ART. XI.—*On Nitrate of Ethyl*; by M. CAREY LEA, Philadelphia.

Action of Reducing Agents. Acetic Acid and Iron.—Acetic acid mixed with nitrate of ethyl was made to act on iron filings. On the application of a gentle heat a violent action set in, and most of the nitrate of ethyl was driven off undecomposed. The tube of a Liebig's condenser was therefore attached so that the distillate might constantly flow back, and heat was applied until the whole of the nitrate of ethyl was acted on. A considerable quantity of deutoxyd of nitrogen was evolved and some nitrite of ethyl. Finally caustic soda was added and the gaseous products were conducted into water. A very considerable quantity of ammonia was thus obtained but no ethyl bases could be distinguished.

From a considerable number of experiments I am disposed to think that the ethyl bases are produced in but a limited number of reactions, and that in many cases when they would seem to be possible products, ordinary ammonia is alone formed. For example, it appeared not improbable, that by acting on dry ethylosulphate of ammonia[*] $C_4H_5(NH_4)O_2 2SO_3$; with caustic lime, ethylamine would be formed simultaneously with hydrated sulphate of lime $CaO\,SO_3+2HO$, according to the equation

$$C_4H_5(NH_4)O_2\,2SO_3+CaO=(CaO\,SO_3+2HO)+\left.\begin{matrix}C_4H_5\\H_2\end{matrix}\right\}N,SO_3\dagger$$

but experiment showed that this was not the case, ammonia alone was disengaged.

Sodium.—The evolution of both deutoxyd of nitrogen and nitrite of ethyl indicate that by the reaction of iron and acetic acid the nitric acid in combination with the ethyl may be deprived not only of one, but even of three atoms of oxygen. In view of this easy and far reaching reduction, it is curious to find that nitrate of ethyl is scarcely acted upon by metallic sodium which even retains its lustre for some time when immersed in the ether. If a few drops of alcohol be added to the nitrate of ethyl, the sodium attacks the alcohol and when this is exhausted the sodium remains in the liquid for hours, as brilliant as a piece of silver.

Production of a Saccharoid Substance?—When nitrate of ethyl is made to act upon ammmonia in sealed tubes, secondary products appear to be also formed. When the hydrochlorates of ethyl bases obtained in this way are evaporated down previously to final distillation with caustic alkali, they are brownish and have a strong odor of burnt sugar. The residue after distillation was examined for sugar or allied substance, but it could not then be detected and the odor had disappeared.

Boutlerow has lately described[‡] a remarkable reaction which indicates the probable production of a sugar for the first time by complete synthesis. It was obtained by the action of alkalies on dioxymethylene $\text{Ꞓ}_2H_4\Theta_2$. It seems possible that dioxyethylene might, in the reaction of nitrate of ethyl on ammonia,

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[*] By exposure over sulphuric acid in vacuo for several weeks, crystals of ethylosulphate of ammonia near an inch in length and diameter were obtained.

[†] Ethylamine is capable of forming an anhydrous carbonate and probably also an anhydrous sulphate.

[‡] Bulletin de la Soc. Ch. de Paris, No. 5, Seánce du 26 Juillet, 1861.

be found in small quantities and lead, when the crude contents of the pressure tubes are first distilled with caustic alkali, to the formation of a substance analogous to Boutlerow's methylenitane in the ethyl series.

Further remarks on the preparation of the Ethyl bases by means of Nitrate of Ethyl, and their separation.

Frequent repetition of the process which I have previously described* confirms me in my opinion of its advantages. Nitrate of ethyl is obtained easily and abundantly. From 480 grammes of alcohol of 40° Baumé, I have obtained 231 of nitrate of ethyl, and even a still larger proportion. It is essential in operating upon quantities of half a litre or over, of the mixture of alcohol and nitric acid to first raise the alcohol to a boiling heat and dissolve the urea in it, and then add the nitric acid, otherwise it may attack the alcohol while the urea remains undissolved at the bottom of the vessel, and thus cause the whole process to fail. I have prepared six or seven pounds of nitrate of ethyl in this way with very little trouble.

In acting upon the nitrate of ethyl with ammonia, it is necessary that the pressure tubes should be extremely strong and should never be more than one-half full. Saline baths are not to be used.

Triethylamine appears to be only an occasional product of this reaction.

In employing the process which I have recommended for removing the ammonia, viz: converting the mixed bases into sulphates and exhausting with absolute alcohol, it does not answer well to add sulphuric acid to the crude products obtained from the pressure tubes, because it is impossible to know the exact quantity of sulphuric acid required to expel the nitric acid. If too little be employed, some nitrate of ammonia might remain and dissolve in the alcohol. If too much, bisulphate of ammonia may be formed, and this likewise would dissolve to some extent in the alcohol and contaminate the product. It is therefore necessary to distil the crude products with caustic alkali, neutralize exactly with SO_3 and then evaporate to dryness and exhaust with alcohol as described in the paper here referred to.

In employing picric acid to separate the ethyl bases, each picrate, after having been purified by recrystallizations, is to be treated with chlorhydric acid. The greater part of the picric acid separates, and a further portion by evaporating the liquid. Some however remains, and it is important to get rid of it, because picric acid when distilled with aqueous caustic alkali evolves ammonia, which would thus contaminate the ethyl base.

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* This Journal, July, 1861.

This is effected as follows. After the chlorhydrate of the ethyl base has been evaporated as far as possible without crystallization, a very little carbonate of potash is to be added and the solution stirred at intervals. Almost every trace of picric acid is thus precipitated.

In the final distillation of the chlorhydrate with caustic alkali, if there remains any trace of picric acid, an infinitesimal quantity is apt to be carried over, imparting a yellow tinge to the distillate. This may be prevented by adding before distillation a very small quantity of animal charcoal.