(10) $HgCl_2 + py = HgCl_2.py + 13,387$ cal.
(11) $3HgCl_2.2C_5H_5N + py = 3HgCl_2.py + 14,922$ cal.
(11*a*) or $HgCl_2.{}^2/_3C_5H_5N + py = HgCl_2.py + 4,974$ cal.
(12) $3HgCl_2 + 2C_5H_5N = 3HgCl_2.2C_5H_5N + 25,239$ cal.
(12*a*) or $HgCl_2 + {}^2/_3C_5H_5N = HgCl_2.{}^2/_3C_5H_5N + 8,413$ cal.
(10) $HgCl_2 + py = HgCl_2.py + 13,387$ cal.
(13) $HgCl_2.C_5H_5N + py = HgCl_2.py + 1,932$ cal.
(14) $HgCl_2 + C_5H_5N = HgCl_2.C_5H_5N + 11,455$ cal.

(10) $HgCl_2 + py = HgCl_2.py + 13,387$ cal.
(15) $HgCl_2.2C_5H_5N + py = HgCl_2.py - 5,359$ cal.
(16) $HgCl_2 + 2C_5H_5N = HgCl_2.2C_5H_5N + 18,746$ cal.

(16) $HgCl_2 + 2C_5H_5N = HgCl_2.2C_5H_5N + 18,746$ cal.
(14) $HgCl_2 + C_5H_5N = HgCl_2.C_5H_5N + 11,455$ cal.
(17) $HgCl_2.C_5H_5N + C_5H_5N = HgCl_2.2C_5H_5N + 7,291$ cal.

(18) $HgI_2 + py = HgI_2.py + 9,974$ cal.
(19) $HgI_2.2C_5H_5N + py = HgI_2.py - 4,921$ cal.
(20) $HgI_2 + 2C_5H_5N = HgI_2.2C_5H_5N + 14,895$ cal.

Summary.

(1) It is evident that the thermal effect accompanying the combination of metallic salts with organic compounds of crystallization may in many cases be of considerable magnitude; in fact, the values are comparable with the analogous heats of hydration of such substances as sodium sulphate.

(2) A satisfactory apparatus for the measurement of heats of solution and specific heats of solutions has been devised and described. It has been applied to the measurement of the heats of solution in pyridine of silver nitrate, silver thiocyanate, mercuric chloride, and mercuric iodide and their compounds with pyridine. The values thus obtained have been used in calculating the "heats of pyridination" of these latter compounds.

MADISON, WIS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CINCINNATI.]

ALIPHATIC HYDROXYLAMMONIUM SALTS AND HYDROXAMIC ACIDS WITH HALOGEN SUBSTITUENTS.

BY LAUDER WILLIAM JONES AND LOUIS F. WERNER.

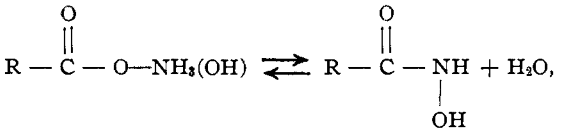
Received December 7, 1916.

A few experiments described in scattered articles indicate that aliphatic hydroxamic acids and their derivatives will be found to show a pronounced tendency to undergo the Beckmann rearrangement in a manner quite similar to that so frequently observed in the study of aromatic hydroxamic acids. Many interesting reactions of this type suggest themselves when the possible rearrangements of simple aliphatic hydroxamic acids with halogen substituents are considered. It is our intention to make a study of the hydroxamic acids described in this article from this point of view.

The only aliphatic hydroxamic acid of this class isolated, so far, is monochloroacethydroxamic acid prepared by Francesconi and Bastianini[1] through the interaction of monochloroacetamide and hydroxylammonium chloride. Their account of this substance was very meager; a few of its properties, including the melting point (108°), were recorded, but no further study of the acid was made. Angelo and Angelico[2] treated a solution of bromoacetaldehyde with "nitrohydroxylamin säure." Among the products of this reaction, the presence of a hydroxamic acid, possibly bromoacethydroxamic acid, was shown by the intense red color imparted to the liquid when ferric chloride was added, but no attempt was made to isolate the acid.

Since this is practically all of the information concerning halogen substituted aliphatic hydroxamic acids to be gained from the literature, it became necessary to devise satisfactory methods by means of which these compounds might be prepared in sufficient quantities to permit of their study from many other angles. The experiments described in this article were undertaken with this particular object in view.

Jones and Oesper[3] showed that hydroxylammonium formate and hydroxylammonium acetate, at temperatures slightly above their melting points, were converted, partially at least, into the corresponding hydroxamic acids,



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-NH_3(OH) \rightleftarrows R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle OH}{|}}{NH}+H_2O,$$

a method analogous to the one commonly employed to prepare amides from ammonium salts of organic acids. In order to try out this plan, it became necessary to make solid hydroxylammonium salts of some of the simpler halogen substituted organic acids. Monochloro-, dichloro-, and trichloroacetic acids were chosen for this purpose. The solid hydroxylammonium salts of monochloro-, dichloro-, and trichloroacetic acids were obtained easily by mixing the calculated amount of free hydroxylamine and the respective acids at 0°. Owing to the fact that the bromine and the iodine in monobromo- and monoiodoacetic acids were so readily replaceable, complications arose when hydroxylamine was allowed to interact with these acids. So that, as yet, the hydroxylammonium salt of these two acids have not been obtained in a pure condition.

When these chloroacetates were heated to their melting points, variable amounts of the corresponding hydroxamic acids were formed. But the instability of the chloroacethydroxamic acids at temperatures near

[1] *Gazz. chim.*, **34**, 428, 434 (1904).

[2] *Ibid.*, **23**, 239 (1903).

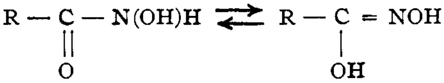
[3] *Am. Chem. J.*, **42**, 515 (1909).

their melting points, which lie very close to the melting points of the salts themselves, rendered the method impractical as a means of preparing the necessary quantities of these hydroxamic acids.

Monochloroacethydroxamic Acid. — Pure monochloroacethydroxamic acid was easily obtained by the action of an alcoholic solution of hydroxylamine upon monochloroacetic ethyl ester. The same method has given successful results in the making of dichloroacethydroxamic acid.

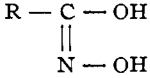
Monochloroacethydroxamic acid obtained in this way was found to melt at 92–93°. When this solid was kept for several days, although no apparent change in the external appearance of the crystals was observed, it no longer melted at 92–93°, but at 108°. Analysis showed that both substances possessed the same composition, as well as the characteristic chemical properties of monochloroacethydroxamic acid. The modification which melted at 92–93° gave an acetyl derivative which melted at 85°, while the form which melted at 108° yielded an acetyl derivative melting at 67°.

It has long been expected that, sooner or later, representatives of tautomeric amides, or hydroxyamides,

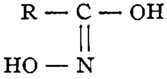


$$R - \underset{\underset{O}{\|}}{C} - N(OH)H \rightleftarrows R - \underset{\underset{OH}{|}}{C} = NOH$$

would make their appearance, and that, for at least one pair of isomers, sufficient evidence might be presented to establish this relationship in a manner so convincing that no question of physical isomerism (polymorphism) could enter. Furthermore, in these cases, there is another complexity to be dealt with, since the hydroximic formula suggests the possibility of stereoisomers as well.

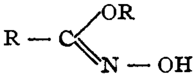


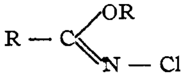
$$R - \underset{\underset{N - OH}{\|}}{C} - OH$$



$$R - \underset{\underset{HO - N}{\|}}{C} - OH$$

The existence of such geometrical isomers is rendered somewhat more probable by the occurrence of pairs of stereoisomers among the closely related hydroximic esters and chloroimido esters.



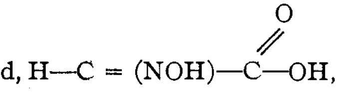


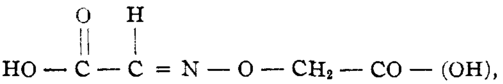
In the literature, to be sure, there may be found conflicting statements concerning the properties of a particular hydroxamic acid; but these cases have generally turned out to be printers' errors, or records of observations based upon the study of impure materials, and, as yet, it has been impossible to get sufficient evidence to substantiate the claim of isomerism in either sense mentioned above. Lossen found that almost all of the aromatic hydroxamic acids studied by him could be obtained in more than one crystalline form, which he considered to be physical isomers. However, it has not been established with certainty that this is true in all instances. The fact that in the case of the two forms of monochloroacethydroxamic acid two different acetyl derivatives have been prepared suggests that the difference between the two forms may not be due to physical isomerism, but to *real structural isomerism* (or to stereoisomerism). These compounds will be studied further from this point of view.

Monobromoacethydroxamic Acid and Monoiodoacethydroxamic Acid.—When attempts were made to prepare monobromoacethydroxamic acid and monoiodoacethydroxamic acid by the action of free hydroxylamine upon the esters of monobromoacetic acid and of monoiodoacetic acid, unexpected complications arose owing to the fact that hydroxylamine reacted with the bromine and the iodine in these compounds so readily, that immediately after mixing the alcoholic solutions of ester and hydroxylamine, crystalline precipitates formed which were found to be basic hydroxylammonium salts,

$$(NH_2(OH))_2,HBr \qquad (NH_2(OH))_2,HI.$$

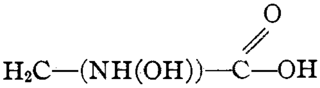
Various other products, including small amounts of the desired hydroxamic acids, accompanied these salts.

In view of the fact that Hantzsch and Wild[1] had found that an alkaline solution of hydroxylamine acted upon monochloroacetic acid to give oximidoacetic acid,  $\mathrm{H{-}C{=}(NOH){-}\overset{\overset{O}{/\!/}}{C}{-}OH}$, and another acid which they named "oximidoacetoacetic acid,"



$$\mathrm{HO-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{C}=N-O-CH_2-CO-(OH)},$$

a careful search for esters of these two acids was made. During the search for these substances, a new crystalline compound, which contained no bromine, or iodine, was isolated. It melted at 65° and possessed the empirical formula $C_8H_{15}O_5N$. At first it was assumed that this substance might be the diethyl ester of oximidoacetoacetic acid; but the empirical formula of the latter would be $C_8H_{13}O_5N$, and no oximidoacetic acid, or its ester, could be detected among the reaction products.

A second formula suggested itself. It is probable that the first product of the reaction between hydroxylamine and monochloroacetic acid, as Hantzsch and Wild implied, was hydroxylaminoacetic acid,  $\mathrm{H_2C{-}(NH(OH)){-}\overset{\overset{O}{/\!/}}{C}{-}OH}$. If the ethyl ester of this acid were formed

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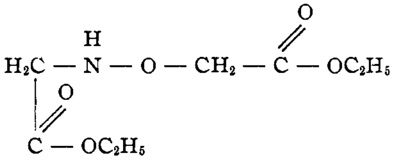
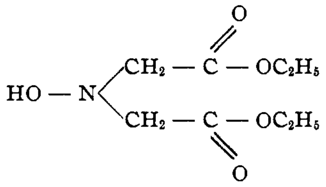
[1] Hantzsch and Wild, *Ann.*, **289**, 295 (1896).

during the interaction of hydroxylamine upon the ester of monobromoacetic acid or of monoiodoacetic acid, it might react with a second molecule of the ester of the halogen acid to give either α,β- or β,β-disubstituted hydroxylamine derivatives ($C_8H_{15}O_5N$) of the following structural formulas:



or



Since the new compound reduced silver nitrate and Fehling's solution rapidly, a fact not entirely consistent with the first formula, although hydroxylamino acids are quite readily oxidized to oximido acids, the second formula seems to be more probable. The reducing action suggested a relationship to β,β-dialkyl hydroxylamines, which are known to be extremely sensitive to oxidizing agents. This formula has not been established conclusively by analytic and synthetic methods.

Because of these difficulties, the two methods described above were abandoned as a means of preparing monobromo- and monoiodoacethydroxamic acids. These acids were finally made successfully by the action of monobromoacetyl bromine and of monoiodoacetyl chloride upon water solutions of hydroxylammonium chloride to which two equivalents of sodium carbonate had been added.

EXPERIMENTAL PART.

I. Hydroxylammonium Salts.

1. **Hydroxylammonium Monochloroacetate,** $ClCH_2.CO(ONH_3(OH))$.—Five grams of hydroxylamine were cooled to 0°, and a little less than the calculated amount of monochloroacetic acid, previously melted, was added in small portions. The mixture was stirred vigorously to insure thorough commingling of the ingredients. When all of the acid had been added, a mass of snow-white crystals was obtained which was collected and drained. When the filtrate was concentrated *in vacuo*, an additional amount of the crystals was obtained. The salt was purified by recrystallization from boiling alcohol, from which it separated in well developed crystals. The melting point was 124–125°.

0.2312 g. gave 22.6 cc. N_2 at 27° and 736 mm.
Calc. for $C_2H_6O_3NCl$: N, 10.98. Found: N, 10.74.

Ferric chloride added to a water solution of the salt gave no color reaction. If, however, the salt was melted and kept at a temperature one or two degrees above its melting point for a few minutes, a solution of the residue in water gave an intense violet color with ferric chloride and a brilliant green precipitate with copper acetate. These reactions show that the hydroxylammonium salt was converted, partially at least, into the corresponding hydroxamic acid

$$ClCH_2.CO(ONH_3OH) \rightleftarrows ClCH_2—CO(NH(OH)) + H_2O.$$

2. **Hydroxylammonium Dichloroacetate,** $Cl_2CH.CO(ONH_3(OH))$.—Five grams of hydroxylamine, cooled by ice, were treated with the calculated amount of dichloroacetic acid. The mixture, which soon solidified, was collected and drained. The salt was found to be extremely soluble in water and in alcohol. It was easily purified by suspending it in benzene to which just enough alcohol had been added to cause the salt to dissolve at the boiling point of the mixed solvent. In this way, fine, glistening crystals were secured. The salt melted, with decomposition, at 116–116.5°. By slow evaporation of an alcoholic solution, or the mother liquor separated from the crude crystals, large crystals, sometimes two or three inches in length, could be obtained.

0.3576 g. gave 29.4 cc. N_2 at 24° and 744.4 mm.
Calc. for $C_2H_5O_3NCl_2$: N, 8.65. Found: N, 8.99.

The salt, dissolved in water, gave no color reaction with ferric chloride. The solution was acid to litmus and reduced silver nitrate immediately. When the dry salt was heated for several minutes at a temperature one or two degrees above the melting point, and the residue was dissolved in water, ferric chloride gave an intense color reaction, indicating a transformation into the corresponding hydroxamic acid.

3. **Hydroxylammonium Trichloroacetate,** $Cl_3C.CO(ONH_3(OH))$.—Eight grams of free hydroxylamine, cooled to 0°, were treated with the calculated amount of trichloroacetic acid, previously melted. The acid was added gradually and the mixture was stirred thoroughly. On one occasion, when proper precautions were not taken, an explosion resulted, caused, probably, by local heating of the hydroxylamine itself. The thick viscous liquid soon solidified. The salt was collected and drained.

This salt, unlike the two salts described above, was readily soluble in ether, and could be precipitated from this solution by means of ligroin. The pure salt melted at 133–134°.

0.1717 g. gave 0.0787 g. CO_2 and 0.0294 g. H_2O; 0.1770 g. gave 11.3 cc. N_2 at 27° and 745.4 mm.; 0.2711 g. gave 0.5918 g. AgCl.
Calc. for $C_2H_4O_3Cl_3N_5$: C, 12.22; H, 2.05; N, 7.13; Cl, 54.18.
Found: C, 12.48; H, 1.91; N, 6.88; Cl, 53.98.

It was readily soluble in alcohol and in water. The water solution gave no color reaction with ferric chloride. When heated carefully one or two degrees above the melting point, it was converted partially into the corresponding hydroxamic acid. A separation of the unchanged salt from the hydroxamic acid was made by extraction with ether in which the salt was easily soluble, while the trichloroacethydroxamic acid was practically insoluble. But the sensitiveness of the hydroxamic acid, as well as the salt, to heat caused almost all of the substances to dissociate into gaseous products, so that the amount of hydroxamic acid obtained by this method has proved too small for a study of its properties.

II. Hydroxamic Acids.

1. **Monochloroacethydroxamic Acid,** $ClCH_2.CO(NH(OH))$.—Ten grams of ethyl monochloroacetate were dissolved in 25 cc. of alcohol and 2.2 g. of free hydroxylamine were added. The mixture was cooled at first, and then allowed to stand for three hours. A solid separated which was removed by filtration. The filtrate, evaporated *in vacuo*, gave more of the acid. Yield, 80%.

This solid recrystallized from ethyl acetate melted at 92–93°. The fusion turned brown and gas was evolved. Recrystallized from amyl alcohol, from benzene, or from chloroform, it showed the same melting point.

0.2118 g. gave 21.87 cc. N_2 at 27° and 743.5 mm.
Calc. for $C_2H_4O_2ClN$: N, 12.80. Found: N, 12.89.

Treated with acetic anhydride at 70° it gave an acetyl derivative which melted at 85–86°.

When the acid (melting point 92–93°) was kept in an open vessel, the melting point fell, reaching a minimum not far from 62°, but complete fusion did not occur until 74° was recorded. After standing for four days, the melting point was found to be 108–108.5°. The fused substance did not turn brown and there was scarcely any gas evolution. When heated to 70° with acetic anhydride, this form gave an acetyl derivative which melted at 67°.

Recrystallized from ethyl acetate, the acid gave the following figures on analysis:

0.2068 g. gave 0.1658 g. CO_2 and 0.0702 g. H_2O; 0.1815 g. gave 21.9 cc. N_2 at 25° and 739.7 mm.; 0.1674 g. gave 0.1634 g. AgCl.
Calc. for $C_2H_4O_2ClN$: C, 21.83; H, 3.68; N, 12.79; Cl, 32.38.
Found: C, 21.86; H, 3.77; N, 12.91; Cl, 32.00.

Salts.—An alcoholic solution of the acid treated with sodium ethylate gave a white sodium salt when ether was added. When heated this salt exploded with a brilliant yellow flame. With silver nitrate, a water solution of the silver salt gave a pure white silver salt, which soon turned green, then brown with precipitation of metallic silver. The copper salt formed by addition of copper acetate was a dark green powder which, upon analysis, gave figures correspondingly close with those for a basic copper salt, $C_4H_6O_5N_2Cl_2Cu_2$, similar to the basic copper salt of acethydroxamic acid described by Crismer.

2. **Monobromoacethydroxamic Acid,** $BrCH_2.CO(NH(OH))$.—When a cold alcoholic solution of hydroxylamine was treated with the calculated amount of ethyl monobromoacetate, the mixture became warm, and, in

the course of a few minutes, a white solid separated. This solid was purified by crystallization from alcohol. It melted at 110°, and proved to be "basic" hydroxylammonium bromide, $(NH_2(OH))_2HBr$. This fact was established by converting the substance into benzophenone oxime (melting point 142°), and by analysis.

0.3192 g. gave 0.3975 g. AgBr.

Calc. for $N_2H_7O_2Br_2$: Br, 54.51. Found: Br, 54.55.

A hydroxamic acid was formed simultaneously, since the solution gave an intense color reaction with ferric chloride and gave an insoluble copper salt. But it was not possible to isolate the hydroxamic acid, since it was so badly contaminated with other products, so that only an oil was obtained when the alcoholic solution resulting from the decomposition of the dried copper salt by hydrogen sulfide was evaporated.

If the "basic" hydroxylammonium bromide was not removed, a further reaction occurred. The basic salt gradually disappeared, and upon evaporation of the solution *in vacuo*, a thick, pasty mass remained which still contained some unchanged ethyl ester, and some hydroxamic acid, but the greater part of the solid was normal hydroxylammonium bromide, $NH_3(OH)Br$.

After this solid residue was freed from oil on a porous plate, it was extracted with acetic ethyl ester. A new compound, containing no bromine, was obtained in this way. This new substance was not a hydroxamic acid since it gave no color reaction with ferric chloride and no copper salt with copper acetate. It reduced ammoniacal silver nitrate at once. It was soluble in alcohol, in water, in ether and in petroleum ether from which it crystallized in long slender needles which melted at 65°.

It could be prepared in considerable quantities by treating a methyl-alcoholic solution of hydroxylamine, prepared by mixing sodium methylate with an alcoholic solution of hydroxylammonium chloride, with an equivalent amount of ethyl monobromoacetate. The reaction was complete in three or four days. The alcohol was removed by means of a blast of air, and water was added to the residue. If the solution is not acid, it should be acidified with acetic acid, and then extracted repeatedly with ether. After drying the ether solution with anhydrous sodium sulfate, the ether was evaporated in a current of air. An oil was left which solidified in a short time. The solid, freed from a slight amount of adhering oil, was recrystallized from ligroin, with a little animal charcoal to remove coloring matter. Melting point, 65°. (An interpretation of the reaction and the possible formulas for this compound were considered in the introduction to the experimental part.)

0.2714 g. gave 0.4647 g. CO_2 and 0.19249 H_2O.

0.0892 gave 5.99 cc. N_2 at 30° and 746 mm.

Calc. for $C_8H_{15}NO_5$: C, 46.79; H, 7.37; N, 6.83.

Found: C, 46.69; H, 7.88; N, 7.10.

The simplest empirical formula calculated from the analytical values was $C_8H_{15}NO_5$.

The Preparation of Monobromoacethydroxamic Acid.—Monobromoacethydroxamic acid was finally prepared by mixing 20 g. of bromoacetyl bromide with a solution of one equivalent of hydroxylammonium chloride in 200 cc. of water containing two equivalents of sodium carbonate. The acid bromide was added in small portions, and the mixture was shaken vigorously each time until the portion added disappeared. At all times the temperature was kept below 10°. Finally, any excess of sodium carbonate was decomposed by acetic acid, and the hydroxamic acid was precipitated by means of copper acetate. The copper salt was collected, washed and dried. The yield was nearly quantitative. The analysis showed that the copper salt was a basic salt.

0.6512 g. gave 35.7 cc. N at 22° and 746 mm.
Calc. for $C_4H_4Br_2N_2O_3.2CuOH$: N, 6.23. Found: N, 6.18.

The hydroxamic acid, itself, was obtained by suspending the copper salt in alcohol and treating it with hydrogen sulfide. The alcoholic solution filtered from the copper sulfide was evaporated rapidly in a current of dry air. It was necessary to remove the alcohol rapidly, and at a low temperature, since the hydroxamic acid reacted with alcohol by reversible reaction to give ethyl bromoacetate and free hydroxylamine. The crystals of the hydroxamic acid were recrystallized from ethyl acetate at a temperature not above 60°.

The pure acid melted at 103°. It was soluble in alcohol, in water and in ethyl acetate; only slightly soluble in chloroform, or in benzene, and insoluble in petroleum ether. It gave a cherry red color reaction with a solution of ferric chloride.

0.2772 g. gave 24.4 cc. N_2 at 27° and 745 mm.
Calc. for $C_2H_4BrO_2N$: N, 9.08. Found: N, 9.48.

3. **Monoiodoacethydroxamic Acid,** $ICH_2.CO(NH(OH))$.—When ethyl iodoacetate, dissolved in alcohol, was allowed to interact with the calculated amount of free hydroxylamine, difficulties similar to those described in the case of ethyl monobromoacetate were encountered. Basic hydroxylammonium iodide separated at first. This gradually disappeared, and a mixture resulted from which hydroxylammonium iodide and oily products were obtained by evaporation of the alcohol. From this residue, by the method described above, the same solid, $C_8H_{15}NO_5$, melting at 65°, was isolated. Only a small amount of the desired hydroxamic acid was present.

The Preparation of Monoiodoacethydroxamic Acid.—Fifteen grams of iodocetyl chloride were added gradually to an aqueous solution of hydroxylammonium chloride to which two equivalents of sodium carbonate had been added. The temperature was kept below 10°, and the solution was shaken vigorously as the acid chloride was added. The reaction mixture was neutralized with acetic acid, and treated with an excess of copper acetate. The dark green copper salt proved to be a normal copper salt of iodoacethydroxamic acid,

0.6372 g. gave 35.6 cc. N_2 at 28° and 731 mm.
Calc. for $C_4H_6O_4N_2I_2Cu$: N, 6.05. Found: N, 5.98.

The dried copper salt was suspended in absolute alcohol and decomposed by means of hydrogen sulfide. The filtrate was evaporated rapidly by means of a current of cold air, and the crystals of the hydroxamic acid were purified by recrystallization from ethyl acetate at a temperature not exceeding 60°.

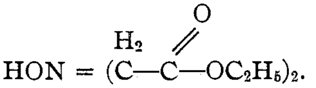
The hydroxamic acid was a white crystalline powder, which melted at 107.5° (corr). It was readily soluble in water, in ethyl and in methyl alcohol, slightly soluble in chloroform and in benzene, but insoluble in petroleum ether. Ethyl acetate was the best solvent for it. It gave a cherry red color reaction with ferric chloride.

0.2982 g. gave 19.6 cc. N_2 at 29° and 739 mm.
Calc. for $C_2H_4O_2NI$: N, 6.97. Found: N, 7.02.

Summary.

The preparation and properties of the hydroxylammonium salts of monochloro-, dichloro- and trichloroacetic acid were described. When heated carefully, these hydroxylammonium salts gave small quantities of the corresponding hydroxamic acids.

The methods of preparation and properties of monochloro-, monobromo-, and monoiodoacethydroxamic acids were described. The action of ethyl monobromoacetate and of monoiodoacetate upon hydroxylamine gave, among other substances, a new compound of the formula $C_8H_{15}NO_5$, which is probably a β,β-disubstituted hydroxylamine of the formula,



$$HON = (\overset{H_2}{C}-\overset{\overset{O}{/\!/}}{C}-OC_2H_5)_2.$$

CINCINNATI, OHIO.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

THE CATALYTIC INFLUENCE OF ACIDS IN LACTONE FORMATION. PART I. VALEROLACTONE.

BY HUGH STOTT TAYLOR AND HAROLD WILBERFORCE CLOSE.

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The accelerating influence of acids on the velocity of a great many chemical reactions has long been known, and the approximate proportionality between this catalyzing power of acids and their hydrogen ion concentration was recognized upon the formulation of the electrolytic