

ART. X.—*On the Reactions of Ethylamine and Diethylamine*; by
M. CAREY LEA, Philadelphia.

THE materials for the following examinations were prepared by the action of nitrate of ethyl upon ammonia in sealed tubes, in the manner which I have described in a previous number of this Journal. The bases were separated from each other by means of picric acid.

ETHYLAMINE.

In order to ascertain the purity of the ethylamine used, and further to test the exactness of the separation by means of picric acid, another platinum determination was made with great care. It gave the following results.

1.3911 grms. substance gave, platinum, .5457	
This corresponds to, per cent	39.23
Theory requires	39.29

A result which taken in connection with analyses already published seems conclusive.

Reactions of Ethylamine.

The reactions of ethylamine with metallic solutions have been more studied than those of the other ethyl bases; the following however do not seem to have been previously described.

Gold, perchlorid,	reddish precipitate, easily soluble in excess of precipitant.
Ruthenium, sesquichlorid,	no precipitate, either immediate or by standing 48 hours. The action of ethylamine differs from that of ammonia not only in producing no precipitate, but also in this, that the liquid after treatment by ammonia, acquires a lilac or lilac brown color, whereas after treatment with ethylamine it assumes a greenish brown or olive shade.
Palladium, protochlorid,	an immediate highly crystalline precipitate which redissolves in part, in excess of the precipitant, forming a colorless solution.
Uranium, nitrate,	yellowish precip. insoluble in excess of precipitant.
Cerium, protochlorid,	perfectly pure protochlorid of cerium prepared according to Holtzman's modification of Hermann's method, gave a dirty precipitate insoluble in excess of the precipitant.

Cerium, nitrate of protoperoxyd,	light brown precipitate, insoluble in excess of the precipitant.
Glucinum, sulphate of glucina,	white, insoluble in excess.
Zirconium, chlorid of zirconia,	white, insoluble in excess.
Molybdenum, protochlorid,	reddish brown, insoluble in excess.
“ bichlorid,	reddish brown, insoluble in excess.

While the analogies which unite ethylamine to ammonia are extremely well marked, the differences in their reactions are also very well defined. Like ammonia, ethylamine redissolves its precipitates from salts of copper, of zinc and of silver, but it also redissolves precipitates from solutions of gold, ruthenium and aluminum which ammonia does not. It is, on the other hand, incapable of redissolving the precipitates from solutions of cobalt, nickel and cadmium. Towards protosalts and salts of protoperoxyd of cerium, glucinum, zirconium, protochlorid and bichlorid of molybdenum, peroxyd of uranium, bismuth and antimony, its behavior is similar to that of ammonia.

It was a matter of interest to observe whether the substance produced by the reaction of ethylamine on solution of terchlorid of gold would exhibit any analogy with that resulting from treatment by ammonia, viz., fulminating gold. The precipitate caused by ethylamine readily dissolved as above stated in excess of the precipitant, this at a gentle heat dried up to a yellow mass, which when heated, melted, turned red, emitted dense white fumes and left a brown spot. No sudden decomposition took place.

The following is a well marked distinctive reaction between ammonia and ethylamine. If bichlorid of tin be treated with ammonia, a precipitate is obtained which scarcely shows any disposition to redissolve in even a large excess of the precipitant. But with ethylamine the precipitate redissolves easily. In the case of ammonia the presence of salammoniac renders the precipitate from a stannic solution, according to Rose, altogether insoluble, whereas in the case of ethylamine, a considerable proportion of chlorhydrate of ethylamine may be added without diminishing the solubility of the precipitate.

Ethylamine, like ammonia, has the property of reddening an alcoholic solution of dinitronaphthaline.

DIETHYLAMINE.

The action of nitrate of ethyl upon ammonia is particularly well suited for obtaining diethylamine on account of the relatively large proportion obtained at once. Further experience, since I published that process, has shown me that the product is even larger than I supposed. The quantity of diethylamine produced is fully as great as that of ethylamine.

Diethylamine obtained by that process was purified by solution of its picrate in ether. A specimen of platinum salt analyzed gave, Pt 35.45 per cent, theory requires 35.45.

Reactions of Diethylamine.

The reactions of diethylamine with metallic solutions have not hitherto been examined. The following were observed :

Cerium, protochlorid,	dirty white precipitate, insoluble in excess of the precipitant.
“ nitrate of protoperoxyd,	light brown precipitate, insoluble in excess of the precipitant.
Zirconium, chlorid of zirconia,	white precip., insoluble in excess.
Gold, terchlorid,	brownish red precipitate, easily soluble in excess of precipitant.
Ruthenium, sesquichlorid,	no precipitate. The color of the solution presents the same characteristics as in the case of ethylamine.
Palladium, protochlorid,	no precipitate from a somewhat dilute solution, but the deep red liquid is instantly decolorized.
Platinum, protochlorid,	no precipitate from a moderately concentrated solution. Hydrochlorate of diethylamine dissolves in protochlorid of platinum to a clear solution, so that if a diethylamine base analogous to Magnus' Green Base exists, it must be very soluble.
“ bichlorid,	No precipitate unless both solutions are very concentrated.
Molybdenum, protochlorid,	red brown, insoluble in excess of precipitant.
“ bichlorid,	red brown, insoluble in excess of precipitant.
Copper, sulphate,	Blue precipitate, very sparingly soluble in excess of the precipitant.
Silver, nitrate,	Brown, easily soluble in excess of the precipitant.
Zinc, sulphate,	White, insoluble in excess of the precipitant.
Cadmium, sulphate,	Same reaction.
Nickel, sulphate,	Pale green, insol. in excess of the precipitant.
Cobalt, protochlorid,	Blue, insoluble in excess of the precipitant.
Aluminium, alum,	White, soluble in excess.
Chromium, chrome alum,	Bluish grey, insoluble in excess.
Lead, acetate,	A small quantity produces no precipitate, a large quantity a white precipitate insoluble in excess.

Lead, nitrate,	An immediate precipitate insoluble in excess.
Mercury, protochlorid,	White, insoluble in excess.
Tin, protochlorid,	Same reaction.
" bichlorid,	White, soluble in excess.
Glucina, sulphate,	White, insoluble in excess.
Manganese, protosulphate,	Pale brown, insoluble in excess.
Magnesia, sulphate,	White, insoluble in excess.
Iron, sesquioxyd, ammonia alum,	Brick red, insoluble in excess.
Antimony, chlorid,	Brick red, insoluble in excess.
" tartar emetic,	At the first moment no precipitate, then a cloudiness and finally a heavy precipitate.
Bismuth, nitrate,	White, insoluble in excess of precipitant.
Uranium, nitrate,	Yellow, insoluble in excess.

Some of these reactions are highly interesting. It has been already shown under the head of ethylamine that in addition to the differences already known to exist between its reactions, and those of ammonia, its behavior towards solutions of gold and ruthenium is highly characteristic. We now see that diethylamine, not only resembles ethylamine in these properties, but shares with it its remarkable capability of redissolving precipitates of alumina. Ethylamine and diethylamine moreover resemble each other and differ from ammonia in their reactions with cadmium, nickel, cobalt, and bichlorid of tin. They both act like ammonia towards solutions of glucina, zirconia, protoxyd and protoperoxyd of cerium, peroxyd of uranium, protoxyd and deutoxyd of molybdenum and many other metals. The only oxyds which all three are capable of redissolving are those of silver and copper. Silver dissolves abundantly in all three; copper much more sparingly in ethylamine than in ammonia, while in diethylamine this property almost disappears, a faint blue color indicates the solution of a mere trace. Unless the aqueous solution of diethylamine is strong, not even a trace of copper is taken up by it.

The action of diethylamine on terchlorid of gold was further examined to ascertain if the resulting compound had any properties corresponding with those of fulminating gold. The clear yellow solution obtained from solution of terchlorid of gold by treatment with diethylamine, dried up to a somewhat crystalline deliquescent mass which when heated, decomposed without the slightest explosion.

It is evident from the above that the relations which exist between ethylamine and diethylamine are much closer than those between ethylamine and ammonia. In fact, in all the above

reactions, they differ in their behavior to palladium and zinc salts only. Protochlorid of palladium is precipitated by ethylamine and not by diethylamine: zinc precipitates are redissolved by ammonia and ethylamine, but not by diethylamine. In view of this remarkable analogy, all clearly distinctive reactions acquire an interest, and the following which I have observed, is very well marked.

If protochlorid of mercury be precipitated with a very large excess of ammonia, the precipitate readily dissolves on the addition of a little acetic acid, the liquid remaining very strongly alkaline. Ethylamine behaves in the same way, but the precipitate caused by diethylamine does not redissolve under the same circumstances. Acetic acid may be added, in fact, until the liquid acquires a decidedly acid reaction without causing a solution.

Diethylamine shares the property of ethylamine and ammonia of reddening alcoholic solution of dinitronaphthaline.

The analysis of the platinum salts of the ethyl bases requires great circumspection in the application of heat, as they decompose at a far lower temperature than the chloroplatinate of ammonium. The diethylamine salt blackens at a temperature at which the upper part of the porcelain crucible remains cool enough for it to be lifted by the fingers.

Action of Iodine on Ethylamine and Diethylamine.

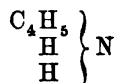
When aqueous diethylamine is poured over iodine in powder, it becomes milky and there collects at the bottom of the vessel a black substance in thick oily drops. These when heated in a platinum spoon give off first violet vapors of iodine, then thick white clouds and finally leave a carbonaceous residue. If this black substance be boiled a few minutes with a large excess of caustic soda, it emits an odor not unlike that produced by the combustion of phosphuretted hydrogen, diminishes in volume, and becomes thicker, so much so as to solidify on cooling. It then when heated, gives off no violet vapors, but only thick white clouds, swells up and leaves an enormously bulky residue of carbon. Ethylamine exhibits a nearly similar reaction. In neither case has the resulting substance the slightest explosive properties, as might be expected from the reaction of ammonia under similar circumstances.

The compound formed in the case of ethylamine has been examined by Wurtz and found to have the formula $C_4H_5I_2N$. By this result, the researches of Gladstone into the constitution of the so-called iodid of nitrogen, reliable in themselves, are supported. The latter chemist found for the explosive substance formed by the action of iodine on ammonia, the constitution

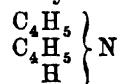
HI₂N. The action of iodine is consequently in both cases exactly analogous, two atoms of hydrogen are replaced by two of iodine.

Gilm therefore seems to be in error in asserting that no substitution-product from ethylamine analogous to so-called iodid of nitrogen (biniodamine) can be obtained.*

This iodine substitution-product from ethylamine and diethylamine, cannot, unfortunately, be obtained in a state of purity sufficient for reliable analysis, otherwise the examination of the diethylamine product would be interesting. For in ethylamine, there are two atoms of the hydrogen of the ammonia type remaining,



and there is no difficulty in supposing them to undergo a substitution by iodine. But in diethylamine there remains but one—



Nevertheless diethylamine under the action of iodine affords a substance exactly resembling that produced from ethylamine. To effect the analysis of a substance having an equivalent in the neighborhood of 300 so as to speak with confidence of the presence or absence of a single equivalent of hydrogen, it would need to be obtainable in a state of perfect purity. This however has not so far been possible.

Isomorphism of Ammonias.

A few experiments made in this direction gave the following results:

Ethylamine alum.—Octahedra of sulphate of ethylamine and alumina were obtained.

Tartrate of diethylamine and soda.—In order to determine whether diethylamine was capable of replacing ammonia in the magnificent crystalline forms of the double tartrates, this salt was formed, but whether crystallized from water or from weak alcohol, only needles could be obtained.

Sulphate of diethylamine and zinc.—In order to determine if diethylamine was capable of replacing ammonia in Mitscherlich's group of double sulphates, RO, SO₃ + MO SO₃ + 6HO; with the characteristic crystal-form, the double sulphate of zinc and diethylamine was formed. A deliquescent solution was obtained which in vacuo over sulphuric acid afforded a crystalline mass, from which no conclusion as to isomorphism could be drawn.

* Jahresbericht der Chemie, 1858, p. 340.

Reaction of Ethyl bases with Dr. Knop's new hydrofluosilicic acid,
 $2\text{HF} + \text{Si}_2\text{F}_6$.

In the *Chemisches Centralblatt* for August 21, 1861, Dr. Knop publishes an account of a very interesting combination which he has obtained by the action of peroxyd of copper and metallic copper on silicofluoric alcohol, and subsequent removal of the copper by sulphydric acid. He thereby obtains an acid $2\text{HF} + \text{Si}_2\text{F}_6$, which exhibits different properties from ordinary hydrofluosilicic acid, $3\text{HF} + 2\text{SiF}_4$, and which he thinks may prove a valuable reagent. It precipitates according to its discoverer, potash and soda completely from their solutions, while with sulphate, chlorhydrate, phosphate and oxalate of ammonia, it gives no precipitate. It appeared to me to be of interest to examine the behavior of this reagent with some of the ethyl bases. I prepared some by Dr. Knop's process; with it obtained immediate precipitates with carbonated and caustic alkalies, hydrochlorate of ammonia afforded no precipitate—results in accordance with his.

Caustic ammonia, afforded the following results: When the acid was in excess, no precipitate was formed, but where the ammonia was in excess, a very abundant caseous precipitate was obtained, which showed little disposition to dissolve in an excess of precipitant, even by standing and with the application of heat. Chlorhydric acid dissolved it somewhat better but still left a considerable portion undissolved.

Ethylamine, when the acid was in excess did not give a precipitate, but when the ethylamine was in excess, the mixture by standing a while, coagulated to a jelly so stiff that the test glass could be inverted, and this with scarcely any loss of transparency. In an excess of the new acid, this jelly redissolved with the exception of a few flakes.

Diethylamine exhibited almost the same reaction as ethylamine, except that the jelly was less transparent, and the solution in excess of the reagent less complete. The acid gives no precipitate with either the chlorhydrate of ethylamine or that of diethylamine. In this respect therefore these ethyl bases resemble ammonia.