stomach, 0.7 grain, equivalent approximately to from 1 to 1½ teaspoonfuls of the officinal 1 per cent. solution.

A comparative quantity of pure nitroglycerine, acidified with tartaric acid, distilled with steam in a similar apparatus, at the same rate, yielded a distillate in which oily drops were observable, and its ethereal extract when evaporated yielded a residue which exploded with the same readiness. A similar examination of other parts in our possession did not reveal any nitroglycerine, and none of the intestines had been taken at the autopsy.

The defendant was convicted of the use of instruments, and the presence of nitroglycerine was not accounted for by the testimony. It was a theory of the prosecuting attorneys, however, that nitroglycerine had been administered, in ignorance, as a heart stimulant.

I am indebted to Dr. F. E. Tuttle and to Dr. F. J. Pond, for their assistance in this work.

CHEMICAL LABORATORY OF THE PENNSYLVANIA
STATE COLLEGE, August 21, 1901.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 57.]

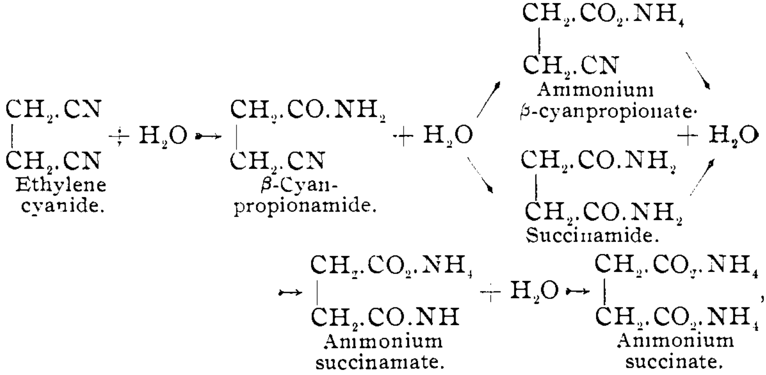
ON THE PRODUCTION OF THE IMIDES OF SUCCINIC AND GLUTARIC ACIDS BY THE PARTIAL HYDRATION OF THE CORRESPONDING NITRILES.[1]

BY MARSTON TAYLOR BOGERT AND DAVID C. ECCLES.

Received November 5, 1901.

THEORETICAL.

THE hydration of ethylene cyanide, by the addition of successive molecules of water, may be represented as follows:



$$\underset{\text{Ethylene cyanide.}}{\begin{array}{l}CH_2.CN\\ |\\ CH_2.CN\end{array}} + H_2O \rightarrow \underset{\beta\text{-Cyanpropionamide.}}{\begin{array}{l}CH_2.CO.NH_2\\ |\\ CH_2.CN\end{array}} + H_2O \begin{array}{l}\nearrow \underset{\text{Ammonium }\beta\text{-cyanpropionate.}}{\begin{array}{l}CH_2.CO_2.NH_4\\ |\\ CH_2.CN\end{array}} \searrow\\ \searrow \underset{\text{Succinamide.}}{\begin{array}{l}CH_2.CO.NH_2\\ |\\ CH_2.CO.NH_2\end{array}} \nearrow\end{array} + H_2O$$

$$\rightarrow \underset{\text{Ammonium succinamate.}}{\begin{array}{l}CH_2.CO_2.NH_4\\ |\\ CH_2.CO.NH\end{array}} + H_2O \rightarrow \underset{\text{Ammonium succinate.}}{\begin{array}{l}CH_2.CO_2.NH_4\\ |\\ CH_2.CO_2.NH_4\end{array}},$$

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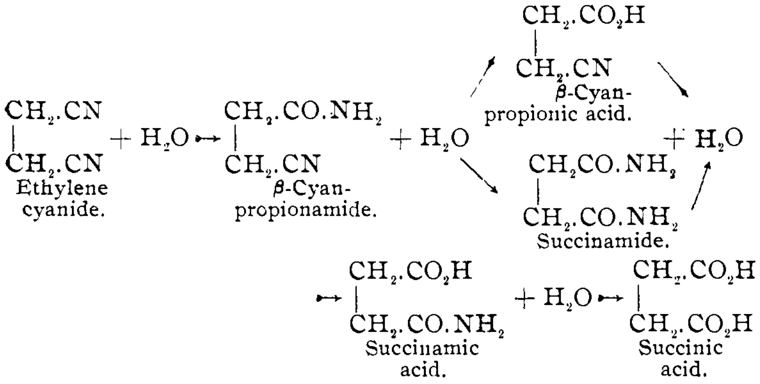
[1] Read before the New York Section of the American Chemical Society, Nov. 1, 1901.

or, if this hydration be carried out in the presence of a strong mineral acid, the products will be as follows:



For the conversion of the nitrile to the acid, therefore, at least four molecules of water are necessary, and the question naturally arises as to what will occur when less than this amount of water is present, say two molecules of water in sealed tubes, and with one equivalent of a mineral acid to set free the cyanpropionic acid from its ammonium salt.

Of course, it was hardly to be expected, in our experiments to answer this question, that the hydration would proceed quantitatively and exclusively along one line, yielding, for example, only amide or cyan acid, but that in all probability any or all of the various hydration products would have to be reckoned with. Under conditions of heat and pressure, however, the addition of exactly two molecules of water to one molecule of the nitrile, and in presence of exactly one equivalent of a strong mineral acid, should yield one and the same major product, no matter what the course of the hydration. That product is the imide.

β-Cyanpropionic acid rearranges to the imide, succinamide loses ammonia with formation of the imide, succinamic acid gives the same body by loss of water, and it has been shown in this laboratory[1] that when succinic acid and its nitrile are heated together in sealed tubes succinimide is the product.

To be sure, these changes to the imide occur at quite different temperatures, the production of the imide from succinic acid and its nitrile, or from succinamide, requiring a temperature of 200°

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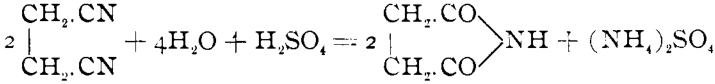
[1] Miller: This Journal. **16**, 443 (1894); Seldner: *Am. Chem. J.*, **17**, 532 (1895); Mathews: This Journal, **20**, 654 (1898).

or over, while succinamic acid probably loses its water at a much lower point, and β-cyanpropionic acid rearranges to the imide at still lower temperatures. It was hoped, consequently, that the temperature at which the reaction took place, and the nature of the by-products separated, might indicate whether the course of the hydration proceeded through the cyanpropionic acid or the amide. The problem is somewhat complicated by the fact that, while only two molecules of water might be added, succinamic acid, although theoretically requiring three molecules for its quantitative production, might be continuously formed in small amount and immediately break up again into imide and water, the net amount of water, therefore, used up in the reaction being but two molecules; the production of the imide might thus occur at low temperatures and still the course of the hydration be through the amide. Then, again, the formation of imide from amic acid is partly reversible:

$$\text{Amic acid} \longleftrightarrow \text{Imide} + H_2O,$$

and succinamic acid and most of its salts change quite easily, in presence of water, to succinic.

The following reaction was taken as the basis of our laboratory work:



$$2\left|\begin{array}{l}CH_2.CN\\ CH_2.CN\end{array}\right. + 4H_2O + H_2SO_4 = 2\left|\begin{array}{l}CH_2.CO\\ CH_2.CO\end{array}\right\rangle NH + (NH_4)_2SO_4.$$

As the ratio of sulphuric acid to water in such a reaction is entirely independent of the particular nitrile to be hydrated, a standard acid was prepared containing sulphuric acid and water in exactly this proportion, and then the required amount measured out volumetrically. In most cases, 5 grams of the nitrile were used at a time, and the reaction carried out in sealed tubes at temperatures varying from 100°–200°.

As expected, the imide was the chief product in all cases. Cyanpropionic acid, cyanpropionamide, and succinic acid were not found in any of the tubes. The absence of β-cyanpropionic acid and its amide is not strange, as the hydration would certainly carry the cyanpropionamide further, and cyanpropionic acid would rearrange to succinimide at the temperature of the reaction. That no succinic acid was found, however, seems to argue that the major part of the imide did not come from continuous formation and breaking down of the amic acid, for the amic acid is so easily hydrated to succinic that in the early stages of the reaction, when small amounts of the amic acid had formed and there was still an excess of uncombined dilute sulphuric acid present, it seems difficult to understand why no trace of succinic acid resulted. Any succinic acid produced in the reaction should have been recovered unchanged, as the temperature was in no case high enough or maintained for a sufficient length of time to cause the acid to combine with the unchanged nitrile and thereby yield the imide.

If the imide did not owe its origin to amic acid, it could not have come from the amide at all, as the temperature was too low to drive ammonia out of the amide. The only remaining explanation is that the chief source of the imide was the rearrangement of the cyanpropionic acid, and that the hydration, therefore, proceeded mainly along this line. Small amounts of succinamide and of succinamic acid were, however, isolated from many of the tubes, the presence of the latter being quite possibly due to a partial rehydration of the imide, to establish the equilibrium between the system-imide, amic acid, water. The production of imide in tubes 5 and 6, where no mineral acid was present, also seems more likely to be due to a decomposition of ammonium cyanpropionate than of ammonium succinamate. That the hydration should tend to complete itself upon one cyanogen group before attacking the next is quite analogous to the action of oxidizing agents, halogens, etc., upon similar straight chain compounds.

As the question of temperature determines the relative yield of imide, it may be said, briefly, that, for the production of succinimide, it is best to heat for about two days at 165°–175°. Below this point the hydration is slow and incomplete ; above it, partial carbonization follows. For glutarimide, a temperature of 180°–200° is desirable.

EXPERIMENTAL PART.

For Succinimide.—Sealed tubes were prepared containing 5 grams of ethylene cyanide, and a mixture of two molecules of water to half a molecule of absolute sulphuric acid (= 3.6 cc. of a sulphuric acid of 1.478 specific gravity). These tubes were heated at various temperatures and for varying lengths of time, the product being a brown crystalline solid usually more or less moist according to the temperature of the reaction and the duration of the heating. The method of working up the contents of the tubes was based upon the following considerations:

The bodies possibly present in the tubes after heating are the various hydration products already indicated, succinimide, ammonium sulphate, excess of sulphuric acid and water. By rubbing up such a mixture with a thin paste of barium carbonate, the excess of sulphuric acid and most of the ammonium sulphate form barium sulphate; cyanpropionic acid, succinamic and succinic acids, yield barium salts; ethylene cyanide, cyanpropionamide, succinamide and succinimide remain unchanged. If the mass be then evaporated, carefully dried, powdered, and extracted with absolute alcohol, ethylene cyanide, cyanpropionamide, and succinimide will be dissolved out, while succinamide remains for the most part insoluble. Ethylene cyanide, cyanpropionamide, and succinimide can then be separated by selection of suitable solvents, etc. The residue insoluble in absolute alcohol may contain succinamide, the barium salts of cyanpropionic, succinamic and succinic acids, barium carbonate and sulphate, ammonium carbonate, and, possibly, a little unchanged ammonium sulphate. By extraction with water, all except barium carbonate and sulphate are dissolved, and ignition of the residue will show no organic matter. Addition of sulphuric acid to the aqueous solution will then liberate the organic acids from their barium salts, when they can be removed by repeated extraction with ether. Finally, if barium carbonate be added to the acid solution after the ether extraction, and the filtrate from precipitated barium sulphate evaporated and the residue ignited, the carbonizing of the residue will show the presence of amide or of acids insoluble in ether, which may then be extracted by proper solvents until the ignition of the residue shows no organic matter.

As examples, the following tubes may be mentioned: Tubes 1, 2, 3, and 4 all contained 5 grams of ethylene cyanide, two molecules of water, and half a molecule of sulphuric acid. They were heated as follows:

No. 1, six hours at 131° to 138°.

No. 2, six hours at 142° to 155°, and then three hours at 158° to 165°.

No. 3, six hours at 154° to 162°.

No. 4, five hours at 160° to 170°, and then six and a half hours at 159° to 165°.

The contents of the tubes were worked up as already outlined. Succinimide was found in all of the tubes, the amount increasing with the rise in temperature and the duration of the heating. No. 1 contained much unchanged cyanide. Small amounts of amic acid occurred in all of these tubes, and traces of what appeared to be amide were separated in several.

No. 5 contained 5 grams of ethylene cyanide, two molecules of water, and no sulphuric or other mineral acid. It was heated for five hours at 153° to 173°. The mixture in the tube then appeared as a brownish liquid containing oily globules, and with a strong odor of ammonia. Most of the cyanide appeared unchanged, as scarcely any imide could be detected.

No. 6 carried 5 grams of the cyanide, one molecule of water, and no mineral acid. It was heated for six hours at 153° to 173°. The tube contents were then brown and semisolid. Succinimide in large amount was separated, a small amount of amic acid, traces of succinamide, but no cyanpropionamide was discovered.

For Glutarimide.—Trimethylene cyanide was heated in sealed tubes with two molecules of water and half a molecule of sulphuric acid, for five to ten hours at 155° to 200°, and the products of the reaction separated in essentially the same manner as for the succinimide tubes. Glutarimide was isolated in large amount (60 per cent. of theory), but no amide or amic acid could be detected, except the imide, the tubes containing only unhydrated cyanide. A temperature of 180° to 200° is necessary for the success of the hydration.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY,
July 1, 1901.

ON THE DETERMINATION OF CITRATE-INSOLUBLE PHOSPHORIC ACID.

BY C. D. HARRIS.

Received October 12, 1901.

THE method used in the laboratory of the North Carolina Department of Agriculture up to recently was as follows:

Two grams of the sample to be analyzed were washed free of water-soluble phosphoric acid. Then 100 cc. of strictly neutral ammonium citrate solution (sp. gr. 1.09) in an 8-ounce Erlenmeyer flask, was heated to 65°, in a water-bath, keeping the