Yttrium material was prepared having only a very faint spectra in 10 cm. layers of saturated solutions of the chloride. It was considered to have not more than one-half per cent. erbium present. The average atomic weight obtained by the oxide-chloride method was 90.12.

This work is being continued, with the hope of preparing pure yttrium oxide for the final determination of the atomic weight of yttrium. It may be well to mention that similar work is under way with samarium and gadolinium.

AN ESTER OF HYDROCOBALTICYANIC ACID.

BY C. E. BOLSER AND L. B. RICHARDSON.

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While hydrocobalticyanic acid, which was discovered by Zwenger[1] in 1847, and many of its metallic salts are substances more or less familiar to chemists, we have been unable to find references to the formation of esters of the acid. It occurred to us that it might be possible to synthesize some of these substances, and that their conduct might afford information as to the structure of this class of compounds. We have been successful in producing but one of them, the ethyl compound; and that probably not in a state of absolute purity; but the reactions which it may be made to undergo are of some interest in the study of the general nature of the class of substances to which hydrocobalticyanic acid, hydroferricyanic acid, etc., belong.

The general method used for the preparation of the ethyl ester was the usual treatment of the silver salt of the acid, suspended in alcohol, with ethyl iodide. Inasmuch as the acid is rather unstable at high temperatures, the reaction was carried on at the boiling point of the mixture. No decomposition seemed to take place under these circumstances, and the gradual yellowing of the suspended solid, indicating the formation of silver iodide, showed that the desired reaction was taking place. The exact course of procedure was as follows:

Twenty grams of potassium cobalticyanide were precipitated by silver nitrate in excess, and the silver cobalticyanide, washed with very dilute nitric acid, then with water, and finally with alcohol, was placed in a liter flask. The flask was fitted with a return condenser. 250 cc. of 95% alcohol were added, and the mixture was heated to the boiling point. An amount of ethyl iodide slightly in excess of the theoretical quantity was then poured in, and the boiling continued for an hour. The hot mixture was filtered rapidly, and the filtrate evaporated at once under reduced pressure (40 mm.). It is most important that this evaporation take place immediately; otherwise the iodine produced by the decomposition of the excess of ethyl iodide contaminates the products, and can be removed from

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[1] *Ann.*, 62, 157.

it only with the utmost difficulty. It is equally important that the evaporation should be carried on under reduced pressure; the decomposition of the ester, which takes place to a slight extent under the best of conditions, is very considerable if the evaporation takes place at the atmospheric pressure. The residue obtained was dissolved in water, filtered, and again evaporated as before, the evaporation being continued until the greater part of the solid separated out; the thick mass was filtered on a suction filter, and the residue dried upon a porous plate. The dried product from a number of these operations was combined and recrystallized from water under reduced pressure in the same way as above. It was found advantageous to carry on the preparation in small quantities rather than in large lots.

The yield produced by the operation outlined above was variable, even under the most careful regulation of conditions. In the best series we obtained from 55 g. of the potassium cobalticyanide, run in three lots, 10.5 g. of the ester. The theoretical yield for complete conversion is 43.7 g.

The product resulting from the second crystallization from water, dried over sulfuric acid for at least a week, produced only a slight opalescence when dissolved in water. This was analyzed for cobalt, nitrogen, carbon, and hydrogen. The salt was evaporated three times with a mixture of concentrated sulfuric and nitric acids, being heated to dull redness after each evaporation. The conversion to cobalt sulfate was complete, the mass dissolving in water without leaving a residue. The cobalt was precipitated as the hydroxide, ignited, and reduced to the metallic condition by hydrogen in the usual way. The nitrogen was determined by the Dumas method. The results were as follows:

Co......	22.44	22.77	22.54	22.88	Calculated for $C_2H_5H_2Co(CN)_6.H_2O$	22.34
N.......	32.19	32.15	...	...	Calculated for $C_2H_5H_2Co(CN)_6.H_2O$	31.84
C.......	35.93	...	...	...	Calculated for $C_2H_5H_2Co(CN)_6.H_2O$	36.36
H.......	3.21	...	...	...	Calculated for $C_2H_5H_2Co(CN)_6.H_2O$	3.41

Owing to the formation of cobalt carbide in the combustion of carbon, we experienced the same difficulty as that described by Zwenger in the analysis of the acid. It was not possible to determin the water of crystallization directly owing to the fact that the ester decomposes at a low temperature.

Ethyl dihydrogen cobalticyanide resembles, in many respects, the acid from which it is derived. It separates from concentrated aqueous solution as a yellowish white mass, but, unlike the acid, does not show well defined crystallin form. When heated somewhat above 100° it begins to lose its water of crystallization and becomes blue in color, growing darker as the temperature is raised. It seems to be somewhat unstable even at 100° as the residue obtained from the evaporation of an aqueous solution which has been boiled shows a marked turbidity when the attempt is made to redissolve it in water. The dry compound is hygroscopic, absorbing enough water from moist air to become very pasty. A most marked characteristic of the compound is its great solubility in water, ether, acetone, and other ordinary solvents. The anhydrous alcohol solution is green, and the substance obtained by evaporation of this solution is distinctly amorphous in character. This confirms the presence of water of crystallization in the substance obtained from the evaporation of an aqueous solution. Its ready solubility and the ease with which it decomposes makes its preparation in the pure condition a difficult matter. The best criterion of purity is the completeness with which the substance dissolves in water. The purest sample which we obtained gave a slight opalescence upon solution. Upon standing in a desiccator over sulfuric acid at room temperature it slowly decomposed. A sample preserved for eight months in this way had a decided odor, dissolved in water, leaving a considerable residue, and gave a cobalt analysis nearly a per cent. higher than when freshly prepared.

According to the conclusion reached from the analysis the compound contains two replaceable hydrogen atoms. It should then be possible to form metallic salts of ethyl dihydrogen cobalticyanide. By the addition of silver nitrate to a solution of the ester we obtained a white precipitate which should be $Ag_2C_2H_5Co(CN)_6$. This compound, like the normal silver salt of the acid, is a white amorphous substance, which is extremely difficult to purify by washing, and which upon drying becomes a white, hornlike mass. Under these conditions we could hardly hope to obtain an absolutely pure compound, but the determination of its silver content might be expected to confirm our conclusions as to the number of replaceable hydrogen atoms in the ester. The result was as follows:

Silver found, 48.51; calculated for $Ag(C_2H_5)_2Co(CN)_6$............ 28.16
calculated for $Ag_2C_2H_5Co(CN)_6$............. 46.72
calculated for $Ag_3Co(CN)_6$................. 59.68

The ester also forms a copper salt, very similar in appearance to that obtained from the acid.

Upon moistening the substance with a solution of sodium hydroxide at room temperature, an odor, which seemed to be that characteristic of an isocyanide, was perceived. This action came as much of a surprise and was at first attributed to an accidental impurity of the sample examined. Upon repeating the operation with other specimens the same reaction was observed to go on. A more careful examination was then determined upon, with the object of making sure that the substance was actually, as it seemed to be, ethyl isocyanide. This was done by converting the gas evolved by the action of sodium hydroxide (heated), through the corresponding amine, to ethyl alcohol, to which the iodoform test was applied. The result was the production of a small quantity of iodoform, having the proper melting point.

It was thus evident that the substance produced by the action of sodium hydroxide upon the ester was, in fact, ethyl isocyanide. This points to a linkage between the ethyl group and nitrogen. If, on the other hand, all the substance subjected to the NaOH reaction had decomposed in this way the quantity of iodoform obtained would have been very much larger than was the case. We have proven that at least a part of the compound, probably a small part, contains the ethyl group linked with nitrogen. We have not shown that the remainder is an isomeride in which the group is linked with carbon, but perhaps the conclusion is warranted that this is the case, and that the two components are related in much the same manner as are cyanides and isocyanides of organic radicals. The transformation of isocyanides into cyanides upon heating is well known, and might explain the presence of isomerides in this case.

It would be quite possible that in the $K_3Co(CN)_6$ used in the preparation of the $Ag_3Co(CN)_6$ at the beginning of the process a small amount of potassium cyanide remained as an impurity. This would then be converted into AgCN.KCN, which in reaction with ethyl iodide would produce $C_2H_5NC.AgCN$, and eventually C_2H_5NC, either during the boiling with ethyl iodide in alcoholic solution, or later on in the reaction with sodium hydroxide. Suspecting this possibility, we tried to detect the odor of ethyl isocyanide when $Ag_3Co(CN)_6$ was boiled with ethyl iodide. We did not obtain a trace. We then duplicated our experimental conditions, using the merest trace of silver cyanide in place of $Ag_3Co(CN)_6$. We obtained a definit isocyanide odor, which was not increased upon the addition of sodium hydroxide.

The experimental data obtained are not sufficient to enable us to assign a formula to the compound which would explain the above reaction. It is enough to say that an ester of hydrocobalticyanic acid exists—and possibly esters of other similar acids—in which the alkyl group is attached to nitrogen.

It seemed possible that the formation of the ester containing the ethyl group linked to nitrogen might be due to the use of the silver salt of the acid in its preparation, and that an ester produced without using a silver salt might contain the ethyl group otherwise linked. The attempt was made, therefore, to prepare the compound by the action of absolute alcohol upon hydrocobalticyanic acid in the presence of hydrochloric acid. It was found, however, that upon passing dry hydrochloric acid into a solution of the acid in absolute alcohol this acid was at once precipitated. Any action, therefore, might be expected to be slow. In the hope that some result might be obtained, the mixture was allowed to stand under pressure for three months, fresh hydrochloric acid being passed in from time to time. The mixture soon turned green, but even at the end the precipitated acid seemed to be little diminished in quantity. The reaction mixture was filtered, and the filtrate evaporated under reduced pressure, the residue taken up in water and evaporated as before. From 5 g. of the acid a yield of 0.6 g. was obtained. Upon treatment of this substance with sodium hydroxide the same reaction, as indicated by the isocyanide odor, was obtained as before. The substance remaining upon the filter paper, after a thorough washing with alcohol, gave no such reaction; it was probably unchanged acid. The presence of the ester in the residue from the soluble portion was thus indicated, but analysis of this residue shows that it contains but a small quantity.

Co obtained	24.43
Co in $H_3Co(CN)_6.H_2O$, calculated	25.00
Co in $C_2H_5H_2Co(CN)_6.H_2O$, calculated	22.35

The product was evidently a mixture of a small quantity of the ester with a larger quantity of the free acid; a result which might have been expected from the course of the reaction.

This shows that the formation of the ester in which the alkyl group is linked with nitrogen is not dependent upon the presence of a silver salt in its preparation.

The attempt was made to prepare a corresponding ester of hydroferricyanic acid, by the action of ethyl iodide upon the silver salt. Such a compound, if formed, is evidently decomposed at once. Contrary to our experience in the preparation of the ester of hydrocobalticyanic acid a perceptible odor of an isocyanide was noted in the reaction flask. Upon evaporation of the filtered solution no homogeneous product was obtained.

Summary.

1. Ethyl dihydrogen cobalticyanide has been prepared by one reaction, and in an impure condition by another.

2. The composition of the substance has been confirmed by the preparation of disilver ethyl cobalticyanide.

3. The decomposition of the ester brought about by the action of sodium hydroxide indicates that at least in some of its molecules the ethyl group is attached to nitrogen, with the strong probability that in others the ethyl group is otherwise linked.

4. The attempt to prepare the corresponding ester of hydroferricyanic acid failed.

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THE CHEMICAL SIGNIFICANCE OF CRYSTALLIN FORM.

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When in 1669 Nicholas Steno discovered that a given crystallin angle possesses always a constant value for any given substance, an important circumstance concerning the chemical significance of crystallin form was