

2. The evidence indicates that some iodine substituted aliphatic acids are more stable than the analogous bromine compounds.

3. α -Halogen substituted acids are more stable than isomeric β -halogen substituted acids.

4. The effect of position on the stability of a halogen substituted acid is greater than the identity of the halogen.

5. The replacement of a hydrogen atom on the carbon atom carrying the halogen by an aliphatic radicle renders the acids less stable.

6. The replacement of a second hydrogen atom on the carbon atom carrying the halogen by an aliphatic radicle greatly decreases the stability of the acid.

7. The larger the aliphatic group substituted the more unstable the acid becomes.

8. The presence of a second halogen in the α -position of the acid (irrespective of the replacement of that second halogen) renders the removal of the first halogen in either the α - or β -positions more difficult.

The writer is indebted to W. A. Drushel for his coöperation in this work.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY.]

THE NEUTRAL AMMONIUM SALTS OF ORGANIC ACIDS AND THEIR SUBSTITUTED DERIVATIVES.

[SEVENTH COMMUNICATION.¹]

BY LEROY McMASTER AND LETA WRIGHT.

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This work is a continuation of the preparation and investigation of the properties of neutral ammonium salts of organic acids and their substituted derivatives. The salts described in this paper were prepared by the same general method as was used in the previous investigations, *i. e.*, by passing dry ammonia into solutions of the acids in anhydrous organic solvents. We have thus prepared and studied the ammonium salts of 1,2,3-methylhydroxybenzoic, 1,3,4-methylhydroxybenzoic, 1,4,3-methylhydroxybenzoic, 1,2,4-dihydroxybenzoic, 1,2,5-dihydroxybenzoic, 1,2,4-dinitrobenzoic, *o*-nitrocinnamic, *m*-nitrocinnamic, *p*-nitrocinnamic, α -naphthoic, β -naphthoic, *m*-nitrobenzenesulfonic, *m*-aminobenzenesulfonic (metanilic) 1,2,4-nitrotoluenesulfonic, 1,4-naphthylaminesulfonic (naphthionic), 1,4-naphtholsulfonic, 1,5-naphtholsulfonic, benzilic, oxanilic and phenyl-

¹ For previous papers on this subject see *Am. Chem. J.*, **49**, 84-7 (1913); *Chem. News*, **108**, 136-7 (1913); *Am. Chem. J.*, **49**, 294-301 (1913); *Chem. News*, **108**, 182-3, 193-4 (1913); *THIS JOURNAL*, **36**, 742-7 (1914); *Chem. News*, **110**, 212-4 (1914); *THIS JOURNAL*, **36**, 1916-25 (1914); *Chem. News*, **110**, 224-8 (1914); *THIS JOURNAL*, **37**, 2181-8 (1915); *Chem. News*, **112**, 187-9 (1915); *THIS JOURNAL*, **38**, 1785-1803 (1916); *Chem. News*, **114**, 217-221, 224-227, 238-239 (1916).

propionic acids. After the salts were precipitated and tested for neutrality they were quickly filtered by suction, washed with anhydrous ether and allowed to stand for a short time in a vacuum desiccator.

Substituted Benzoic Acids. Methylhydroxybenzoic Acids.

There are 10 acids of the formula $\text{CH}_3\text{C}_6\text{H}_3(\text{OH})\text{CO}_2\text{H}$ known,¹ and are sometimes called the cresotinic acids. We have been able to procure from Kahlbaum the 1-methyl-2-hydroxy-3-carboxylic acid, the 1-methyl-3-hydroxy-4-carboxylic acid, and the 1-methyl-4-hydroxy-3-carboxylic acid. All three of them gave neutral ammonium salts.

Ammonium Salt of the 1-Methyl-2-hydroxy Acid.—Hübner² worked with some of the salts of this acid, but not with the ammonium salt. No record can be found of its preparation. A very stable salt is formed when an ether solution of the acid is saturated with dry ammonia. It dries in the form of pink-tinted needles which tend to adhere to each other to form cotton-like masses. The salt is exceedingly soluble in ethyl alcohol and will not precipitate from a mixture made of equal parts of alcohol and ether. It is also soluble in methyl alcohol and acetone, slightly soluble in ethyl acetate, and insoluble in ether, chloroform and benzene. The aqueous solution of the salt does not hydrolyze. The salt is not hygroscopic and does not lose ammonia when dried at 100°. Moist air causes it to lose ammonia slowly.

Calc. for $\text{CH}_3\text{C}_6\text{H}_3(\text{OH})\text{CO}_2(\text{NH}_4)$: N, 8.29%. Found: 8.31%.

Ammonium Salt of the 1-Methyl-3-hydroxy Acid.—No reference to this salt is made in the literature. A quantitative yield was obtained when it was precipitated from an ether solution of the acid. It formed in beautiful, pure white needles which, like those of the preceding salt, formed into lustrous, cotton-like masses. When the ammonia was passed into the acid solution, an amorphous, semi-transparent mass formed at first, which very soon changed to a voluminous precipitate of needles, which are not deliquescent. The salt is soluble in methyl and ethyl alcohols and acetone, slightly soluble in ethyl acetate, and insoluble in ether and benzene. It is not quite as stable as the preceding salt, since moist air decomposes it rather readily. Dry air at 50° for 1 hour has no effect on the salt, while at 100° it decomposes slightly within 30 minutes. Its aqueous solution remains neutral and the salt does not hydrolyze.

Calc. for $\text{CH}_3\text{C}_6\text{H}_3(\text{OH})\text{CO}_2(\text{NH}_4)$: N, 8.29%. Found: 8.27%.

Ammonium Salt of the 1-Methyl-4-hydroxy Acid.—When ammonia was passed into an ether solution of the acid, there was first formed an amorphous mass, which soon changed to a white, cotton-like mass of needles.

¹ *Ber.*, 16, 1966 (1883).

² *Monatsh.*, 15, 725 (1894).

This was similar to the action taking place in the preparation of the two preceding salts. We attempted to prepare this salt also in an ethyl acetate solution of the acid since we had found that the 1,2,3- and the 1,3,4-salts were only slightly soluble in that solvent. No yield was obtained as the salt was found to be readily soluble in ethyl acetate. It is also very soluble in water, methyl and ethyl alcohols and acetic acid but only slightly soluble in benzene. It is not hygroscopic and its neutral aqueous solution does not hydrolyze.

The salt is a little less stable than its two preceding isomers, but even as that it is quite stable. At ordinary temperatures it does not decompose in dry air, and when heated at 50° for 1 hour it decomposes but slightly. Moist air at ordinary temperatures decomposes it slowly. When heated to 100°, the salt decomposes into ammonia and the acid. The literature makes no mention of this salt so far as we can find.

Calc. for $\text{CH}_3\text{C}_6\text{H}_3(\text{OH})\text{CO}_2(\text{NH}_4)$: N, 8.29%. Found: 8.30%.

All three of these salts have a faint phenol odor, which is also characteristic of the free acids. It should be noted that all of them precipitate from ether solutions of the acids in the form of needle-like crystals. It has been found that a majority of the ammonium salts prepared in ether form as non-crystalline bodies.

Dihydroxybenzoic Acids.

Ammonium 1,2,4-Dihydroxybenzoate.—Since the acid is called resorcylic acid, another name for the salt would be ammonium resorcylate. The acid formed an orange-red solution with ether, from which the salt precipitated as a delicately colored pink powder. It precipitated immediately and in rather voluminous quantities. This delicately colored salt shared with the free acid the property of making highly colored solutions. With water a light brown solution was formed, which, upon the addition of sodium hydroxide solution, changed to a dark rich, red-brown color. Ammonium resorcylate is soluble in both methyl and ethyl alcohols, but is insoluble in ethyl acetate, ether, benzene and acetone. It decomposes slightly in dry air at 50° after 40 minutes, and rapidly gives off ammonia when the temperature has been 100° for a half hour. Its solution with water remains neutral for some time. The salt is not hygroscopic.

Calc. for $\text{C}_6\text{H}_3(\text{OH})_2\text{CO}_2(\text{NH}_4)$: N, 8.19%. Found: 8.25%.

Ammonium 1,2,5-Dihydroxybenzoate or Ammonium Gentisate.—The acid formed with ethyl acetate a dark brown solution, from which ammonia precipitated a dark, gelatinous, pasty mass; but, on shaking and on further addition of ammonia, this gelatinous mass was replaced by a light brown, amorphous powder. The color became lighter, and when precipitation was complete the precipitate was almost white. When it was dried and powdered it was a very slightly colored substance, but, after standing for

5 months, the color was somewhat darker, probably on account of slight decomposition. The salt forms a neutral solution with water, and is soluble in acetic acid and methyl alcohol, slightly soluble in ethyl alcohol, but insoluble in ether, ethyl acetate, benzene and chloroform. Acetone very slightly dissolves it. It does not lose ammonia on exposure to dry air at 50°, and even at 100° there is but very little loss after some length of time. The salt is not deliquescent.

Calc. for $C_6H_5(OH)_2CO_2(NH_4)$: N, 8.19%. Found: 8.19%.

A Dinitrobenzoic Acid.

Ammonium 1,2,4-Dinitrobenzoate.—The ammonium 1,3,5-dinitrobenzoate¹ has been prepared in this laboratory in ether solution and found to be a white, amorphous powder, having a slight yellowish tinge. We have also prepared the 1,2,4-salt in ether. When the ammonia was passed into an ether solution of the acid, a transparent, yellowish, gelatinous mass was first formed. This soon changed to a yellowish white, flocculent precipitate and then to an amorphous powder. After drying, the salt was found to have the same color as the 1,3,5-body. It is not as stable in the air as the latter salt for it gives off ammonia very slowly in dry air and rapidly in moist air. The temperature of the dry air does not seem to affect the rate of decomposition of the salt. The 1,3,5-salt is stable in dry air and loses its ammonia only very slowly in moist air. Neither salt is deliquescent. The aqueous solution of the 1,3,5-salt does not hydrolyze even on standing for several days, while that of the 1,2,4-salt is neutral at first but becomes acid after several hours. A peculiar difference between the two salts is to be observed in their solubilities. The 1,3,5-salt is soluble in all the ordinary organic solvents except ether, though not very readily in acetone; the 1,2,4-salt is practically insoluble in all the organic solvents except methyl alcohol.

In determining the ammonium nitrogen high results were always obtained so we made determinations of the total nitrogen.

Calc. for $C_6H_3(NO_2)_2CO_2(NH_4)$: total N, 18.35%. Found: 18.32%.

The Nitrocinnamic Acids.

Ammonium *o*-Nitrocinnamate.—The free acid was found to be insoluble in all the usual organic solvents except acetone, in which it is very slightly soluble. Moreover, the ammonium salt is very soluble in most of the solvents, except ethyl acetate and benzene in which it is insoluble. Acetone dissolves the salt but slightly.

When ammonia was passed into a suspension of the acid in ethyl alcohol, a precipitate formed which went into solution at once. It could not be reprecipitated by any reagent obtainable since its solubility in ethyl alcohol is so great. When a suspension of the acid in ether was saturated

¹ THIS JOURNAL, 38, 2187 (1915).

with ammonia, a yellow, amorphous precipitate, lighter in color than the free acid, which has a rich yellow color, was formed. Tests for neutrality and analysis proved this precipitate to be the neutral ammonium salt. The salt is not deliquescent and its aqueous solution does not hydrolyze. In dry air the salt does not lose ammonia but does so in moist air.

Calc. for $C_8H_6(NO_2)CO_2(NH_4)$: ammonium N, 6.67%. Found: 6.62%.

Calc. for $C_9H_{10}N_2O_4$: total N, 13.33%. Found: 13.31%.

Ammonium *m*-Nitrocinnamate.—The free acid is insoluble in the organic solvents, except in ethyl acetate. When an ethyl acetate solution of the acid was saturated with ammonia, a white, curdy mass formed, which changed almost at once to a very fine, noncrystalline substance. It was very difficult to dry this precipitate. It was not possible to drain off the solvent, even with strong suction; so the pasty mass was placed for about an hour in a vacuum desiccator. It was then ground to a fine, chalky powder, which loses its ammonia very slowly in a moist atmosphere. The salt is not hygroscopic, and its aqueous solution remains neutral for several hours. The salt was found to be a rather difficultly soluble compound. It is most soluble in acetic acid, and only sparingly so in water, methyl alcohol and acetone. It is insoluble in ethyl alcohol, ether and benzene.

The salt decomposes very slowly in hot, dry air. At 50° for 30 minutes the decomposition is slow, but at 100° for 15 minutes ammonia is rapidly given off. Analysis of the salt prepared in ethyl acetate proved it to be the neutral body.

Calc. for $C_8H_6(NO_2)CO_2(NH_4)$: total N, 13.33%. Found: 13.34%.

Ammonium *p*-Nitrocinnamate.—As in the two preceding cases, difficulty was encountered in getting the acid into solution. The acid was so very slightly soluble in all the organic solvents that we tried a suspension of it in ethyl alcohol; but, as was the case with the *o*-salt, this ammonium salt was so soluble in the alcohol that it would not precipitate nor could we precipitate it by adding large amounts of other solvents to the alcohol solution. When a suspension of the acid in ether was tried, we obtained a fine, yellow powder of the neutral ammonium salt. This salt was soluble in water with difficulty, readily soluble in methyl alcohol, ethyl acetate and ethyl alcohol, slightly soluble in acetone but insoluble in ether, chloroform and benzene. It decomposed at 50° . The salt is not hygroscopic and its aqueous solution hydrolyzes very slowly.

Calc. for $C_8H_6(NO_2)CO_2(NH_4)$: total N, 13.33%. Found: 13.32%.

Most of the neutral ammonium salts so far prepared have been found to be readily soluble in water, but these three nitro-salts were unusually difficult to dissolve in water. Ammonium cinnamate,¹ previously prepared, was

¹ *Am. Chem. J.*, 49, 300 (1913).

found to be much more soluble in water than these three nitro-derivatives. However, the ammonium nitrocinnamates resemble the ammonium cinnamate in many respects. When ammonia is conducted into an ether solution of cinnamic acid, a gelatinous precipitate is first obtained which later changes to an amorphous form. The same phenomenon occurs in the formation of the *m*-nitrocinnamate in ethyl acetate but not in the formation of the *o*- and *p*-salts in ether. We could find no record of any of these salts having been previously prepared even in aqueous solution.

The Naphthoic Acids.

Ammonium α -Naphthoate.—The barium, calcium and silver salts of α -naphthoic acid have been prepared by Hofman,¹ but no reference to the ammonium salt can be found. The acid is not soluble in ether, but is easily soluble in hot ethyl alcohol. However, the ammonium salt is so very soluble in alcohol that it is impossible to precipitate it in this medium even in the presence of a large amount of ether. It was, therefore, necessary to pass the ammonia into a suspension of the acid in ether, whereupon the ammonium salt quickly formed as a fine, white powder. The aqueous solution is neutral and does not hydrolyze for a number of hours. The salt is not hygroscopic and does not give off ammonia in dry air at room temperature. Moist air decomposes the salt slowly. When heated to 50° in dry air decomposition is perceptible after 40 minutes. After 10 minutes at 100° it is rapidly broken up, giving off ammonia freely.

The salt is very soluble in methyl and ethyl alcohols, moderately soluble in acetone and acetic acid, and insoluble in ether, chloroform, ethyl acetate and benzene.

Calc. for $C_{10}H_7CO_2(NH_4)$: N, 7.41%. Found: 7.40%.

Ammonium β -Naphthoate.—A number² of the salts of β -naphthoic acid have been made and studied, but there is no record of the neutral ammonium salt. The acid is readily soluble in both ether and ethyl alcohol and the ammonium salt can be prepared in either solvent. When prepared in ether it forms as a pure white, amorphous powder. Its aqueous solution does not hydrolyze. The salt dries quickly, is not hygroscopic, and does not give off ammonia in dry air at ordinary temperatures. In moist air ammonia is given off. At 50° in dry air for 30 minutes the salt decomposes, and at 100° marked decomposition takes place within 15 minutes.

The salt is insoluble in ethyl acetate, chloroform, acetone, ether and benzene and only slightly soluble in ethyl alcohol. Except for certain differences in solubility, the properties of this salt closely resemble those of the α -salt.

Calc. for $C_{10}H_7CO_2(NH_4)$: N, 7.41%. Found: 7.39%.

¹ *Ber.*, 1, 39 (1868).

² Vieth, *Ann.*, 180, 305 (1876); Merz and Mühlhäuser, *Z. Chem.*, 5, 70 (1869).

Sulfonic Acids.

The literature mentions a few ammonium salts of the sulfonic acids prepared in aqueous solution, but their properties are very inadequately described. Having never applied our general method to the preparation of ammonium salts of this class of acids, we turned our attention to the preparation of some of them. Our results show that they can thus be readily made.

Ammonium *m*-Nitrobenzenesulfonate.—Limpricht¹ describes this salt as crystallizing in clear leaflets without water of crystallization, but gives nothing further of its properties. We prepared this salt in an ether solution as a white, bulky, noncrystalline compound. The salt dries quickly in the air and is very stable. It is not deliquescent, and does not give off ammonia in moist air nor in dry air at any temperature up to 100°. At this temperature there is no evidence of any decomposition. The salt is soluble in water, to which it imparts a neutral reaction for at least several days. We could not prepare it in an ethyl alcohol solution on account of its solubility in that solvent. The salt is slightly soluble in methyl alcohol, and insoluble in chloroform, ether and acetone.

Calc. for $C_6H_4(NO_2)SO_3(NH_4)$: ammonium N, 6.36%. Found: 6.37%.

Ammonium *m*-Aminobenzenesulfonate or Ammonium Metanilate.—It was found that the acid is insoluble in ether and soluble in alcoholic ammonia. The ammonium salt was probably formed, but would not precipitate on account of its solubility in the ethyl alcohol. After saturating this alcohol solution with ammonia, an attempt was made to precipitate the salt by adding an excess of ether. A white, colloidal product resulted, which could not be filtered even on an alundum crucible. The mixture was allowed to stand for a number of days and, after the ether had evaporated, a clear, yellowish solution remained. Upon further evaporation, the alcoholic solution became darker in color and finally turned red. No crystals separated until practically all the solvent had evaporated, whereupon large, dark red, thick plates appeared. They gave a neutral reaction when dissolved in water. This aqueous solution, which was reddish in color, did not hydrolyze until it had stood for 2 days. The salt was stable at ordinary temperatures and slowly decomposed in dry air at 50°. It was decomposed readily in moist air.

Calc. for $C_6H_4(NH_2)SO_3(NH_4)$: ammonium N, 7.37%. Found: 7.38%.

Ammonium 1,2,4-Nitrotoluenesulfonate.—Jenssen² mentions this salt but tells nothing about it except that it crystallizes in long, fine needles, and is not decomposed at 190°. An attempt was made to precipitate it in ethyl alcohol, because it was thought that a better crystalline form could be obtained from alcohol than from ether. But though there was some

¹ *Ann.*, 177, 73 (1875).

² *Ibid.*, 172, 232 (1874).

precipitation, it took place very slowly and very incompletely. The free acid was found to be insoluble in ether, but the ammonium salt came out beautifully when a suspension of the acid in ether was saturated with ammonia. The white precipitate was amorphous in form, and all of the free acid was converted into the salt. There was a slight amount of heat generated in this precipitation. This is unusual for it has been found that almost always there is no heat generated when ether is used. The salt is not deliquescent. In dry air at 50° , there was evidence of some decomposition of the salt after 30 minutes, but the rate was not much increased when the temperature was raised to 100° . Moist air decomposed it slowly. It was found to be slightly soluble in methyl alcohol, still less so in acetone and insoluble in ether and chloroform. It is slightly soluble in ethyl alcohol. The aqueous solution is neutral and does not hydrolyze readily.

Calc. for $\text{CH}_3\text{C}_6\text{H}_3(\text{NO}_2)\text{SO}_3(\text{NH}_4)$: ammonium N, 5.98%. Found: 6.02%.

The ammonium nitrotoluenesulfonate is less stable than the nitrobenzenesulfonate, but in other ways the salts resemble each other. The ammonium nitrotoluenesulfonate has a peculiar odor which is not noticeable with the ammonium nitrobenzenesulfonate.

Ammonium 1,4-Naphthylaminesulfonate.—The ammonium salt of this acid known as naphthionic acid is not mentioned in the literature. It was found that the acid is a very insoluble substance. A suspension of the acid in ethyl acetate was used for making the ammonium salt. It was easy to see it changing over to the salt, for the acid is a chalky white, amorphous powder, while the ammonium salt is pinkish brown in color and possesses a distinct crystalline form. Ammonium naphthionate is soluble in methyl and ethyl alcohols, and warm water. It is only slightly soluble in cold water. In solution it gives a red and blue fluorescence, which is characteristic of the salts¹ of naphthionic acid. The lead salt crystallizes in small, red grains, while the crystals of the ammonium salt are small pinkish brown grains. The ammonium salt forms a neutral aqueous solution which does not hydrolyze within 3 hours. The salt is stable in dry air at 50° , but after 30 minutes at 100° , there is a faintly perceptible change imparted to the color of sensitive red litmus paper. Moist air causes the salt to give off ammonia. It does not deliquesce.

Calc. for $\text{C}_{10}\text{H}_6(\text{NH}_2)\text{SO}_3(\text{NH}_4)$: ammonium N, 5.83%. Found: 5.86%.

Ammonium 1,4-Naphtholsulfonate.—There is no reference to this salt in the literature, though a number of other salts of the free acid, which is called "Neville, Winther's acid," have been investigated.² The acid is a very insoluble substance, but methyl alcohol and ethyl alcohol dissolve it slightly. The salt is very soluble in methyl alcohol, but was precipitated by adding to the solution 10 times its volume of anhydrous ether. It was

¹ Piria, *Ann.*, 78, 31 (1851).

² *Ber.*, 13, 1949 (1880); *Ann.*, 273, 107 (1893).

almost impossible to free the salt of the excess of solvent. It rapidly decomposed in dry and in moist air at ordinary temperatures, and its water solution, though neutral for about 3 minutes, quickly hydrolyzed and gave an acid reaction. The salt is a light brown powder, a "cocoa" colored substance, while the free acid is slightly pink. By the time the salt was thoroughly dry (a period of several days), analysis showed that it had greatly decomposed.

The salt was also prepared in a benzene suspension of the acid, and the same brown colored powder was obtained. It dried very much more readily than the methyl alcohol product, but it gave off ammonia very rapidly. It was analyzed a few hours after it was made, and the results showed that it had then more than half decomposed, although it had been either in a vacuum desiccator or in a tightly stoppered bottle during the meantime. At first a water solution of the freshly prepared salt showed a neutral reaction, but it soon hydrolyzed. The salt is insoluble in ether, chloroform, acetone, ethyl acetate and benzene.

Ammonium 1,5-Naphtholsulfonate.—It was thought best to prepare this salt from an ether suspension, since it was found that it was, like the 1,4-salt, very soluble in methyl alcohol, which is the only medium in which the free acid is easily soluble. The salt was quickly filtered and dried. It dried quickly to a finely divided, brownish powder, an aqueous solution of which gave a neutral test for a period of 10 minutes. Dry air at ordinary temperatures does not decompose it within a period of 15 minutes, but after that it does. It quickly decomposes at 50° in dry air, and moist air at ordinary temperatures decomposes it readily.

Both this 1,5-salt and the salt of Nevile, Winther's acid are very soluble in methyl alcohol, somewhat soluble in ethyl alcohol, and insoluble in ether, ethyl acetate, benzene, chloroform and acetone. The 1,4-salt is also insoluble in acetic acid, while the 1,5-salt shows a slight solubility in this medium. The latter salt, as well as the former, lost ammonia so readily that one analysis showed only 2.25% N. The correct value is 5.81%.

Other Acids.

Ammonium Benzilate.—There is no record of this salt ever having been prepared, though other salts of benzoic acid have been studied.¹ The free acid is soluble in methyl and ethyl alcohols, ether and ethyl acetate, but ammonia will not precipitate the salt from any of these solutions. In ether, a precipitate did form at first as an amorphous, white powder, but on addition of more ammonia this changed to a sticky half-transparent mass, which in turn dissolved when still more ammonia was added. Finally a benzene suspension was treated with ammonia. The fine, white needles of the free acid were very rapidly changed over into a yellowish mass exactly like that encountered in one stage of the ether solution treatment.

¹ Symons and Zincke, *Ann.*, 171, 131 (1874).

This mass did not change in appearance materially for a period of 3 hours, during which time ammonia was constantly bubbled through the solution. At the end of that time the flask was removed and stoppered. It was allowed to stand for 2 days and then small transparent crystals were seen distributed over the bottom and sides of the flask. The mass that had been soft and sticky had become hard, and when broken up it was found to consist of the same small granular crystals which coated the flask. These crystals were filtered and dried in a vacuum for a short time, and tested for neutrality and stability. Their aqueous solution was neutral. They are not deliquescent. Moist air slowly decomposes the salt, and dry air at 50° causes it to lose ammonia after 30 minutes.

Calc. for $(C_6H_5)_2C(OH)CO_2(NH_4)$: N, 5.71%. Found: 5.71%.

This diphenylhydroxyammonium acetate resembles very much more closely the salts of phenylacetic acid and its substituted derivatives than it does that of glycolic acid itself. It has been found by one of us that ammonium phenylacetate and the substituted phenylacetates are stable salts, some of which are yellowish in color; they give off ammonia slowly in moist air, and they can all be prepared in alcohol. This is not true of the benzilate and that fact constitutes the only point of resemblance between the benzilate and glycolate itself. Ammonium glycolate¹ rapidly loses ammonia in the air and is hygroscopic. Also, a water solution of ammonium glycolate hydrolyzes very readily, and one of ammonium benzilate does not.

Ammonium Oxanilate.—This salt has been prepared and some of its properties studied.² It is described as plates, slightly soluble in cold water and cold alcohol, but very soluble in hot water and hot alcohol. It is also stated that it begins to lose its ammonia at 190°.

The neutral salt can be precipitated from an ether suspension of the acid in the form of a curdy mass or as a flaky precipitate from a methyl or ethyl alcohol solution of the acid. Considerable heat was developed when the ammonia was passed into the alcohol solutions and it was necessary to keep the solutions cold. Flaky, yellowish white crystals precipitated. When perfectly dry, the salt is composed of fine, white needles.

The salt is soluble with difficulty in cold water, to which it imparts a neutral reaction. The aqueous solution does not hydrolyze. It is only slightly soluble in methyl and ethyl alcohols, and insoluble in acetone, ether and benzene. The salt is not deliquescent and gives off no ammonia in dry air until heated above 100°. Laurent and Gerhardt found that at 190° this salt began to lose ammonia and at the same time a little aniline was formed and finally there remained oxanilide. On gently heating, we also found aniline to be formed. In moist air ammonia is slowly given off.

¹ McMaster and Magill, *THIS JOURNAL*, **38**, 1788 (1916).

² Laurent and Gerhardt, *Ann.*, **68**, 20 (1848); Aschan, *Ber.*, **23**, 1821 (1890).

Calc. for $\text{NH}(\text{C}_6\text{H}_5)\text{CO}\cdot\text{CO}_2(\text{NH}_4)$: total N, 15.38%. Found: 15.36%.

Ammonium Phenylpropiolate.—Phenylpropionic acid, which contains a triple bond, is the first acid of its type whose ammonium salt has been studied in this laboratory. There is no record of the salt having been made elsewhere. It was precipitated in an ether solution of the free acid. A little heat was developed during the saturation with ammonia, which is an unusual occurrence with ether solutions. The salt is a pure white powder, having a slight odor. It is somewhat soluble in ethyl alcohol, very soluble in methyl alcohol, and insoluble in chloroform, acetone, benzene and ether. An aqueous solution is neutral for about 2 hours, after which time it slowly hydrolyzes and gives an acid reaction. Moist air causes it to lose ammonia, but in dry air at 50° it remains unchanged for about 1 hour before it begins to lose ammonia slowly. The salt is not hygroscopic.

Calc. for $\text{C}_6\text{H}_5\text{C}\cdot\text{CCO}_2(\text{NH}_4)$: N, 8.59%. Found: 8.62%.

Work is still in progress in this laboratory on the ammonium salts of organic acids.

St. Louis, Mo.

[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIOCHEMISTRY, UNIVERSITY OF MINNESOTA.]

AN OPTICAL METHOD FOR THE DETERMINATION OF MALIC AND TARTARIC ACIDS IN THE SAME SOLUTIONS.¹

By J. J. WILLAMAN.

Received January 25, 1918.

Introduction.

For several years the question of optical methods for malic and for tartaric acids has been before the conventions of the Association of Official Agricultural Chemists. Such progress was made in the case of malic acid that a polariscopic method was incorporated in the official methods of the Association in 1916.² The method involves the increase in optical activity caused by uranyl acetate, a reaction first observed by Walden.³ A method for tartaric acid was not so successfully evolved, although its optical activity is likewise strongly increased by uranyl acetate.⁴

Where both acids occur in the same solution, a special problem arises. There is no way now known by which they can be separated quantitatively; hence any method for their determination must depend upon

¹ Published with the approval of the Director as Paper No. 111, Journal Series Minnesota Agricultural Experiment Station.

² "Methods of Analysis," *J. Assoc. Off. Agr. Chemists*, 1916.

³ Walden, "Über ein neues, die Drehungsgrösse steigerndes Mittel," *Ber.*, [3] 30, 2889-2895 (1897).

⁴ P. B. Dunbar, "The Determination of Tartaric Acid," *U. S. Dept. Agr. Bur. Chem. Circ.*, 106 (1912).