ART. XXIII.—*On the Production of the Methyl Bases, and on the Preparation of Nitrate of Methyl;* by M. CAREY LEA, Philadelphia.

(1.) *On the Production of the Methyl Bases.*

HAVING found in the nitrate of ethyl so convenient a source for the production of the ethyl bases, I was naturally led to endeavor to employ it for the preparation of the corresponding substances in the methyl series, and the result proved eminently satisfactory.

When nitrate of methyl was placed in a sealed tube and immersed in water at 120° F. for an hour or two, a crystallization already took place. In a subsequent experiment it was found that complete decomposition was effected in about three hours at a temperature of 180° to 190° F. But with methylic nitrate we may dispense with sealed tubes altogether, in which respect the methylic bases are more easily obtained than the ethylic.

Bottles provided with well ground stoppers are filled one-third full with a mixture of nitrate of methyl and of the strongest liquid ammonia, in the proportion of 14 parts by volume of nitrate of methyl to 15 of liquid ammonia. The liquid ammonia which I used was a thoroughly saturated solution of the gas. In from five to seven days decomposition is complete and the nitrate of methyl has disappeared. This time may be somewhat reduced by frequent agitation, and by placing the bottles on the second day at a temperature of 90° F., and on the third at 100°. In this way three days complete the process. It is not even necessary to secure the stoppers, if the operation is performed at ordinary temperatures.

The solution then contains ammonia, methylamine, and at least one more substituted ammonia. The separation of the methyl bases is a matter of extraordinary difficulty. I am now engaged in studying it and hope to publish my results at a future time.

(2.) *On the Production of Nitrate of Methyl.*

For the production of nitrate of methyl but one process appears to have been proposed, and that is to be found in all our text-books, English, German and French. Two parts of powdered nitre are to be distilled in a capacious flask with a recently prepared mixture of 5 parts wood spirit and 10 oil of vitriol. Judging from the reactions of ethylic alcohol, it did not appear to me probable that such a proceeding could succeed. It was tried, however, and with the following results.

The substances were placed in a flask capable of containing twenty times their united volume, which was connected with a

Liebig's condenser by a wide delivery tube. For a few minutes no action was perceptible, but it soon set in, with rapidly increasing violence. Torrents of gaseous products with deep red fumes of oxyds of nitrogen, were evolved, and presently the apparatus blew up with a loud explosion, and had not due precautions been taken with a view to a possible unpleasant conclusion, personal inconvenience might have resulted, for the 3-litre flask was shattered into very small pieces, which were thrown to a considerable distance. The quantities operated upon were small, 50 grammes of methylic alcohol and proportionate quantities of the other substances. No heat was applied.

It is scarcely probable that the gases were evolved in such quantities as to have caused the explosion. It seems more likely that the heat generated by the reaction was sufficient to raise the temperature of the interior of the flask to 150° C., at or below which point, according to Dumas, the vapor of methylic nitrate explodes.

I have had no difficulty, however, in preparing this ether by a different process. By dissolving a considerable quantity of urea or nitrate of urea in methylic alcohol, it supports the action of nitric acid with the utmost facility. The following are the proportions which I have employed.

Into a retort of the capacity of a litre, 200 c. c. of purified wood spirit are placed and about 40 grammes of nitrate of urea are added and heat applied. When solution has nearly taken place, 150 c. c. of nitric acid free from the lower oxyds of nitrogen,* sp. gr. 1·31, are added, and the mixture is distilled to one-third. 170 c. c. of wood spirit and 130 of nitric acid are then added and distilled to the same point. Finally 150 c. c. wood spirit and 110 nitric acid with 10 grammes of nitrate of urea are added, and distilled to the same point as before. It is useless to carry the distillation further than the point here specified, not that it is accompanied by any inconvenience, but because nitrate of methyl ceases to be evolved. The temperature rises very high at the close of the distillation.

The operation may be carried on rapidly. We are recommended in the text-books to carry off the vapors very carefully in preparing nitrate of methyl, on account of the production of cyanhydric acid as a by-product. In chemical laboratories there is doubtless generally rather too little precaution taken than too much against noxious vapors, but in the present case, I have carefully examined the distillate, both in the old process, which failed, and in that which I here propose, and I could find no

* Freedom from the lower oxyds is an essential condition of success. That nitric acid is colorless is not in itself a sufficient indication of purity in this respect. An acid which causes the least darkening to a solution of ferrous sulphate is wholly unfit for use in the preparation of either methylic or ethylic nitrate.

trace of cyanhydric acid either by the iron or the silver tests, or by conversion into sulphocyanid. Both the ether itself and the watery part of the distillate were tested. As however it is impossible without special analysis to know what impurities may be present in so variable a substance as commercial wood spirit, it is difficult to foresee what substances may be generated in its decomposition, but I think I am justified in concluding that cyanhydric acid is not generated by the action of nitric acid upon methylic alcohol; at least not in the presence of urea.

Treated as above described, 420 grammes of wood spirit yielded a distillate from which by agitation with solution of salt, there separated the very large quantity of 300 grammes crude nitrate of methyl. This may be subsequently agitated with a little weak solution of carbonated alkali.

The wood spirit before use should be distilled with one-third of its bulk of very strong (almost saturated) solution of caustic soda, to decompose any acetate of methyl which may be present. This operation must be performed over the water bath.

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