.
Magnesium-salts	White precipitate of the hydrate of the earth, insoluble in an excess of the base.
Aluminum-salts	White gelatinous precipitate, soluble in a considerable excess of the base.
Chromium-salts	Greenish precipitate of the hydrated sesquioxide, insoluble in an excess of the base.
Nickel-salts	Apple-green hydrate of the protoxide, insoluble in excess.
Cobalt-salts	Pink hydrate of the protoxide, insoluble in excess.
Manganese-salts	Whitish precipitate of the hydrated protoxide, insoluble in excess.
Iron-salts.	
Protoxide	Green precipitate of the hydrated protoxide, insoluble in excess.
Sesquioxide	Brown precipitate of the hydrated sesquioxide, insoluble in excess.
Zinc-salts	White hydrate of the protoxide, soluble in excess.
Lead-salts	White hydrate of the protoxide, soluble in excess.
Silver-salts	Brown protoxide, insoluble in excess.
Mercury-salts.	
Suboxide	Black suboxide, insoluble in excess.
Protoxide	Red precipitate, probably of a double salt, becoming yellow protoxide by addition of excess.
Copper-salts	Blue hydrated protoxide, insoluble in excess, becoming black by ebullition.
Cadmium-salts	White hydrated protoxide, insoluble in excess.
Bismuth-salts	White hydrated teroxide, insoluble in excess.
Antimony-salts (Teroxide)	White hydrated teroxide, soluble in excess.
Tin-salts.	
Protoxide	White hydrated protoxide, soluble in excess.
Binoxide	White hydrated binoxide, soluble in excess.
Gold-salts	Yellow precipitate of the double compound.
Platinum-salts	Yellow precipitate of the double compound.

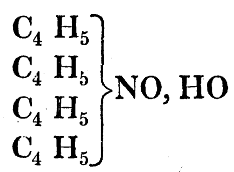
It is evident that the salts of the metals, with the exception of those of chromium, whose oxide does not redissolve in an excess of the base, exhibit the same reactions with potassa and oxide of tetrethylammonium.

Although I did not anticipate great results from the experiment, I have submitted the new base to the action of the galvanic current, the pile being disposed as in Berzelius's original experiment on the formation of the ammonium-amalgam.

However, no phenomenon, other than the decomposition of water, was observed. This decomposition certainly appeared to be facilitated, especially if the base was employed in the form of sulphate. Nor had potassium-amalgam the slightest effect upon oxide of tetrethylammonium.

I must still mention a peculiar reaction, somewhat singular at the first glance, which takes place on adding the concentrated oxide to alkaline solutions of iodide of potassium, when the crystalline iodide of tetrethylammonium is at once precipitated. I need scarcely remark that this phenomenon is due to the insolubility of the iodide in alkaline solutions, and not to the new base possessing a greater affinity for iodine than potassium, whose oxide is thus actually liberated.

A moderately concentrated solution of oxide of tetrethylammonium may be boiled without alteration; it is only in a very advanced stage of evaporation that decomposition gradually sets in. The change occurs even in the water-bath, as soon as the base becomes nearly dry. On evaporating, however, under the bell of the air-pump in the presence of sulphuric acid and lime, the base may be obtained in the dry state. I have endeavoured to obtain it in this manner in a condition fit for analysis, but all my attempts have been hitherto in vain; a concentrated solution of the oxide, when placed in a vacuum, deposits, after some days' exposure, long hair-like needles, which are, however, deliquescent in the extreme, and attract carbonic acid with great avidity. In both respects they are scarcely inferior to potassa. By remaining longer *in vacuo*, these crystals disappear again, and the whole liquid dries up to a semisolid mass, which also deliquesces rapidly, and becomes carbonated on exposure to the air. As there was not the slightest chance of getting this substance into a combustion-tube, I endeavoured to ascertain its composition, by decomposing a known quantity of the iodide with protoxide of silver, evaporating *in vacuo* in a glass dish, which on removing from the air-pump, could be covered with a glass plate, and determining the weight of the solid mass remaining. These experiments, however, have not led to any decisive results. Soon after the formation of the crystals, the liquid becomes coated with a thin pellicle, which retards the evaporation to such an extent, that even after a fortnight's exposure the mass still continues to lose in weight; but by that time, however carefully the air was excluded, the base has partly been converted into carbonate. Some similar experiments, made in the amyl-series, which I shall describe in another part of this paper, have been attended with more success. From these experiments it may be inferred by analogy, that the residue remaining on evaporating a solution of oxide of tetrethylammonium is the hydrate



$$\left.\begin{matrix}C_4\,H_5\\C_4\,H_5\\C_4\,H_5\\C_4\,H_5\end{matrix}\right\}NO,\,HO$$

corresponding to hydrate of potassa. The hair-like crystals contain evidently in addition several equivalents of water of crystallization; they may possibly be analogous to the well-known crystallized hydrate of potassa KO, HO+4 Aq, which is formed at low temperatures.

It was above stated that the residuary substance left on evaporating a solution of the oxide of tetrethylammonium is decomposed, even at the temperature of boiling water. During this change a powerful ammoniacal odour is evolved, the substance strongly intumesces, and is by degrees perfectly volatilized. If this process be conducted in an appropriate apparatus, it is found that the base, under these circumstances, yields three products of decomposition, namely, water, an highly alkaline oil, rather soluble in water, and a colourless inflammable gas. The oily base has all the properties of triethylamine; it was identified moreover by the analysis of its characteristic platinum-salt.

0·2257 grm. of platinum-salt gave on ignition 0·0725 grm. of platinum.

	Theoretical percentage.	Experimental percentage.
Platinum	32·12	32·12

The inflammable gas evolved was pure olefiant gas; it was perfectly absorbed by bromine water, proving the absence of hydrocarbons not belonging to the family $C_n H_n$, and the oily liquid formed had all the properties of the Dutch liquid. It readily solidified into a crystalline mass when exposed to a freezing mixture, a deportment whereby the olefiant gas compound may be easily distinguished from the corresponding compounds of propylene, butylene and amylene.

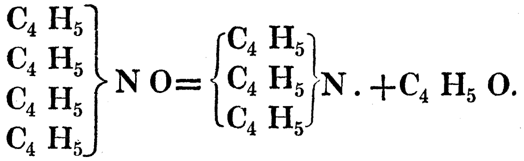
Hence the metamorphosis of oxide of tetrethylammonium under the influence of heat is represented by the following equation:—

$$\left.\begin{matrix} C_4 H_5 \\ C_4 H_5 \\ C_4 H_5 \\ C_4 H_5 \end{matrix}\right\} NO,\ HO = 2HO + \left\{\begin{matrix} C_4 H_5 \\ C_4 H_5 \\ C_4 H_5 \end{matrix}\right\} N + C_4H_4.$$

This change is not only interesting as an additional corroboration of the formula of the base, but likewise as affording a new source from which triethylamine may be obtained in a state of perfect purity; for as I shall show presently, the oxide may be also prepared from very impure mixtures of the lower ethyl-bases, and even from ammonia directly.

This, too, deserves to be noticed, as a new instance of the failure of the analogy between iodide and oxide of ethyl (ether)—a fact which was pointed out long ago by MM. Laurent and Gerhardt, and most indubitably demonstrated by the recent investigations of Dr. Williamson. If the decomposition by heat of oxide of tetrethylammonium was perfectly analogous to that of the iodide, we should expect to see the former split into triethylamine and oxide of ethyl (ether).

$$\left.\begin{matrix} C_4 H_5 \\ C_4 H_5 \\ C_4 H_5 \\ C_4 H_5 \end{matrix}\right\} N\ I = \left\{\begin{matrix} C_4 H_5 \\ C_4 H_5 \\ C_4 H_5 \end{matrix}\right\} N + C_4 H_5\ I.$$



$$\left.\begin{matrix}C_4\,H_5\\C_4\,H_5\\C_4\,H_5\\C_4\,H_5\end{matrix}\right\}N\,O=\left\{\begin{matrix}C_4\,H_5\\C_4\,H_5\\C_4\,H_5\end{matrix}\right\}N.+C_4\,H_5\,O.$$

But, as I have stated above, this decomposition yields, instead of ether, water and olefiant gas.

I have prepared several of the salts of tetrethylammonium. The sulphate, the nitrate, the phosphate, the carbonate, the hydrochlorate and the hydrobromate, all crystallize. But these salts are extremely soluble, and, with the exception of the carbonate, deliquescent, and but little adapted to analysis. They may be obtained either by directly saturating the oxide with the respective acids, or by double decomposition. The phosphate is conveniently prepared by gently heating a solution of the iodide with an excess of phosphate of silver, when, according to the silver-salt employed, either the common phosphate, or the pyrophosphate, &c. may be obtained. The phosphate thus obtained is strongly alkaline, like the tribasic soda-salt.

Tetrethylammonium forms a great number of beautiful double salts, of which I have examined a few.

Platinum-salt.—On adding a solution of bichloride of platinum to the chloride, an orange-yellow precipitate appears at once, which in every respect resembles the corresponding potassium- or ammonium-compound.

Like the latter, it is slightly soluble in water, and less so in alcohol and in ether; like the latter, it may be crystallized in beautiful octahedrons. The salt was repeatedly prepared. The specimens used for analysis I., II. and III., were precipitated from the pure chloride obtained by saturating the oxide with hydrochloric acid; specimens IV. and V., simply by removing the iodine from the iodide by nitrate of silver, acidifying with hydrochloric acid, and adding bichloride of platinum to the mixture of nitrate and chloride thus obtained. The latter circumstance may have caused the trifling discrepancy, which will be observed in the numbers below.

I. 0·3837 grm. of platinum-salt gave 0·4065 grm. of carbonic acid, and 0·2100 grm. of water.

II. 0·3586 grm. of platinum-salt gave 0·1056 grm. of platinum.

III. 0·2784 grm. of platinum-salt gave 0·0816 grm. of platinum.

IV. 0·5228 grm. of platinum-salt gave 0·1526 grm. of platinum.

V. 0·6782 grm. of platinum-salt gave 0·1977 grm. of platinum.

	Percentage-composition.				
	I.	II.	III.	IV.	V.
Carbon . . .	28·89	——	——	——	——
Hydrogen . .	6·08	——	——	——	——
Platinum . .	——	29·48	29·35	29·19	29·16

The formula

$$C_{16}\,H_{20}\,N\,Cl,\,Pt\,Cl_2=\left\{\begin{array}{l}C_4\,H_5\\C_4\,H_5\\C_4\,H_5\\C_4\,H_5\end{array}\right\}N\,Cl,\,Pt\,Cl_2$$

requires the following values, which I collate with the experimental numbers.

	Theory.		Mean of Experiment.
16 equivs. of Carbon	96	28·63	28·89
20 equivs. of Hydrogen . . .	20	5·95	6·08
1 equiv. of Nitrogen	14	4·20	——
3 equivs. of Chlorine	106·5	31·78	——
1 equiv. of Platinum	98·68	29·44	29·27
1 equiv. of Platinum-salt . .	335·18	100·00	

Gold-Salt.—It is formed by mixing the solution of the two chlorides, when a lemon-yellow precipitate takes place, which is but slightly soluble in cold water or hydrochloric acid. Before analysis it was recrystallized from boiling water. I was satisfied with a determination of the metal in this compound.

I. 0·2555 grm. of gold-salt gave 0·1075 grm. of gold.

II. 0·4344 grm. of gold-salt gave 0·1822 grm. of gold.

The formula

$$\left.\begin{array}{l}C_4\,H_5\\C_4\,H_5\\C_4\,H_5\\C_4\,H_5\end{array}\right\}N\,Cl,\,Au\,Cl_3$$

requires the following values:—

	Theory.		Mean of Experiment.
1 equiv. of Chloride of Tetrethylammonium	165·50	35·32	——
3 equivs. of Chlorine	106·50	22·72	——
1 equiv. of Gold	196·66	41·96	42·00
1 equiv. of Gold-salt	468·66	100·00	

Mercury-Salts.—a. *Chlorine-Compound.*—On adding an excess of protochloride of mercury to a nearly neutral solution of the chloride, a beautiful crystalline white precipitate is formed, which is soluble in water and in hydrochloric acid, especially on ebullition. From the boiling solution it is deposited on cooling in plates of a greasy appearance. The analysis refers to two different preparations, the same specimen being used for I. and II. The mercury was determined as protosulphide.

I. 0·4595 grm. of substance gave 0·3147 grm. of protosulphide of mercury.

II. 0·3960 grm. of substance gave 0·4020 grm. of chloride of silver.

III. 0·5530 grm. of substance gave 0·5580 grm. of chloride of silver.

	Percentage.		
	I.	II.	III.
Mercury	59·01	——	——
Chlorine	——	25·11	25·00

The only expression into which these numbers may be translated is the formula

$$\left.\begin{array}{l}C_4\,H_5\\C_4\,H_5\\C_4\,H_5\\C_4\,H_5\end{array}\right\}N\,Cl,\ 5Hg\,Cl,$$

which requires the following values:—

	Theory.		Mean of Experiment.
1 equiv. of Tetrethylammonium . .	130	15·49	——
6 equivs. of Chlorine	213	25·20	25·05
5 equivs. of Mercury	500	59·31	59·01
1 equiv. of Mercury-salt	843	100·00	

This somewhat peculiar composition, though chloride of mercury is known to join other compounds in rather unusual proportions, induced me to prepare an analogous iodine-compound, which on analysis was found to have a corresponding formula.

b. *Iodine-Compound.*—This substance was prepared in two different ways. Protiodide of mercury, when boiled with a solution of iodide of tetrethylammonium, loses at once its red colour, and is converted into a yellow compound, which fuses and collects as a transparent layer at the bottom of the vessel. On cooling it solidifies to a brittle mass, with crystalline fracture (I.). The same substance is obtained by adding a large excess of protochloride of mercury to a solution of iodide of tetrethylammonium. A whitish crystalline precipitate is produced, which consists of a mixture of the double salt just mentioned, with a large amount of the corresponding chlorine-compound*. By boiling with water the latter is removed, the former remaining behind (II.).

I. 0·7305 grm. of salt gave 0·7402 grm. of iodide of silver.

II. 0·8258 grm. of salt gave 0·8270 grm. of iodide of silver.

	Percentage.	
	I.	II.
Iodine.	54·34	53·99

The formula

$$\left.\begin{array}{l}C_4\,H_5\\C_4\,H_5\\C_4\,H_5\\C_4\,H_5\end{array}\right\}N\,I,\ 5Hg\,I$$

---

* 6 equivs. of iodide of tetrethylammonium and 30 equivs. of protochloride of mercury, contain the elements of 1 equiv. of the iodide of mercury double salt and of 5 equivs. of the chloride of mercury compound.

requires the following values:—

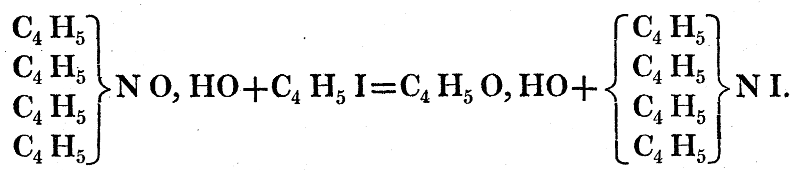
	Theory.		Mean of Experiment.
1 equiv. of Tetrethylammonium . . .	130·00	9·37	——
6 equivs. of Iodine.	758·16	54·61	53·76
5 equivs of Mercury	500·00	36·02	——
1 equiv. of Mercury-salt	1388·16	100·00	

The new oxide forms several other double compounds; but as their analysis would have scarcely given additional elucidation to the subject, I have omitted to study them in detail.

The action of various chemical agents upon the compounds of tetrethylammonium gives rise to a series of very remarkable substances. Chlorine, bromine and iodine, convert the base into substitution-products, in which the basic character of the original atom has disappeared; of these the bromine-compound is distinguished by its splendid appearance, crystallizing as it does from alcohol in long magnificent orange-yellow needles. The iodine-compound, too, is very beautiful; it forms either on addition of iodine-solution to the base, or on evaporating a solution of the iodide exposed to the action of the air. In fact it is difficult to avoid the formation of this substance in recrystallizing iodide of tetrethylammonium. Cyanic acid yields with the base a crystalline compound, a sort of urea, which is remarkable for its composition, inasmuch as it may be viewed as ordinary urea, in which the four equivalents of hydrogen are replaced by ethyl. I hope to communicate shortly a full account of these several substances.

The preceding sketch, incomplete as it is, sufficiently exhibits the leading features of the new class of substances, of which tetrethylammonium and its compounds are the prototypes. It is at once evident that there is a marked difference between these latter and the bases which I have described in my former memoir. Irrespectively of the non-volatility of the new basic oxide, which forms in itself a line of demarcation, there are many other properties not less distinctive which attract our attention. The consecutive replacement of the several hydrogen-equivalents of ammonia induces a gradual change in the properties of the original atom; ethylamine is almost as soluble in water as ammonia itself; in diethylamine this property is less marked; and finally, triethylamine is still less soluble. But another equivalent of ethyl being added, the substance changes altogether in property; it becomes soluble in water in all proportions, in fact so soluble that it can scarcely be obtained in the dry state. A perfectly analogous, although reverse deportment, is exhibited by the platinum-salts of the various bases; here we find that the solubility of the salts augments with the degree of ethylation, the salt of triethylamine being soluble in the extreme, while suddenly the tetrethylammonium-compound becomes not more soluble than the ammonium-compound itself. It is evident that ethylamine, diethylamine and triethylamine are compound ammonias; the tetrethylated base is a compound oxide of ammonium.

It now remained only to submit the new base again to the action of iodide of ethyl. An experiment on a small scale showed that the two compounds do not fail to act promptly upon one another. The mixture, after an hour's ebullition in a sealed tube, solidified into a beautiful crystalline mass. In order to obtain a precise notion of this reaction, I repeated this experiment upon a grand scale. Two ounces of iodide of tetrethylammonium were caustified by protoxide of silver, and then submitted to the action of about half a pound of iodide of ethyl. The mixture was kept boiling in a glass flask, provided with a long tube, in which the volatilized substances were condensed and returned to the seat of the reaction. During the whole process not a trace of permanent gas was disengaged. After a day's ebullition the solution had become neutral, and deposited on cooling magnificent crystals of iodide of tetrethylammonium, which were identified by analysis. In fact, for the determinations III. and V., mentioned at the analysis of the platinum-compound, the salts had been prepared with the base obtained in this manner. On submitting the mother-liquor of the crystals to distillation in such a manner as to collect only the most volatile products, a considerable amount of perfectly pure alcohol was obtained, which was identified by a careful comparison of all its properties. The action of iodide of ethyl upon oxide of tetrethylammonium is therefore represented by the following equation—



$$\left.\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}N\,O, HO+C_4H_5I=C_4H_5O, HO+\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}N\,I.$$

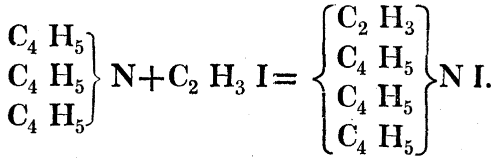
I have since found that metallic oxides, such as protoxide of silver, in the presence of water, all exert the same action on iodide of ethyl; in this case a metallic iodide is formed, alcohol being reproduced.

The experiment just described shows that, as might have been expected, the ethylation cannot be carried on *ad infinitum*, and that the oxide of tetrethylammonium is the highest term attainable in the ethyl-series. The latter substance continues to act upon iodide of ethyl, but the change affects solely the iodide of ethyl, while the base is no longer altered.

The preceding researches are, in themselves, sufficient to establish the point of theory which is here in question; still I hoped to gain a broader basis for raising general conclusions by collecting some additional facts. The repetition in the methyl- or amyl-series of an experiment already made in the ethyl-series, resembles, it is true, the working of a design in blue or green, which has been previously printed in red. Nevertheless, irrespectively of the farther elaboration of the theory of homologues, which is still wanted, such experiments lead frequently to new and unexpected observations, which often amply repay the trouble and tediousness of such inquiries. I therefore made the experiments which yielded the following results:—

Action of Iodide of Methyl upon Triethylamine.

A mixture of triethylamine and iodide of methyl solidifies, after some time, to a crystalline mass, even at the common temperature. On ebullition the change takes place instantaneously. The crystalline compound thus produced may be viewed as the iodide of an organic metal, containing, together with nitrogen, one equivalent of methyl, and three of ethyl.



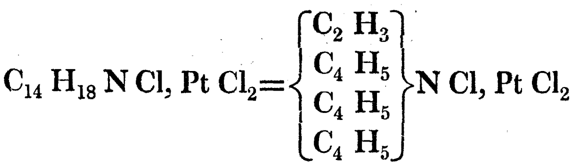
$$\left.\begin{matrix}C_4\,H_5\\C_4\,H_5\\C_4\,H_5\end{matrix}\right\}N+C_2\,H_3\,I=\left\{\begin{matrix}C_2\,H_3\\C_4\,H_5\\C_4\,H_5\\C_4\,H_5\end{matrix}\right\}N\,I.$$

In accordance with the nomenclature I have proposed for the preceding substance, this compound may be called iodide of methylotriethylammonium. And here is perhaps the place to ask for indulgence, for the *sesquipedalia verba*, which I am using in the account of this investigation, and of which the worst, I fear, are still to come. However, the use of these barbarous names has the advantage of conveying an idea of the composition of the substances under examination in the shortest and most impressive manner. Moreover, none of these names are likely to remain in science; all these substances, which are prepared solely for the elucidation of a principle, will be forgotten as soon as the object is gained; they resemble paving-stones, each of which is very important in laying down a street, though no interest is attached to the blocks themselves, as soon as we are passing along the level road.

Iodide of methylotriethylammonium has all the properties which I have enumerated when speaking of the preceding compound. It is extremely soluble, forming a perfectly neutral, very bitter solution. On adding potassa to this solution, a heavy oily liquid is precipitated, which gradually solidifies. This is the unchanged iodide, which, like the corresponding tetrethylammonium-compound, is less soluble in alkaline solutions than in water. The iodide is readily decomposed by protoxide of silver, whereby the oxide is obtained in solution, which is caustic and bitter in the extreme. *In vacuo* it dries up to a crystalline compound, analogous to oxide of tetrethylammonium, the properties of which present the same difficulties to analysis. I have fixed the composition of this compound by the analysis of the beautiful platinum-precipitate, which is formed on adding the bichloride to a solution of the base saturated with hydrochloric acid.

0·3530 grm. of platinum-salt gave 0·1075 grm. of platinum.

To the formula



$$C_{14}\,H_{18}\,N\,Cl,\,Pt\,Cl_2=\left\{\begin{matrix}C_2\,H_3\\C_4\,H_5\\C_4\,H_5\\C_4\,H_5\end{matrix}\right\}N\,Cl,\,Pt\,Cl_2$$

correspond the following values:—

	Theory.		Experiment.
1 equiv. of Methylotriethylammonium .	116·00	36·15	——
3 equivs. of Chlorine	106·50	33·15	——
1 equiv. of Platinum	98·68	30·70	30·48
1 equiv. of Platinum-salt	321·18	100·00	

I have not studied this substance very minutely; it forms crystalline salts with sulphuric, nitric, oxalic and hydrochloric acids.

ACTION OF IODIDE OF AMYL UPON TRIETHYLAMINE.

The experiment was conducted in a perfectly similar manner, and the results obtained are perfectly analogous. The action however is by no means as rapid as in the preceding cases, the amyl-substances being invariably much more inert than the corresponding terms in the ethyl- and methyl-series. In order to complete the process, it is necessary to heat the mixture in sealed tubes for two or three days. The iodide of amylotriethylammonium, for this is the new compound, forms remarkably fine crystals, which exhibit the fatty lustre and touch peculiar to the amyl-compounds. It is extremely soluble in water and alcohol, insoluble in ether. The solutions have the bitter taste of quinine. On adding potassa or carbonate of potassa, the iodide separates as an oil, which rapidly shoots into brilliant needles. The salt when slightly moist fuses at 100° C. to a clear oily liquid, which becomes solid on cooling and perfect desiccation, and gradually assumes a yellow tint.

The iodine-determination gave the following result:—

0·4210 grm. of iodide gave 0·3310 grm. of iodide of silver.

The formula

$$C_{22}\,H_{24}\,N\,I = \left\{\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \\ C_{10}\,H_{11} \end{matrix}\right\} N\,I$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Amylotriethylammonium . . .	172·0	57·51	——
1 equiv. of Iodine	127·1	42·49	42·51
1 equiv. of Iodine-compound	299·1	100·00	

When boiled with protoxide of silver the base is liberated and dissolves, forming an alkaline liquid of extremely bitter taste. The alkaline properties are however less marked than in the preceding bases. On evaporation the oxide of amylotriethylammonium remains in form of a syrup, which I have never seen assuming the crystalline form, perhaps because I have not allowed it to stand for a sufficiently long time. The sulphate and oxalate of this base, when evaporated in the bell of the air-pump, leave a syrupy or gummy residue like the base itself. The nitrate, however, and the hydrochlorate form beautiful crystals, the former hard, permanent needles of a cooling taste; the latter, leaves which are extremely deliquescent. The solution of the hydrochlorate is not precipitated by bichloride of platinum unless very concentrated. The salt once formed however is far less soluble. From a boiling solution in water it shoots into most magnificent orange-yellow needles, sometimes half an inch in length.

On ignition, 0·2620 grm. of platinum-salt gave 0·0675 grm. of platinum.

The values corresponding to the formula

$$C_{22}\,H_{26}\,N\,Cl,\,Pt\,Cl_2 = \left.\left\{\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \\ C_{10}\,H_{11} \end{matrix}\right\}\right. N\,Cl,\,Pt\,Cl_2$$

are

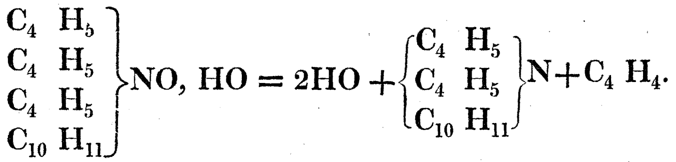
	Theory.		Experiment.
1 equiv. of Amylotriethylammonium . . .	172·00	45·60	——
3 equivs. of Chlorine	106·50	28·24	——
1 equiv. of Platinum	98·68	26·16	25·76
1 equiv. of Platinum-salt	377·18	100·00	

The percentage of the platinum is unusually low when compared with the theoretical value, a fact which I suppose is due to the recrystallization of the salt. In several cases I have observed that the platinum-salts of these bases undergo a slight decomposition under these circumstances, which is not indicated by the appearance of the recrystallized salt, but which is invariably pointed out by a diminution of the amount of platinum. I am not as yet acquainted with the mode of this change. In the present instance I have not repeated the experiment, because the mode of formation, the analysis of the iodide, and moreover the decomposition of the base, preclude all doubts respecting the formula of the compound under examination.

The remarkable change exhibited by oxide of tetrethylammonium, when submitted to the action of heat, necessarily induced me to study the deportment of the amylotriethylated base under similar circumstances. This study appeared to promise some farther revelations respecting the molecular constitution of this body, a hope in which I was not deceived. I had no doubt in my mind that the process alluded to would give rise to the formation of a nitrile-base, but there were two alternatives which presented themselves as to the nature of this base. The question arose, Will an equivalent of ethyl or amyl be broken up in this decomposition? This question had to be decided by experiment.

Action of Heat on Oxide of Amylotriethylammonium.

Oxide of amylotriethylammonium, when subjected to distillation, begins to froth as soon as the solution becomes concentrated, after which decomposition rapidly sets in. The products of this decomposition are water, an oily substance, and a transparent inflammable gas. The latter, by the method I have indicated when speaking of the decomposition of oxide of tetrethylammonium, was proved to be perfectly pure olefiant gas, when the composition of the oily liquid was no longer doubtful. It was evident that this substance must be a nitrile-base containing two equivalents of ethyl and one equivalent of amyl.



$$\left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \\ C_{10}\,H_{11}\end{matrix}\right\}NO,\ HO = 2HO + \left\{\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_{10}\,H_{11}\end{matrix}\right\}N + C_4\,H_4.$$

Experiment has entirely confirmed this view. Diethylamylamine—for this is the name which appertains to the new compound—has a peculiar, not unpleasant aromatic odour, and an analogous somewhat bitter taste, is lighter than water, in which it scarcely dissolves, imparting to it a slight but decided alkaline reaction. It combines with acids less readily than do the bases which occupy a lower position in the system. The salts with sulphuric, nitric, oxalic and hydrochloric acids, crystallize beautifully, but are deliquescent. Diethylamylamine, when dried over hydrate of potassa and rectified, exhibits a perfectly constant boiling-point at 154° C.

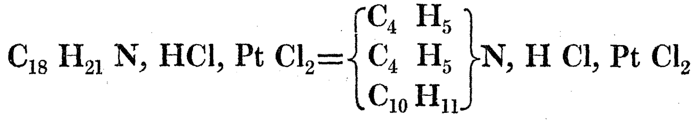
I have fixed the composition of this base, as usual, by the analysis of the platinum-salt. This compound is obtained by concentrating a mixture of the hydrochlorate with bichloride of platinum, when it shoots into long magnificent orange-yellow prisms.

I. 0·3405 grm. of platinum-salt gave 0·0955 grm. of platinum.

II. 0·3805 grm. of platinum-salt gave 0·1065 grm. of platinum.

	Percentage.	
	I.	II.
Platinum	28·04	28·02

The formula



$$C_{18}\,H_{21}\,N,\ HCl,\ Pt\,Cl_2 = \left\{\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_{10}\,H_{11}\end{matrix}\right\}N,\ H\,Cl,\ Pt\,Cl_2$$

requires

	Theory.		Experiment.
1 equiv. of Hydrochlorate of Diethylamylamine	179·50	51·40	——
2 equivs. of Chlorine	71·00	20·34	——
1 equiv of Platinum	98·68	28·26	28·03
1 equiv. of Platinum-salt	349·18	100·00	

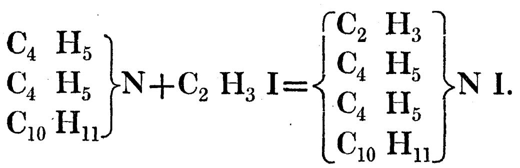
The formula of diethylamylamine is moreover supported by the boiling-point. This compound differs from diethylamine by $C_{18}H_{21}N - C_8H_{11}N = C_{10}H_{10} = 5C_2H_2$. I have lately prepared diethylamine on a larger scale, and found its boiling-point to be 57° C.; on starting from this number, the boiling-point of diethylamylamine should be $57 + (5 \times 19) = 152°$. The experimental boiling-point is 154°.

Having seen by the preceding experiments that ethyl, as it were, yields its place to amyl, the idea naturally suggested itself to inquire into the mutual relations of ethyl and methyl under similar circumstances. For this purpose I might have studied the action of heat upon oxide of methylotriethylammonium; however, as I had some grammes of diethylamylamine at my disposal, I preferred to methylate this compound, and examine the new body thus obtained.

Action of Iodide of Methyl upon Diethylamylamine.

On adding iodide of methyl to diethylamylamine, the phenomena which I have already several times described are repeated in turn. The action in this case however is so violent that the iodide must be added very gradually, for on suddenly mixing, the liquid is projected from the vessel with a sort of explosion; on account of the low boiling-point of the methyl-compound, it is advisable to mix in a tubulated retort provided with a condenser.

On cooling the mixture solidifies into a hard white crystalline mass, consisting of a new iodide, for which, in accordance with the nomenclature which I have adopted, I propose the name iodide of methylodiethylamylammonium.



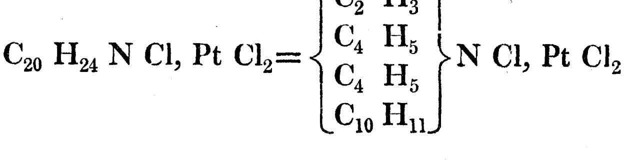
$$\left.\begin{matrix}C_4\,H_5\\C_4\,H_5\\C_{10}\,H_{11}\end{matrix}\right\}N + C_2\,H_3\,I = \left\{\begin{matrix}C_2\,H_3\\C_4\,H_5\\C_4\,H_5\\C_{10}\,H_{11}\end{matrix}\right\}N\,I.$$

The new iodide, like the preceding analogues, is extremely soluble in water, forming a very bitter solution, from which it is reprecipitated by potassa in oily globules, which solidify again but slowly.

When digested with protoxide of silver, the iodide yields the oxide in form of a powerful alkaline solution, which forms crystalline salts with sulphuric, nitric and hydrochloric acid. The hydrochlorate of methylodiethylamylammonium gives with bichloride of platinum a beautiful salt, by the analysis of which the composition of the substance was established.

0·2015 grm. of platinum-salt gave 0·0550 grm. of platinum.

The values corresponding to the formula



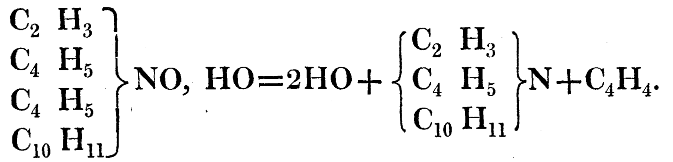
$$C_{20}\,H_{24}\,N\,Cl,\,Pt\,Cl_2 = \left\{\begin{matrix}C_2\,H_3\\C_4\,H_5\\C_4\,H_5\\C_{10}\,H_{11}\end{matrix}\right\}N\,Cl,\,Pt\,Cl_2$$

are the following:—

	Theory.		Experiment.
1 equiv. of Methylodiethylamylammonium . .	158·00	43·50	——
3 equivs. of Chlorine	106·50	29·33	——
1 equiv. of Platinum	98·68	27·17	27·29
1 equiv. of Platinum-salt	363·18	100·00	

Action of Heat upon Oxide of Methylodiethylamylammonium.

When submitted to distillation this compound is decomposed like the analogous substances, the product being water, pure olefiant gas, which was identified as formerly, and a very remarkable nitrile-base, containing the three different alcohol-radicals, an ammonia, in fact, in which the first equiv. of hydrogen is replaced by methyl, the second by ethyl, the third by amyl, and which receives the name methylethylamylamine.



$$\left.\begin{matrix}C_2\,H_3\\C_4\,H_5\\C_4\,H_5\\C_{10}\,H_{11}\end{matrix}\right\}NO,\ HO=2HO+\left\{\begin{matrix}C_2\,H_3\\C_4\,H_5\\C_{10}\,H_{11}\end{matrix}\right\}N+C_4H_4.$$

This reaction shows that ethyl yields its place even to methyl, a fact which could not have been anticipated from analogy, methyl occupying a lower position than ethyl in the system. The above deportment is moreover remarkable, when considered in another point of view. The elimination of methyl in the case under examination would have given rise to the formation of methylene* $C_2\,H_2$, a substance the existence of which is still very problematical.

Methylethylamylamine is a transparent oil of a fragrant odour and an analogous taste. Both these properties are much more marked than those of diethylamylamine, which it resembles in most respects. It is somewhat more soluble in water than the latter, and of a more decided alkaline character. When dried over potassa and rectified, the new base boils constantly at 135°. Hence its boiling-point is $154-135=19°$ lower than that of diethylamylamine, a difference which is in perfect accordance with H. Kopp's rule.

Methylethylamylamine dissolves but slowly in the acids, forming salts which resemble those of the diethylamylated bases. The hydrochlorate gives with bichloride of platinum a beautiful double salt, which is extremely soluble in water. It is usually precipitated on mixing the highly concentrated solutions, or on evaporating the mixture, in oily globules of a deep orange-yellow, which gradually solidify into magnificent needles.

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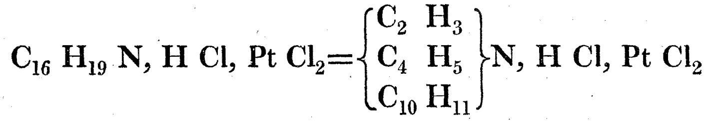
* In their paper on Methylalcohol, Dumas and Peligot (Ann. Ch. Phys. [2] lviii. 5) state that methylene is formed by passing the vapour of chloride of methyl through a red-hot tube. The gas obtained by this process did not however very accurately exhibit the composition $C_n\,H_n$, nor are any experiments for the determination of the value of *n* recorded.

On analysis 0·4155 grm. of platinum-salt gave 0·1212 grm. of platinum.

The formula



$$C_{16}\,H_{19}\,N,\,H\,Cl,\,Pt\,Cl_2=\left.\begin{cases}C_2\,H_3\\C_4\,H_5\\C_{10}\,H_{11}\end{cases}\right\}N,\,H\,Cl,\,Pt\,Cl_2$$

requires

	Theory.		Experiment.
1 equiv. of Hydrochlorate of Methylethylamylamine	165·50	49·38	——
2 equivs. of Chlorine	71·00	21·18	——
1 equiv. of Platinum	98·68	29·44	29·36
1 equiv. of Platinum-salt	335·18	100·00	

In the preceding experiments, the radicals of the alcohols $C_n\,H_{(n+2)}\,O_2$ have been exclusively used as replacing materials. However, as might have been expected, nitrile-bases containing a radical which is not homologous but only analogous to the two others, exhibit exactly the same deportment when submitted to the action of iodide of methyl, of ethyl or of amyl. In order to establish this point, I had to return once more to the aniline-series.

ACTION OF IODIDE OF ETHYL UPON DIETHYLANILINE.

In my former paper* I have recorded a few experiments on the action of bromide of ethyl upon diethylaniline. The results, unintelligible to me at that period, are now perfectly clear. I have since repeated these reactions, substituting the iodide for the bromide on account of its more prompt action. Diethylaniline is perfectly soluble in iodide of ethyl; on exposing the mixture, sealed in tubes, to the temperature of boiling water, the liquid column gradually separates into two layers, the lower one increasing in bulk with the time of exposure, and solidifying on cooling into a semi-solid crystalline mass. The reaction is terminated, when, after half a day's ebullition, the volume of the lower layer, which is the new iodide in the fused state, ceases to increase.

The mixture is now distilled with water in order to separate an excess of either diethylaniline or iodide of ethyl, when a strongly acid solution of iodide of phenylotriethylammonium is obtained, which usually contains a small quantity of hydriodate of diethylaniline, as may be inferred from the oily precipitate produced in the solution by potassa, which does not redissolve on addition of more water.

Digestion with protoxide of silver separates the two bases, one of which, diethylaniline, being insoluble in water, remains mixed with the oxide and iodide of silver; the other, the oxide of phenylotriethylammonium, forming a powerfully alkaline solution of a strongly bitter taste.

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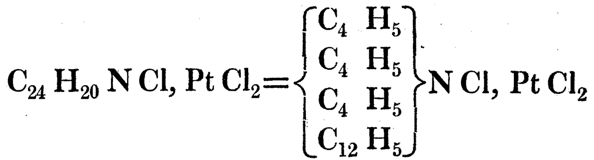
* Philosophical Transactions, 1850, Part I. p. 107.

After having ascertained by treatment with ether that the solution did not retain a trace of diethylaniline, it was saturated with hydrochloric acid and mixed with bichloride of platinum, when at once a pale-yellow, apparently amorphous precipitate was thrown down, which was scarcely soluble in water and insoluble in alcohol and ether.

0·4055 grm. of platinum-salt gave 0·1045 grm. of platinum.

To the formula



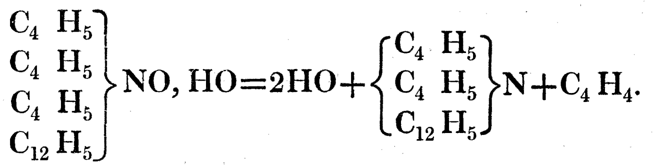
$$C_{24}H_{20}NCl, PtCl_2 = \left.\begin{array}{l} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_{12}H_5 \end{array}\right\} NCl, PtCl_2$$

correspond the following values :—

	Theory.		Experiment.
1 equiv. of Phenylotriethylammonium . .	178·00	46·45	——
3 equivs. of Chlorine	106·50	27·80	——
1 equiv. of Platinum	98·68	25·75	25·77
1 equiv. of Platinum-salt	383·18	100·00	

I have not examined any farther the compounds of this base; I have only ascertained that the sulphate, nitrate, oxalate and hydrochlorate crystallize, although with difficulty.

When oxide of phenylotriethylammonium is submitted to the action of heat, it yields, as might have been expected, water, olefiant gas and diethylophenylamine (diethylaniline).



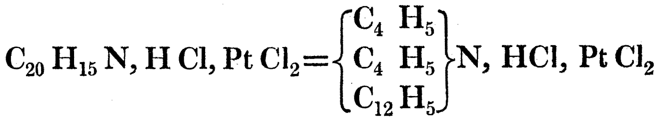
$$\left.\begin{array}{l} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_{12}H_5 \end{array}\right\} NO, HO = 2HO + \left.\begin{array}{l} C_4H_5 \\ C_4H_5 \\ C_{12}H_5 \end{array}\right\} N + C_4H_4.$$

The olefiant gas was identified by the conversion into the bromine-compound, the diethylaniline by the analysis of the characteristic platinum-salt.

0·2965 grm. of platinum-salt gave 0·0820 grm. of platinum.

This corresponds to 27·65 per cent. of platinum.

The formula



$$C_{20}H_{15}N, HCl, PtCl_2 = \left.\begin{array}{l} C_4H_5 \\ C_4H_5 \\ C_{12}H_5 \end{array}\right\} N, HCl, PtCl_2$$

requires 27·78 per cent. of platinum.

Action of Iodide of Methyl upon Ethylamylaniline.

Ethylamylaniline, which I formerly obtained* by the action of bromide of amyl upon ethylaniline, or of bromide of ethyl upon amylaniline, may be formed with the

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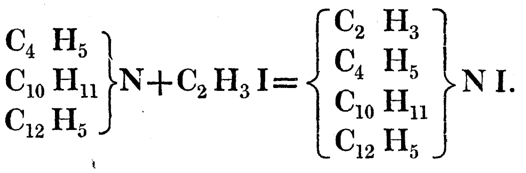
* Philosophical Transactions, 1850, Part I. p. 117.

same, or greater facility, by exposing the latter base to iodide of ethyl. When submitted to the action of iodide of methyl at the temperature of boiling water for three or four days, ethylamylaniline exhibits all the phenomena described in the preceding paragraph. The lower layer, which solidifies, is a mixture of hydriodate of ethylamylaniline and iodide of methylethylamylophenylammonium. *Sit venia verbo*!



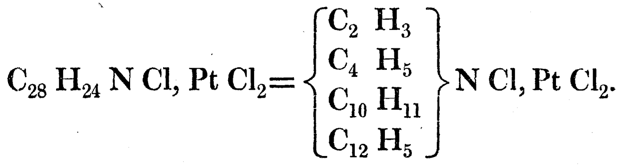
$$\left.\begin{matrix}C_4\,H_5\\C_{10}\,H_{11}\\C_{12}\,H_5\end{matrix}\right\}N+C_2\,H_3\,I=\left\{\begin{matrix}C_2\,H_3\\C_4\,H_5\\C_{10}\,H_{11}\\C_{12}\,H_5\end{matrix}\right\}N\,I.$$

The corresponding oxide is obtained as the preceding one, namely, by treating the clear solution of the two iodine-compounds, previously freed by ebullition from an excess of iodide of methyl, or ethylamylaniline, with protoxide of silver, when unchanged ethylamylaniline and the base with the long name separate. The latter remaining in solution (and forming a very bitter liquid of a strongly alkaline reaction), whilst the former is insoluble, there was no difficulty in obtaining a pure platinum-salt whereby to prove the composition of the compound in question. This salt is a pale-yellow amorphous precipitate, very slightly soluble in water.

On analysis—

0·4335 grm. of the platinum-salt gave 0·1045 grm. of the platinum.

I collate the percentage number corresponding to this result with the theoretical value of the formula—

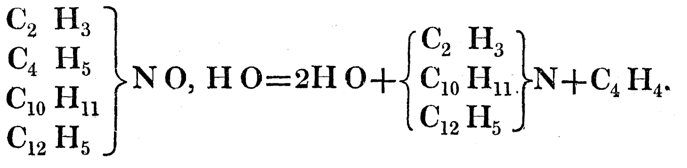


$$C_{28}\,H_{24}\,N\,Cl,\,Pt\,Cl_2=\left\{\begin{matrix}C_2\,H_3\\C_4\,H_5\\C_{10}\,H_{11}\\C_{12}\,H_5\end{matrix}\right\}N\,Cl,\,Pt\,Cl_2.$$

	Theory.		Experiment.
1 equiv. of Methylethylamylophenylammonium . .	206·00	50·01	——
3 equivs. of Chlorine	106·50	26·00	——
1 equiv. of Platinum	98·68	23·99	24·11
1 equiv. of Platinum-salt	411·18	100·00	

This compound is certainly remarkable for the diversity of its components, for it contains the radicals of not less than four different alcohols!

As to the action of heat upon the oxide under examination, there could be scarcely any doubt after the result of the preceding investigation. Still I have established by experiment that in this reaction olefiant gas is eliminated, whilst a new nitrile-base, containing methyl, amyl and phenyl, is generated.



$$\left.\begin{matrix}C_2\,H_3\\C_4\,H_5\\C_{10}\,H_{11}\\C_{12}\,H_5\end{matrix}\right\}N\,O,\,H\,O=2H\,O+\left\{\begin{matrix}C_2\,H_3\\C_{10}\,H_{11}\\C_{12}\,H_5\end{matrix}\right\}N+C_4\,H_4.$$

Methylamylophenylamine is an oil of an odour similar to that of amylaniline; it is almost insoluble in water: I have not prepared enough of this compound to determine the boiling-point, which at all events is very high. It forms a crystalline platinum-salt, whose analysis was sufficient to establish its composition.

0·3795 grm. of platinum-salt gave 0·0866 grm. of platinum.

The formula

$$C_{24}H_{19}N, HCl, PtCl_2 = \left.\begin{matrix} C_2 H_3 \\ C_{10} H_{11} \\ C_{12} H_5 \end{matrix}\right\} N, HCl, PtCl_2,$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Hydrochlorate of Methylamylaniline . .	213·5	55·72	——
2 equivs. of Chlorine	71·0	18·53	——
1 equiv. of Platinum	98·68	25·75	25·81
1 equiv. of Platinum-salt	383·18	100·00	

The paragraphs now following are devoted to a brief account of several bases belonging to the methyl- and amyl-series.

Bases of the Methyl-series.

The experiments described under this head were originally undertaken by my friend Captain Reynolds, who by many occupations unfortunately was prevented from continuing the investigation, so that I am obliged to take alone the responsibility of the following statements.

Action of Ammonia upon Iodide of Methyl.

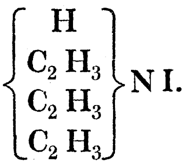
If iodide of methyl be treated with a concentrated aqueous solution of ammonia, the former is rapidly dissolved, the completion of the reaction being indicated by the liquid assuming a yellowish tint. On opening the boiler-tube the liquid is found to be strongly acid, and to contain not less than five different iodides, namely—

Iodide of Ammonium . . . . $\left.\begin{matrix} H \\ H \\ H \\ H \end{matrix}\right\} NI$

Iodide of Methylammonium . . . . $\left.\begin{matrix} H \\ H \\ H \\ C_2 H_3 \end{matrix}\right\} NI.$

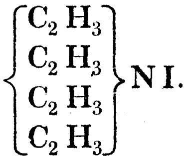
Iodide of Dimethylammonium . . . . $\left.\begin{matrix} H \\ H \\ C_2 H_3 \\ C_2 H_3 \end{matrix}\right\} NI.$

Iodide of Trimethylammonium . . . . . .



$$\left\{\begin{matrix}H\\C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right\}N\,I.$$

Iodide of Tetramethylammonium . . . . . .



$$\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right\}N\,I.$$

Of these five compounds, the first and the last are formed in considerable excess. Of the remainder I have as yet only been able to establish the presence of the iodide of methylammonium by numbers. The two others I have not as yet obtained in sufficiently large quantity and of the requisite purity. The solution of this mixture deposits, on cooling, magnificent dazzling-white hard flat needles, sometimes of an inch in length, which are very difficultly soluble in cold water, and may be obtained in the state of purity by washing with cold and recrystallizing from boiling water. These crystals are the iodide of tetramethylammonium, all the other salts remaining in the mother-liquor, which rapidly turns brown on exposure to the atmosphere. The facility with which ammonia acts upon iodide of methyl, renders it unnecessary to perform the process at a high temperature. The reaction is accomplished after some days, even at the common temperature, if an alcoholic solution be employed, after some hours, a considerable amount of heat being disengaged.

Iodide of Tetramethylammonium.

This substance possesses the family-features of the group. It is soluble in water, but far less so than the corresponding ethyl-compound, forming a perfectly neutral solution of an extremely bitter taste. It is almost insoluble in absolute alcohol, insoluble in ether. Like the ethyl-compounds, this salt is far less soluble in potassa than in pure water.

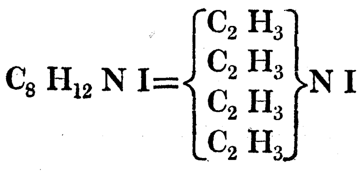
On analysis the following results were obtained:—

I. 0·4753 grm. of iodide gave 0·5519 grm. of iodide of silver.

II. 0·4256 grm. of iodide gave 0·4973 grm. of iodide of silver.

	Percentage.	
	I.	II.
Iodine	62·75	63·14

The formula



$$C_8H_{12}N\,I=\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right\}N\,I$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Tetramethylammonium . . .	74·0	36·75	——
1 equiv. of Iodine	127·1	63·25	62·94
1 equiv. of Iodine-compound	201·1	100·00	

The action of protoxide of silver upon the iodine-compound is perfectly analogous to that which it exerts upon the ethyl-body. The oxide of tetramethylammonium thus liberated is endowed with scarcely less marked properties than the ethyl-base. When evaporated over sulphuric acid *in vacuo*, it likewise dries up to a crystalline mass, attracting moisture and carbonic acid with the greatest avidity; saturated with acids, it yields crystallizable salts. I have prepared the sulphate, oxalate, nitrate and chloride; the nitrate especially crystallizes well, in long brilliant needles.

The chloride yields with bichloride of platinum a magnificent double salt, which is less insoluble than the corresponding salt in the ethyl-series; it crystallizes in perfectly regular octohedrons of a deep orange colour. When recrystallized from boiling water, this salt exhibits the peculiarity to which I have alluded previously (see p. 374), of yielding a smaller percentage of platinum. Analysis I. was made with the precipitated, analysis II. and III. with the recrystallized salt.

I. 0·2695 grm. of platinum-salt gave 0·0950 grm. of platinum.
II. 0·1925 grm. of platinum-salt gave 0·0670 grm. of platinum.
III. 0·3420 grm. of platinum-salt gave 0·1190 grm. of platinum.

	Percentage.		
	I.	II.	III.
Platinum	35·21	34·86	34·79

Values corresponding to the formula:—

$$C_8\,H_{12}\,N\,Cl,\,Pt\,Cl_2 = \left.\left\{\begin{matrix} C_2\,H_3 \\ C_2\,H_3 \\ C_2\,H_3 \\ C_2\,H_3 \end{matrix}\right.\right\} N\,Cl,\,Pt\,Cl_2$$

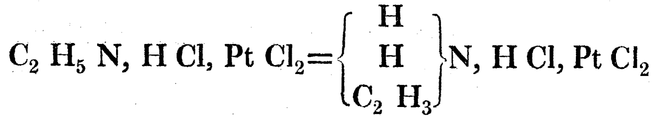
	Theory.		Experiment.
1 equiv. of Tetramethylammonium . .	74·00	26·50	——
3 equivs. of Chlorine	106·50	38·15	——
1 equiv. of Platinum	98·68	35·35	35·21
1 equiv. of Platinum-salt	279·18	100·00	

I was exceedingly desirous to submit this oxide to the action of heat; for this process, provided the methyl-base followed the deportment of its ethyl-fellow, promised to give me the long-desired methylene $C_2\,H_2$. Oxide of tetramethylammonium, when heated violently, intumesces, and is completely volatilized; the product of the distillation is an extremely volatile and powerfully alkaline liquid; but. strange to say, during the whole process not a trace of gas is disengaged. I have repeatedly performed the experiment with exactly the same result. Here then we meet with a new mode of decomposition, and unless I am much mistaken, with a decomposition of a very peculiar character. I have made a few experiments with the basic liquid disengaged, but as I have not as yet arrived at perfectly definite results, I refrain from entering into farther details.

The mother-liquor of iodide of tetramethylammonium, which contains chiefly iodide of ammonium, together with small quantities of the intermediate iodides, yields all the corresponding bases by distillation with potassa. However, the ammonia prevails in the distillate to such an extent, that the attempt to effect a separation would have been hopeless. It was only by precipitating the liquid with bichloride of platinum, and separating the more soluble from the less soluble salts, that I succeeded in obtaining evidence of the presence of the intermediate bases. As yet I have been able to prepare only the methylamine-salt in a state of tolerable purity, of which I subjoin the analysis.

0·1415 grm. of platinum-salt gave 0·0590 grm.=41·69 per cent. of platinum.

The formula



$$C_2\,H_5\,N,\,H\,Cl,\,Pt\,Cl_2=\left.\begin{cases}H\\H\\C_2\,H_3\end{cases}\right\}N,\,H\,Cl,\,Pt\,Cl_2$$

requires 41·61 per cent. of platinum.

Bases of the Amyl-Series.

While I was engaged with the investigation of the lower ethyl-bases, Messrs. William and Alfred Bennett, who at that period were studying in the Laboratory of the College of Chemistry, undertook, at my request, the examination of the corresponding bodies in the amyl-series. Prevented from completing their researches by leaving London, these gentlemen have placed their results at my disposal, which I have verified in every respect, and which I subjoin, together with a series of experiments of my own, especially on the oxide of tetramylammonium.

Amylamine.

Ammonia acts but very slowly upon iodide of amyl, and the product of the reaction contains, as in the methyl-series, not less than five iodides. Among these the iodides of amylammonium and diamylammonium are present in the smallest quantity. The preparation of amylamine succeeds much better according to the process of M. Wurtz, namely, by submitting cyanate of amyl to the action of hydrate of potassa.

ACTION OF BROMIDE OF AMYL UPON AMYLAMINE.

Diamylamine.

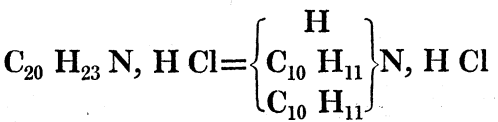
The formation of diamylamine takes place even in the cold, although slowly. At the temperature of boiling water, a mixture of amylamine and bromide of amyl is rapidly converted into a beautiful white crystalline mass of hydrobromate of diamylamine, which is purified, and decomposed in the usual manner. When purified, diamylamine is a light oily substance, very little soluble in water, to which it imparts, however, an alkaline reaction. Its aromatic odour is peculiar, not unpleasant, and reminds us of amylamine; its taste hot and pungent; it boils at about 170°. From want of pure material, the boiling-point could not be determined with accuracy.

Diamylamine forms very beautiful crystalline salts with the acids, which are all rather insoluble in water. The hydrochlorate is almost insoluble in cold water, but may be recrystallized from boiling water. This solution yields with bichloride of platinum a double salt, which is rather soluble, and separates frequently, in the first instance, in the form of oily drops, which become gradually crystalline.

It was by the analysis of these two salts that the composition of diamylamine was fixed.

0·2545 grm. of hydrochlorate gave 0·1852 grm. of chloride of silver.

The formula



$$C_{20}H_{23}N, HCl = \left.\left\{\begin{matrix} H \\ C_{10}H_{11} \\ C_{10}H_{11} \end{matrix}\right.\right\} N, HCl$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Diamylamine	157·0	81·14	——
1 equiv. of Hydrochloric Acid	36·5	18·86	18·51
1 equiv. of Hydrochlorate of Diamylamine .	193·5	100·00	

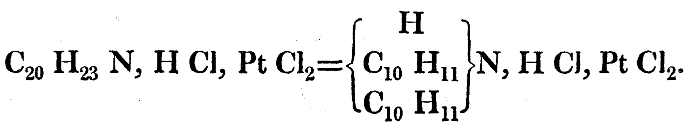
These numbers show that the hydrochlorate employed was not perfectly pure; however, the two following platinum-salts leave no doubt respecting the base under examination.

I. 0·1634 grm. of platinum-salt gave 0·0444 grm. of platinum.

II. 0·1805 grm. of platinum-salt gave 0·0488 grm. of platinum.

	Percentage.	
	I.	II.
Platinum	27·17	27·04

The following theoretical values correspond to the formula



$$C_{20}H_{23}N, HCl, PtCl_2 = \left.\left\{\begin{matrix} H \\ C_{10}H_{11} \\ C_{10}H_{11} \end{matrix}\right.\right\} N, HCl, PtCl_2.$$

	Theory.		Experiment.
1 equiv. of Hydrochlorate of Diamylamine	193·50	53·29	——
2 equivs. of Chlorine	71·00	19·54	——
1 equiv. of Platinum	98·68	27·17	27·10
1 equiv. of Platinum-salt	363·18	100·00	

ACTION OF BROMIDE OF AMYL UPON DIAMYLAMINE.

Triamylamine.

This base arises from diamylamine in the same manner as the latter from amylamine. It is moreover obtained, and at once in a state of purity, by exposing oxide of tetramylammonium, which I shall describe presently, to a high temperature; prepared by either way, this substance resembles in most of its physical and chemical characters diamylamine; it boils however at a much higher temperature, namely, at 257°. Its composition was fixed as that of diamylamine, by the analysis of the hydrochlorate and of the platinum-salt, the former being a very characteristic salt, which separates at once in nacreous plates on adding hydrochloric acid to the base, the latter being a viscid salt gradually solidifying to a crystalline mass.

0·1022 grm. of the hydrochlorate gave 0·0551 grm. of chloride of silver.

The formula

$$C_{30}\,H_{33}\,N,\,H\,Cl=\left.\left\{\begin{matrix}C_{10}\,H_{11}\\C_{10}\,H_{11}\\C_{10}\,H_{11}\end{matrix}\right.\right\}N,\,H\,Cl$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Triamylamine	227·00	86·15	——
1 equiv. of Hydrochloric Acid	36·50	13·85	13·73
1 equiv. of Hydrochlorate of Triamylamine	263·50	100·00	

The following platinum-determinations were made with three different salts: I, and II. were prepared with triamylamine, obtained by the action of bromide of amyl upon diamylamine; salt III. was made with the base resulting from the decomposition of oxide of tetramylammonium.

I. 0·3270 grm. of platinum-salt gave 0·0750 grm. of platinum.
II. 0·2182 grm. of platinum-salt gave 0·0500 grm. of platinum.
III. 0·3795 grm. of platinum-salt gave 0·0860 grm. of platinum.

	Percentage.		
	I.	II.	III.
Platinum	22·90	22·91	22·66

The theoretical values of the formula

$$C_{30}\,H_{33}\,N,\,H\,Cl,\,Pt\,Cl_2 = \left.\begin{array}{l} C_{10}\,H_{11} \\ C_{10}\,H_{11} \\ C_{10}\,H_{11} \end{array}\right\}N,\,H\,Cl,\,Pt\,Cl_2$$

are as follows:—

	Theory.		Experiment.
1 equiv. of Hydrochlorate of Triamylamine .	263·50	60·82	——
2 equivs. of Chlorine	71·00	16·40	——
1 equiv. of Platinum	98·68	22·78	22·82
1 equiv. of Platinum-salt	433·18	100·00	

Action of Iodide of Amyl upon Amylamine and upon Ammonia.

Oxide of Tetramylammonium.

A mixture of triamylamine and iodide of amyl solidifies after two or three days' ebullition to a solid, somewhat fat-like mass of iodide of tetramylammonium. A similar effect is produced by boiling an excess of iodide of amyl with a concentrated solution of ammonia. This reaction, however, takes place very slowly; in fact, the diminution of affinities characterizing the amyl-compounds in general was in none of these cases more marked. After two or three days' ebullition the volume of the ether appeared scarcely diminished; but then a gradual change occurred, the heavy amyl-compound rising and floating upon the solution of the new iodide which was formed. After a fortnight's ebullition the aqueous layer began to solidify, when allowed to cool; but even after keeping the mixture for a period of three weeks in ebullition, on opening the boiler-tube the reaction was found to be far from complete.

The semi-solid mixture thus obtained was subjected to distillation, first alone, in order to recover the iodide of amyl not acted upon; then with potassa, to separate ammonia and the lower amyl-bases. The alkaline liquid contained a small quantity of iodide of tetramylammonium in solution, which crystallized on cooling in fat-like leaves; the larger quantity, however, of this substance collected at the bottom of the vessel in form of a heavy oil, which solidified on cooling to a hard mass of the appearance of stearin.

The new iodide resembles in its general properties the corresponding compounds I have previously described. Like them it is soluble, but only with difficulty, in water, forming a most intensely bitter liquid, and reprecipitated from this solution in the crystalline form by the addition of the alkalies. On drying, the iodide assumes a slightly yellowish tint.

0·3890 grm. of the iodide gave 0·2130 grm. of iodide of silver.

The theoretical values of the formula

$$C_{40}\,H_{44}\,N\,I = \left\{\begin{matrix} C_{10}\,H_{11} \\ C_{10}\,H_{11} \\ C_{10}\,H_{11} \\ C_{10}\,H_{11} \end{matrix}\right\} N\,I$$

are as follows:—

	Theory.		Experiment.
1 equiv. of Tetramylammonium . . .	298·0	70·11	——
1 equiv. of Iodine	127·1	29·89	29·60
1 equiv. of Iodide	425·1	100·00	

On boiling the iodide with protoxide of silver, an alkaline, very bitter solution of the oxide of tetramylammonium is obtained. This substance is evidently far less soluble in water than the corresponding bases in the methyl- and ethyl-series. It would almost appear as if this compound stood to the methyl- and ethyl-bases as an alkaline earth does to potassa and soda.

On adding potassa to a solution of oxide of tetramylammonium, the base rises in the form of an oily layer on the surface of the liquid. The same separation is observed when the solution is much evaporated; in the latter case the oily layer gradually solidifies. On allowing a moderately concentrated solution of this base to stand for some time in a vessel in which it is protected from carbonic acid, magnificent perfectly definite crystals, sometimes an inch in length and in thickness, are deposited; they are but moderately deliquescent, and attract but slowly carbonic acid from the air. These crystals are the hydrate of tetramylammonium, containing a certain amount of water of crystallization. I have not yet been able to determine the number of equivalents. On heating these crystals, they fuse in their water of crystallization, and yield on evaporation in the water-bath a viscid semi-solid transparent mass, which is the hydrated oxide of tetramylammonium,

$$\left.\begin{matrix} C_{10}\,H_{11} \\ C_{10}\,H_{11} \\ C_{10}\,H_{11} \\ C_{10}\,H_{11} \end{matrix}\right\} N\,O,\,HO.$$

This substance is extremely deliquescent, and opposes to an ordinary analysis the same obstacles which I met with in the case of tetrethylammonium. I succeeded, however, in the following manner, in determining with tolerable accuracy the composition of this mass. Having observed that this oxide is far less easily decomposed by heat than the corresponding ethyl-compound, I endeavoured to determine the state of hydration in which the oxide remained, by decomposing a known quantity of the iodide with protoxide of silver, and evaporating the solution thus obtained in a glass vessel, through which a current of air previously dried and decarbonated by potassa was passed at the temperature of boiling water. On weighing the residue, the amount of water retained by the oxide was given. The results obtained in this way, although not perfectly accurate on account of the oxide yielding a small quantity of triamylamine even at 100°, before the last traces of water of crystallization are expelled, nevertheless leave but little doubt respecting the nature of the residue. In an experiment of this kind

1·0610 grm. of iodide of tetramylammonium left 0·8000 grm. of residue.

This corresponds to 75·43 per cent.; if the viscid residue had been the pure monohydrated oxide I should have found 74·10 per cent.

I hope to repeat this experiment at a lower temperature, and also to determine the amount of water of crystallization in the crystallized compound; the latter is soon reproduced on adding again a moderate quantity of water to the viscid hydrate.

I have just now mentioned that the oxide, when heated in the water-bath, yields a small quantity of triamylamine. At a higher temperature this reaction proceeds with perfect regularity; an inflammable carbohydrogen being disengaged, together with the base. There can be scarcely any doubt that the former is amylene. This substance boils at a rather low temperature, 39°, and was therefore partly collected as gas. Another portion however dissolved in the triamylamine, from which it was expelled by ebullition after the base had been fixed by addition of hydrochloric acid. The analysis of the triamylamine obtained in this reaction has been mentioned at page 386. Hence the decomposition of oxide of tetramylammonium is perfectly analogous to that of its analogues in the ethyl-series, and is represented by the equation

$$\left.\begin{matrix} C_{10}\,H_{11} \\ C_{10}\,H_{11} \\ C_{10}\,H_{11} \\ C_{10}\,H_{11} \end{matrix}\right\} NO,\ HO = 2HO + \left\{\begin{matrix} C_{10}\,H_{11} \\ C_{10}\,H_{11} \\ C_{10}\,H_{11} \end{matrix}\right\} N + C_{10}\,H_{10}.$$

Oxide of tetramylammonium is distinguished by forming crystalline salts of remarkable beauty. The sulphate crystallizes in long hair-like filaments, the nitrate in needles, the oxalate in splendid large perfectly defined plates, of a very bitter taste, and extremely deliquescent. The chloride crystallizes in leaves with palm-like ramifications; it is likewise deliquescent, but less so than the preceding salt. The solution of the chloride yields with bichloride of platinum a pale-yellow curdy precipitate, which gradually solidifies into beautiful orange-yellow needles.

On analysis the following results were obtained:—

0·2420 grm. of platinum-salt gave 0·0475 grm. of platinum.

The theoretical numbers of the formula

$$C_{40}\,H_{44}\,N\,Cl,\ Pt\,Cl_2 = \left\{\begin{matrix} C_{10}\,H_{11} \\ C_{10}\,H_{11} \\ C_{10}\,H_{11} \\ C_{10}\,H_{11} \end{matrix}\right\} N\,Cl,\ Pt\,Cl_2$$

are as follows:—

	Theory.		Experiment.
1 equiv. of Tetramylammonium . . .	298·0	59·21	——
3 equivs. of Chlorine	106·5	21·19	——
1 equiv. of Platinum	98·68	19·60	19·63
1 equiv. of Platinum-salt	503·18	100·00	

The analysis of the tetramylammonium-salt concludes the experimental part of this paper; and here I cannot but make mention publicly of the valuable assistance which Mr. James S. Brazier, Senior Assistant in the Royal College of Chemistry, has given me during the prosecution of these inquiries. I thankfully acknowledge the aid of this able young chemist, whose experimental skill is equalled by his love of science.

Before passing on to some general considerations, which the experiments detailed in the preceding paper suggest, it appears to be desirable to condense the whole of the materials into a synoptical form. The appended Table requires no commentary; it contains the formulæ of the alkaloids described in this and the preceding memoir, exhibiting in a clear light the arrangement of the molecules composing them, and the manner in which the various compounds are interchained.

TYPE.	AMIDOGEN-BASES.		IMIDOGEN-BASES.		NITRILE-BASES.		ANALOGUES OF OXIDE OF AMMONIUM.	
Ammonia (Amine) $\left\{\begin{matrix}H\\H\\H\end{matrix}\right\}N.$	Aniline (Phenylamine)	$\left\{\begin{matrix}H\\H\\C_{12}H_5\end{matrix}\right\}N.$	Ethylaniline (Ethylophenylamine)	$\left\{\begin{matrix}H\\C_4H_5\\C_{12}H_5\end{matrix}\right\}N.$	Diethylaniline (Diethylophenylamine)	$\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_{12}H_5\end{matrix}\right\}N.$	Oxide of Triethylophenylammonium	$\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_{12}H_5\end{matrix}\right\}NO, HO.$
			Methylaniline (Methylophenylamine)	$\left\{\begin{matrix}H\\C_2H_3\\C_{12}H_5\end{matrix}\right\}N.$	Methylethylaniline (Methylethylophenylamine)	$\left\{\begin{matrix}C_2H_3\\C_4H_5\\C_{12}H_5\end{matrix}\right\}N.$		
			Amylaniline (Amylophenylamine)	$\left\{\begin{matrix}H\\C_{10}H_{11}\\C_{12}H_5\end{matrix}\right\}N.$	Diamylaniline (Diamylophenylamine)	$\left\{\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\\C_{12}H_5\end{matrix}\right\}N.$		
					Ethylamylaniline (Ethylamylophenylamine)	$\left\{\begin{matrix}C_4H_5\\C_{10}H_{11}\\C_{12}H_5\end{matrix}\right\}N.$		
					Methylamylaniline (Methylamylophenylamine)	$\left\{\begin{matrix}C_2H_3\\C_{10}H_{11}\\C_{12}H_5\end{matrix}\right\}N.$	Oxide of Methylethylamylophenylammonium	$\left\{\begin{matrix}C_2H_3\\C_4H_5\\C_{10}H_{11}\\C_{12}H_5\end{matrix}\right\}NO, HO.$
	Chloraniline (Chlorophenylamine)	$\left\{\begin{matrix}H\\H\\C_{12}\begin{pmatrix}H_4\\Cl\end{pmatrix}\end{matrix}\right\}N.$	Ethylochloraniline (Ethylochlorophenylamine)	$\left\{\begin{matrix}H\\C_4H_5\\C_{12}\begin{pmatrix}H_4\\Cl\end{pmatrix}\end{matrix}\right\}N.$	Diethylochloraniline (Diethylochlorophenylamine)	$\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_{12}\begin{pmatrix}H_4\\Cl\end{pmatrix}\end{matrix}\right\}N.$		
	Bromaniline (Bromophenylamine)	$\left\{\begin{matrix}H\\H\\C_{12}\begin{pmatrix}H_4\\Br\end{pmatrix}\end{matrix}\right\}N.$	Ethylobromaniline (Ethylobromophenylamine)	$\left\{\begin{matrix}H\\C_4H_5\\C_{12}\begin{pmatrix}H_4\\Br\end{pmatrix}\end{matrix}\right\}N.$				
	Nitraniline (Nitrophenylamine)	$\left\{\begin{matrix}H\\H\\C_{12}\begin{pmatrix}H_4\\NO_4\end{pmatrix}\end{matrix}\right\}N.$	Ethylonitraniline (Ethylonitrophenylamine)	$\left\{\begin{matrix}H\\C_4H_5\\C_{12}\begin{pmatrix}H_4\\NO_4\end{pmatrix}\end{matrix}\right\}N.$				
	Ethylamine (Ethylammonia)	$\left\{\begin{matrix}H\\H\\C_4H_5\end{matrix}\right\}N.$	Diethylamine (Diethylammonia)	$\left\{\begin{matrix}H\\C_4H_5\\C_4H_5\end{matrix}\right\}N.$	Triethylamine (Triethylammonia)	$\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}N.$	Oxide of Tetrethylammonium	$\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}NO, HO.$
					Diethylamylamine (Diethylamylammonia)	$\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_{10}H_{11}\end{matrix}\right\}N.$	Oxide of Triethylamylammonium	$\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_{10}H_{11}\end{matrix}\right\}NO, HO.$
							Oxide of Triethylomethylammonium	$\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_2H_3\end{matrix}\right\}NO, HO.$
					Methylethylamylamine (Methylethylamylammonia)	$\left\{\begin{matrix}C_2H_3\\C_4H_5\\C_{10}H_{11}\end{matrix}\right\}N.$	Oxide of Diethylomethylamylammonium	$\left\{\begin{matrix}C_2H_3\\C_4H_5\\C_4H_5\\C_{10}H_{11}\end{matrix}\right\}NO, HO.$
	Methylamine (Methylammonia)	$\left\{\begin{matrix}H\\H\\C_2H_3\end{matrix}\right\}N.$	Dimethylamine (Dimethylammonia)	$\left\{\begin{matrix}H\\C_2H_3\\C_2H_3\end{matrix}\right\}N.$	Trimethylamine (Trimethylammonia)	$\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right\}N.$	Oxide of Tetramethylammonium	$\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right\}NO, HO.$
	Amylamine (Amylammonia)	$\left\{\begin{matrix}H\\H\\C_{10}H_{11}\end{matrix}\right\}N.$	Diamylamine (Diamylammonia)	$\left\{\begin{matrix}H\\C_{10}H_{11}\\C_{10}H_{11}\end{matrix}\right\}N.$	Triamylamine (Triamylammonia)	$\left\{\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\\C_{10}H_{11}\end{matrix}\right\}N.$	Oxide of Tetramylammonium	$\left\{\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\\C_{10}H_{11}\\C_{10}H_{11}\end{matrix}\right\}NO, HO.$

The preceding researches show that the action of the bromides and iodides of the alcohol-radicals upon ammonia, gives rise to the formation of not less than four distinct groups of organic bases. Of these, the members of three groups, corresponding to ammonia ($H_3 N$), are volatile, while those of the fourth, corresponding to oxide of ammonium ($H_4 N O$), cannot be volatilized without decomposition. The facility with which the members of this last class arise from those of the preceding ones, and the readiness with which their reconversion is effected, renders the former group as it were the connecting link between the volatile and the non-volatile organic alkaloids. I am inclined to attach some importance to the latter point; for the acquisition of a general method, by means of which we may rise from the volatile to the non-volatile bases, is not unlikely to pave the way to the artificial production of the fixed native alkaloids, whose constitution is still shrouded in darkness. We may here remember that a very considerable number of these *fixed* native alkaloids yield *volatile* organic bases when submitted to the action of heat or of potassa,—that is under precisely those conditions under which the new ammonium-compounds, which I have described in this paper, are converted into conjugate ammonias. Thus quinine, cinchonine, strychnine, and pelosine yield among their products of decomposition leucoline (chinoline), while piperine gives picoline (?), and morphine, caffeine, codeine and narcotine have actually been converted into alcohol-bases, the former yielding methylamine, the latter two propylamine*.

I readily admit that those processes are by no means so simple as the passage of oxide of tetrethylammonium into triethylamine, several processes of transformation being in most of these cases accomplished side by side. A certain analogy, however, cannot possibly be denied, although, on account of the more complicated formulæ of the native bases, it cannot as yet be traced in simple equations. In some instances the connection even now appears almost palpable. If we compare the formulæ of quinine and of leucoline, the volatile base derived from its destruction, we are surprised to find that these substances exhibit the same elementary difference which we observe between oxide of tetramethylammonium and methylamine.

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* M. WERTHEIM, the discoverer of this base, believes that it stands to the unknown propyl-alcohol in the same relation which exists between methylamine, ethylamine and amylamine on the one hand, and methylic, ethylic and amylic alcohol on the other. It deserves, however, to be noticed that the formula $C_6 H_9 N$ for this compound, as determined by experiment, expresses not only propylamine but also trimethylamine and even methylethylamine,

$$C_6 H_9 N = \left.\begin{cases} H \\ H \\ C_6 H_7 \end{cases}\right\} N = \left.\begin{cases} C_2 H_3 \\ C_2 H_3 \\ C_2 H_3 \end{cases}\right\} N = \left.\begin{cases} H \\ C_2 H_3 \\ C_4 H_5 \end{cases}\right\} N.$$

In the absence of decisive reactions, it remains doubtful which of these formulæ represents the base obtained by the action of soda-lime on narcotine; I may state here that propylamine, as prepared by WERTHEIM'S process, and the liquid containing trimethylamine, for as yet I have not obtained this substance perfectly pure, exhibit the same remarkable fishy odour. It deserves moreover to be remarked that Dr. ANDERSON found that propylamine occurs, associated with methylamine, among the basic products of the decomposition of codeine.

$$\underbrace{C_{20}\,H_{12}\,N\,O_2}_{\text{Quinine.}}-C_2\,H_4\,O_2=\underbrace{C_{18}\,H_8\,N}_{\text{Leucoline.}}$$

$$\underbrace{C_8\,H_{13}\,N\,O_2}_{\substack{\text{Hydrated oxide}\\\text{of Tetramethyl-}\\\text{ammonium.}}}-C_2\,H_4\,O_2=\underbrace{C_6\,H_9\,N}_{\substack{\text{Trimethyl-}\\\text{amine.}}}$$

Accordingly, we might expect that the action of iodide of methyl upon leucoline, and the subsequent decomposition of the iodide produced by means of protoxide of silver, would enable us to reconvert leucoline in this manner into quinine. This metamorphosis would be the more interesting, as it would open a source for the artificial production of quinine; leucoline being, as is well known, contained in considerable quantity in the basic portion of coal-tar naphtha. It may be stated here that leucoline, which is a substance remarkable for its antipathy to the crystalline form, when submitted to the action of iodide of methyl, solidifies at once into a splendid mass of crystals of a new iodide*, which in fact resembles in its outward appearance hydriodate of quinine, and which is still under examination. I am, however, by no means sanguine as to the result of this experiment, for the above play of formulæ rests as yet on a very precarious foundation; neither the formula of quinine nor that of leucoline being established beyond a doubt. Nevertheless, I intend to complete this investigation, because even if no other result is obtained, yet by means of this process new data for ultimately fixing the formulæ of quinine and leucoline may be found.

In conclusion, it may not be out of place to consider how far the preceding researches affect the received views regarding the constitution of the ammonia-salts. Without reproducing all the arguments brought forward by the supporters of the various theories, we may remember that, irrespectively of the impossibility of isolating ammonium itself, the instability of its oxide has been adduced as one of the most important objections against the assumption of the ammonium-theory as originally suggested by AMPÈRE, and subsequently elaborated by BERZELIUS. It deserves to be noticed that BERZELIUS expressly states that he considers the solution of ammonia-gas in water as a solution of the hydrated oxide of ammonium.

This idea, which is but a logical conclusion from the generalization of the facts, is discountenanced to a certain extent by the chemical and physical character of this solution. Everybody knows that, even at the common temperature, this liquid splits again into water and ammonia, while it still exhibits the character of the latter in so marked a manner, as almost to preclude the idea that it had undergone as essential a change as the transformation into oxide of ammonium necessarily must be. Under these circumstances, some interest is attached to the discovery of a series of compound bases, corresponding in their composition to hydrated oxide of ammonium,

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* A similar result is obtained by the action of iodide of ethyl upon conine and nicotine.

from which they differ only by containing methyl, ethyl and amyl in the place of hydrogen, and exhibiting a deportment which agrees much better with the anticipated character of such compounds as suggested by analogy. Here we find a very marked difference between the properties of the compound ammonia, and those of the ammonium-oxide belonging to it; in the latter, we observe no longer any feature which could possibly betray the presence of the former; all their habits, volatility, odour, taste, &c. are totally changed; there is a difference between the two groups which is not inferior to that between ammonia and potassa. The solutions of the new oxides may be boiled for hours without the slightest quantity of the corresponding ammonia being disengaged; several of these oxides, containing more or less water of constitution or crystallization, may actually be obtained in the dry state. It is evident that the arguments mentioned above, as adduced in refutation of the ammonium-theory, cannot well be raised against the compound ammoniums. But who could deny the parallelism of these substances with the Berzelian type,—with the oxide of ammonium?

Again, many have found it difficult to conceive, that in the combination of ammonia with hydrochloric or hydrobromic acid, the hydrogen of the latter should leave the chlorine and bromine, for which it is known to possess so powerful an affinity, in order to unite with ammonia converting it into ammonium. And they were the less inclined to admit of such a disposition of the elements, as every day's experience showed that the alleged chloride or bromide of ammonium was incapable of exchanging oxygen for chlorine or bromine, without losing the additional equivalent of hydrogen again in the form of water. In other terms, the decomposition of sal-ammoniac, by lime, into chloride of calcium, ammonia-gas and water, induced them to consider this salt as a compound of ammonia and hydrochloric acid; for in the conception of the ammonium-theory we should have to assume in this decomposition *two* consecutive changes, the transformation of the chloride into oxide, and the subsequent splitting of the latter into ammoniacal gas and water. I readily admit that the latter view is less simple, but I am inclined to think that this slight inconvenience is altogether overruled by the general advantages of the ammonium-theory, especially for the purposes of instruction, by the facility with which it accounts for all phenomena of transposition and substitution, and by the simple explanation it gives of the isomorphism of the potassium- and ammonium-compounds, which will always be the firmest foundation of this theory. On the other hand, we have to inquire which of the two views comes nearest to truth, and here a comparative consideration of the deportment exhibited by the compound ammoniums may be of some interest. In many respects their properties are more clearly pronounced; and their behaviour is explicit and unequivocal in those very points in which the typical ammonium leaves room for speculation. In the combination of triethylamine with bromide or iodide of ethyl, it is no longer a matter of doubt whether the ethyl leaves the iodine in order to unite more intimately with the triethylamine, for we see that the new iodide thus produced is capable of exchanging its iodine for oxygen without the newly-formed oxide suffering immediate decomposition, as is the case with oxide of ammonium. On the contrary, we find this new oxide endowed with remarkable stability; although under the influence of heat it is liable to the same change which befalls the oxide of ammonium, its corresponding ammonia being reproduced. Here then, in the decomposition of iodide of triethylammonium by metallic oxides, we are obliged by irresistible evidence to acknowledge those very two stages, the assumption of which in the analogous change of iodide of ammonium appeared to us deficient in simplicity and probability.

The conception of ammonium does not in any way imply the notion that the different hydrogen-atoms united with nitrogen in the molecule of the compound metal, retain their position in the molecular system with equal persistency. We are forced by unequivocal facts to admit that the fourth atom of hydrogen is in a peculiar state of mobility, and it is on the facility with which this fourth atom is dislodged from its position that one of the foundations of the ammonia-theory rests. In the compound ammoniums the mobility of the fourth atom of hydrogen, or the hydrocarbon replacing it, still prevails, although less so than in the type itself. The decomposition of the ammonium-bases under the influence of heat is particularly instructive in this respect; oxide of tetrethylammonium loses the fourth equivalent of ethyl in the form of olefiant gas and water; and this deportment might be graphically indicated by writing the formula of this compound in accordance with the ammonia-theory, namely, thus—

$$\left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\}N,\ C_4\,H_5\,O.$$

The iodide accordingly would be represented by the formula

$$\left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\}N,\ C_4\,H_5\,I,$$

an expression which is moreover in perfect harmony with the mode in which this compound is produced, namely, by the direct union of iodide of ethyl with triethylamine.

But now we combine the triethylamine with iodide of amyl, whereby the iodide

$$\left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\}N,\ C_{10}\,H_{11}\,I$$

is formed, which, as we have seen in the preceding pages, may be converted without difficulty into the corresponding oxide; this oxide however cannot possibly be considered as

$$\left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\}N,\ C_{10}\,H_{11}\,O,$$

for the disengagement of olefiant gas under the influence of heat proves to us that it is an ethyl-atom which in this compound occupies the supplemental position, if I may so call it, as represented in the formula

$$\left.\begin{matrix} C_4\ H_5 \\ C_4\ H_5 \\ C_{10}\ H_{11} \end{matrix}\right\} N, C_4\ H_5\ O,$$

and that the iodide, which is not likely to differ in its constitution from the oxide, has likewise to be represented by the formula

$$\left.\begin{matrix} C_4\ H_5 \\ C_4\ H_5 \\ C_{10}\ H_{11} \end{matrix}\right\} N, C_4\ H_5\ I.$$

The preceding considerations clearly show, that, whatever the actual disposition of the molecules in ammonium or its congeners may be, the atoms re-arrange themselves whenever the fourth equivalent of hydrogen, or of its substitute, joins the compound.

This re-arrangement, so evident in the ammonium-bases, containing various hydrocarbons, may be traced moreover in the lower ethyl-bases in a very obvious manner. For as long as there is any basic hydrogen present in the ammonia-skeleton, this hydrogen assumes what I have previously called the supplemental position, whenever the ammonia passes into the state of ammonium by the accession of a radical. Bromide of ethylammonium formed by the combination of ammonia with bromide of ethyl, when decomposed by a metallic oxide, yields ethylammonia, water and a metallic bromide, the oxide of ethylammonium formed in the first instance being decomposed like oxide of ammonium itself. It is this very transposition which we are in the habit of representing by the equation

$$H_3\ N + C_4\ H_5\ Br = C_4\ H_5, H_2\ N, H\ Br.$$

In the preceding pages I have stated some of the reasons which induced me to adopt the idea of an ammonium for the new class of compounds which I have had the honour to place before the Royal Society in the present memoir. I need scarcely mention, that such a step involves as a matter of necessity the assumption of a similar view for all the lower bases which form part of this investigation. It would be inconsistent to speak any longer of hydrochlorate of ethylamine, of hydrobromate of diethylamine, &c.; these salts have henceforward to be called chloride of ethylammonium, bromide of diethylammonium, &c., these compounds being nothing but intermediate substitution-terms between the type and the last derivative. On considering the various chlorides from this point of view, we arrive at the following series:—

Chloride of Ammonium	H_4	N Cl.
Chloride of Ethylammonium	$\left\{\begin{matrix} H_3 \\ C_4\ H_5 \end{matrix}\right\}$	N Cl.

Chloride of Diethylammonium	$\left.\begin{matrix} H_2 \\ (C_4\,H_5)_2 \end{matrix}\right\} N\,Cl.$
Chloride of Triethylammonium	$\left.\begin{matrix} H \\ (C_4\,H_5)_3 \end{matrix}\right\} N\,Cl.$
Chloride of Tetrethylammonium	$(C_4\,H_5)_4\ N\,Cl.$

The idea of an ammonium once adopted, we have to follow it out in as general a form as possible, and hence I perfectly agree with those chemists who consider the salts of Reiset's second base as compounds of the Platammonium (Platosammonium)

$$\left.\begin{matrix} H_3 \\ Pt \end{matrix}\right\} N\,X,$$

the ammoniosulphate of silver as sulphate of argentammonium,

$$\left.\begin{matrix} H_3 \\ Ag \end{matrix}\right\} N\,SO_4,$$

and the ammoniochloride of copper as chloride of cuprammonium,

$$\left.\begin{matrix} H_3 \\ Cu \end{matrix}\right\} N\,Cl.$$

But I would go farther and advocate an analogous constitution for a great number of mercury-compounds, which are now usually considered in a different way. Since the careful experiments of Sir Robert Kane have pointed out the true composition of the white precipitate, chemists are in the habit of viewing this substance as a compound of chloride and amide of mercury,

$$Hg\,H_2\,N,\ Hg\,Cl\,;$$

it may be viewed with equal justice as chloride of dimercurammonium,

$$\left.\begin{matrix} H_2 \\ Hg_2 \end{matrix}\right\} N\,Cl,$$

and would correspond in this form to the chloride of diethylammonium; dimercurammonium, intimately combined with protoxide of mercury, may be assumed in all the various salts of M. Millon's mercury-base. It would be interesting experimentally to follow out in detail the analogy of the mercury-compounds with the series of ethyl bases. Even now the materials at our disposal appear to point to the existence of the other terms. In Mitscherlich's garnet-octohedrons we might perceive a chloride of mercurammonium,

$$\left.\begin{matrix} H_3 \\ Hg \end{matrix}\right\} N\,Cl,$$

while Plantamour's nitride of mercury presents itself as trimercuramine, $Hg_3\,N$; and the red compound obtained by Mitscherlich on heating the white precipitate, might be viewed as a combination of chloride of mercury with chloride of tetramercurammonium,

$$Hg_4\,N\,Cl,\ Hg\,Cl.$$

The ammonium type may be traced even in a class of compounds which has hitherto been regarded in a perfectly different point of view. I refer to the substances produced by the combination of metallic salts with more than one equivalent of ammonia. Protochloride of platinum unites with two equivalents of ammonia, forming the chloride of REISET's first base; in the same manner, sulphate of copper, nitrate of silver, absorb both two equivalents of ammonia, the latter salt even three equivalents. These substances, although containing 2 equivs. of nitrogen, may still be viewed as ammonium-compounds, if we apply to them an interesting observation made by Professor GRAHAM, namely, that ammonia, whenever it joins a compound containing hydrogen, may be regarded as ammonium replacing 1 equiv. of hydrogen. When viewed in this light, the substances above quoted would assume the following formulæ:—

REISET's first chloride	$\left\{\begin{matrix} H_2 \\ Pt \\ (H_4N) \end{matrix}\right\} N\,Cl.$	Chloride of ammonio-platammonium.
Diammoniacal sulphate of copper . .	$\left\{\begin{matrix} H_2 \\ Cu \\ (H_4N)_2 \end{matrix}\right\} N\,SO_4$	Sulphanide of ammonio-cuprammonium.
Diammoniacal nitrate of silver . . .	$\left\{\begin{matrix} H_2 \\ Ag \\ (H_4N) \end{matrix}\right\} N\,NO_6$	Nitranide of ammonio-argentammonium.
Triammoniacal nitrate of silver . .	$\left\{\begin{matrix} H \\ Ag \\ (H_4N)_2 \end{matrix}\right\} N\,NO_6$	Nitranide of diammonio-argentammonium.

I readily admit that here speculation appears rather in advance of experiment. Nevertheless it deserves to be noticed, that among the substances produced by the action of ammonia upon metallic salts, of which so great a variety has been investigated by HENRY ROSE, there is, as far as I know, not a single one containing more than 4 equivs. of ammonia, which still admits of their being included in the idea to which I have alluded.