[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY.]

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

[SIXTH COMMUNICATION.[1]]

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This work is a continuation of the work which has been in progress in this laboratory for several years on the preparation and investigation of the properties of the neutral ammonium salts of organic acids and their substituted derivatives. The salts previously studied were prepared by passing dry ammonia into solutions of the acids in the anhydrous solvents, methyl alcohol, ethyl alcohol, ether, acetone and benzene or in mixtures of some of these solvents. In this work we have made use of these same solvents, except methyl alcohol, and in addition we have used pure ethyl acetate. Naumann[2] found that a great many ammonium salts of organic acids are insoluble in ethyl acetate. Bateman and Conrad[3] have recently found that the ammonium salts of some of the halogenoacetic acids are soluble in this reagent. In view of these facts, we thought it would be of interest to attempt to prepare some of the neutral ammonium salts in ethyl acetate. Several of the salts to be described were thus prepared. We have also tested the solubility of some of the ammonium salts in this solvent.

In the following work the neutral ammonium salts of tribromoacetic, phenylbromoacetic, *o*-nitrophenylacetic, phenylamidoacetic, glycolic, $\alpha$-bromopropionic, $\beta$-iodopropionic, $\beta$-chlorolactic, trichlorobutyric, caprylic, capric, lauric, myristic, $\alpha$-bromopalmitic, $\alpha$-bromostearic, acrylic, $\beta$-chlorocrotonic, erucic, dimethylmalonic, dipropylmalonic, isopropylmalonic, butylmalonic, allylmalonic, benzylmalonic, monobromosuccinic, dibromosuccinic, suberic and chlorofumaric acids have been prepared by passing dry ammonia into solutions of the respective organic acids in the above anhydrous solvents. A number of the properties of the salts were studied. The salts were quickly filtered by suction on alundum crucibles, washed with anhydrous ether, tested for neutrality, transferred to crystallizing dishes and placed for a short time in a vacuum desiccator.

The analysis of the salts consisted in determining the nitrogen by the Kjeldahl method. In all the salts except the phenylamidoacetate, the

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[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).

[2] *Ber.*, 43, 313 (1910).

[3] THIS JOURNAL, 37, 2553 (1915).

nitrogen present as "ammonium" nitrogen was determined, which is equal to the total nitrogen, except for the phenylamidoacetate and the *o*-nitrophenylacetate. In the case of these two salts, total nitrogen was also determined.

## The Substituted Acetic Acids.

**Ammonium Tribromoacetate.**—Schäffer[1] has prepared and investigated the properties of many of the salts of tribromoacetic acid, but did not prepare the ammonium salt. No reference to this salt can be found in the literature. When ammonia was passed into an ether solution of the acid the salt was precipitated as glistening white leaflets, soluble in water, methyl alcohol, ethyl alcohol and ethyl acetate. It is insoluble in ether, chloroform, acetone and benzene. A solution of the salt in water is neutral. The salt is not hygroscopic, and does not give off ammonia in dry or moist air. It decomposes rapidly, with evolution of ammonia, on heating to 50° and completely volatilizes below 100°.

This salt can also be prepared by saturating an alcoholic solution of the acid with ammonia and then adding an equal volume of ether. It has the same crystalline appearance as when it is prepared in ether alone.

Calc. for $CBr_3CO_2(NH_4)$: 4.96%. Found: 4.96% N.

There is a close resemblance in properties between ammonium tribromoacetate and ammonium monobromoacetate prepared by Bateman and Conrad.[2] Both salts crystallize in white leaflets from alcohol, and are soluble in water and ethyl acetate, and insoluble in benzene. The aqueous solution of the monobromo salt slowly hydrolyzes, while the solution of the tribromo salt does not hydrolyze. Neither salt is deliquescent and both are stable in the air. Both salts decompose on warming.

**Ammonium Phenylbromoacetate.**—There is no record of this salt having been prepared, even by the method of neutralization of an aqueous solution of the acid. It can be prepared in ether or ethyl alcohol. When prepared in ether it appears as a white amorphous powder, while it is formed as a crystalline compound in ethyl alcohol. The salt is somewhat hygroscopic and is very soluble in water. The solution, which is neutral at first, rapidly hydrolyzes. It decomposes rapidly in both dry and moist air, and when heated to 50° it decomposes very quickly, ammonia being evolved. The aqueous solution on being mixed with a solution of lead acetate slowly forms a white crystalline precipitate. The neutral ammonium salt is soluble in methyl alcohol, acetic acid and an excess of ethyl alcohol. It is very slightly soluble in acetone, and insoluble in ether and benzene.

Calc. for $C_6H_5CHBrCO_2(NH_4)$: 6.06%. Found: 6.02% N.

**Ammonium *o*-Nitrophenylacetate.**—No reference to this salt can be

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[1] *Ber.*, 4, 371 (1871).

[2] THIS JOURNAL, 37, 2553 (1915).

found in the literature. It readily precipitates from an ether solution in the form of pale yellow crystals. On account of its solubility in ethyl alcohol, it cannot be prepared in this medium; but if an alcoholic ammonia solution of the acid is added to a large amount of ether, the ammonium salt separates in yellow crystals. This salt was also prepared in acetone and in ethyl acetate in the form of yellow crystals. It is only very slightly soluble in these reagents, but is very soluble in water, methyl and ethyl alcohols, and acetic acid. It is insoluble in benzene and chloroform. The salt is not deliquescent and does not become acid in an aqueous solution which stood for twenty-four hours. It is stable in dry and moist air. It does not decompose at 50° but loses ammonia slowly when heated to 100°.

Both the total and the ammonium nitrogen were determined in this salt, and analyses of the salt prepared in the different solvents proved that we had the neutral salt.

Calc. for $C_6H_4NO_2CH_2CO_2(NH_4)$: 7.07% ammonium N. Found: 7.04% (ether); 7.03% (ethyl alc.); 7.06% (acetone); 7.02% (ethyl acetate).

Calc. for $C_8H_{10}N_2O_4$: 14.14% total N. Found: 14.10% (ether); 14.05% (ethyl acetate).

**Ammonium Phenylamidoacetate.**—Phenylamidoacetic acid is insoluble in ethyl alcohol, ether, benzene, ethyl acetate and acetone, but is soluble in water. While our line of work is mainly to prepare the ammonium salts in anhydrous organic solvents, nevertheless we attempted to prepare this compound in aqueous solution since the free acid is insoluble in the above reagents. Furthermore, we could find no reference to the salt having been prepared.

An aqueous solution of the acid was saturated with ammonia and the solution was allowed to evaporate to dryness. Several attempts were made to prepare the neutral salt by this method, but we obtained an acid salt in each case. This was to be expected, as most of the ammonium salts of the organic acids, when thus prepared, are the acid salts and not the neutral salts. Attention has been called to this fact in the introductory statements of the previous papers[1] on this work.

The neutral ammonium salt of phenylamidoacetic acid, however, was prepared by treating an alcoholic suspension of the acid with dry ammonia. Under this condition, the acid gradually passed into solution. Ether was then added to this solution and there was precipitated a salt in the form of a pale greenish gray powder. It was filtered, washed and dried in the usual way. Although the free acid is odorless, the salt thus prepared has a slight odor which is very disagreeable.

The salt is very soluble in water and benzene. It is somewhat soluble in methyl alcohol, ethyl alcohol, ethyl acetate and acetic acid. It is very

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[1] *Loc. cit.*

slightly soluble in acetone, and insoluble in ether and chloroform. The salt can be crystallized from benzene in splendid monoclinic crystals. The aqueous solution, which is neutral at first, slowly hydrolyzes and becomes acid. The salt does not lose ammonia in dry or moist air, but it is slightly deliquescent. When warmed to 50° the salt shows no evidence of decomposition, but at 100° ammonia is given off rapidly.

Calc. for $C_6H_5CHNH_2CO_2(NH_4)$: 16.67%. Found: 16.62% total N.

**Ammonium Glycolate.**—Heintz[1] mentions the acid ammonium salt of glycolic acid and states that it crystallizes as fine needles, which are easily soluble in water and hot alcohol. Ssabanejew[2] describes the preparation of a neutral solution of ammonium glycolate by treating a solution of glycolic acid with the calculated amount of ammonia. The experiment was carried out in a vacuum. On evaporation of the solution, there was obtained the acid salt in needle-like crystals. The literature contains no mention of the preparation of the neutral salt by precipitation.

On passing ammonia into a dilute solution of the acid in ethyl alcohol, a white precipitate of the ammonium salt at first appeared, which soon went into solution since this salt is quite soluble in alcohol. On continuing the addition of the ammonia, heat was developed and no further precipitate formed. The alcoholic solution was allowed to evaporate in the air and there was formed a syrupy liquid and some fan-like crystals. This experiment was repeated several times. The syrupy liquid was found to distil at but a few degrees below the boiling point of pure ethyl glycolate. The liquid was evidently a mixture of the ethyl ester of glycolic acid and ammonium salts of the acid.

Results similar to this have been previously noticed by one of us[3] and by Bateman and Conrad.[4] Heat favors the formation of the esters, and attention was called to the fact in a previous paper on this subject that, when the experiments are carried out in ethyl alcohol, it is necessary to keep the flasks surrounded by cold water, for, when the ammonia is passed into the solution of the acid in alcohol, heat is set free due to the action of the ammonia on the alcohol and also to the heat of neutralization. While in most of our experiments the precipitation flasks have been kept cold when the alcohols were used as solvents for the organic acids, in this case the flask was not kept cold. No doubt that in many of the cases, where the ammonium salts of even fairly strong acids were being prepared in the alcohols and the mixtures kept cold, small amounts of esters were formed. They were removed by the excess of alcohol and by the ether used to wash the salts while in the alundum crucible.

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[1] *Jahresb. Fortschr. Chem.*, 1861, p. 446.

[2] *Chem. Zentr.*, II, 32 (1899).

[3] McMaster, THIS JOURNAL, 36, 1923 (1914).

[4] *Loc. cit.*

However, when a very concentrated alcoholic solution of the glycolic acid was used, the precipitate, which formed at first was not redissolved and very little ester was formed. The most of the acid was converted into the ammonium salt, and the limit of the solubility of this salt in the alcohol present was reached. The salt formed in small salt-like crystals. When recrystallized from alcohol, they appeared in the form of needles.

When dry ammonia was passed into a solution of the acid in acetone, much heat was evolved and a fine white precipitate formed, which almost immediately dissolved to form a brown solution. Owing to the heat evolved, we suspected the formation of some diacetoamine by the action of ammonia on the acetone vapor present. In order to determine whether this was true, we prepared some diacetoamine by passing ammonia and acetone vapor together through a tube heated to 100°. This is the method used by Heintz[1] to prepare diacetoamine. To the diacetoamine was added an acetone solution of glycolic acid. Fine, white crystals were formed which were insoluble in an excess of the diacetoamine. They were presumably a salt,[2] formed by the action of the basic amine on the acid. If the diacetoamine is saturated with ammonia before adding the acid, white crystals form but almost immediately redissolve and form a brown solution. If some dry, neutral ammonium glycolate (preparation of which will be described later) is added to diacetoamine, it readily dissolves and forms the brown solution. From these reactions we have concluded that the white crystals which formed when the ammonia was passed into an acetone solution of the acid and which dissolved almost at once to form a brown solution, consisted of the neutral ammonium salt, soluble in the diacetoamine produced during the experiment as a result of the action of ammonia gas on the vapor of the acetone and the mixture becoming hot. While neutral ammonium salts of the organic acids have been previously prepared in acetone by one[3] of us, the formation of diacetoamine has not been encountered. The reason for this is probably due to the fact that the solutions were kept cool during the passing in of the ammonia, or that the heat of reaction was not so great as in this case. In fact, we repeated the experiment and kept the acetone solution of the glycolic acid cold while passing in the ammonia. No diacetoamine was formed, but it was found necessary to agitate the cold acetone solution of the acid in an atmosphere of ammonia for several hours in order to obtain a yield of the ammonium salt. The salt separated out as fine, white crystals and analysis proved it to be the neutral ammonium salt.

When ammonia was passed into a solution of the acid in benzene, coarse, large crystals formed. Analysis of these crystals showed that they

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[1] *Ann.*, **174**, 133 (1874).

[2] Heintz, *Ibid.*, **198**, 42 (1879); **203**, 336 (1880).

[3] McMaster.

were a mixture of the acid salt and the neutral salt. No further attempt was made to prepare the neutral salt in benzene.

The neutral ammonium salt can be easily prepared in an ethyl acetate solution of the acid. It precipitated as fine, white crystals, very soluble in water. The aqueous solution gives a neutral reaction but soon becomes acid, due to hydrolysis. The salt is also very soluble in methyl alcohol, acetic acid and diacetoamine. It is slightly soluble in ethyl alcohol and ether, and insoluble in ethyl acetate, chloroform, benzene and acetone. It decomposes slowly in dry air and very rapidly in moist air, giving off ammonia. It is also slightly hygroscopic. On warming to 50°, decomposition of the salt took place rapidly, and at 100° the salt was completely decomposed into ammonia and the acid.

Calc. for $CH_2OHCO_2(NH_4)$: 15.05% N. Found: 15.03% (ethyl acetate); 15.01% (acetone).

**Comparison of Results.**—The ammonium salt of phenylacetic acid has been prepared and described in a previous paper by one of us.[1] A comparison of the salts of phenylacetic acid and its substituted derivatives shows many points of similarity. They can all be prepared in alcohol, although phenylamidoacetic acid is insoluble in this medium. The salts of *o*-nitrophenylacetic acid and phenylamidoacetic acid are yellowish in color. The others are white. They are all soluble in water and slightly soluble in acetone, but insoluble in ether and benzene. The phenylbromoacetate and phenylamidoacetate are slightly deliquescent, while the others are not deliquescent. The phenylacetate and phenylbromoacetate give off ammonia slowly in moist air. The others do not give off ammonia in the air.

Ammonium glycolate (hydroxyacetate) is quite unlike the salts of the other substituted acetic acids. It is insoluble in acetone and slightly soluble in ethyl alcohol and ether. It is also insoluble in ethyl acetate, benzene and chloroform. It loses ammonia very rapidly in moist air. Like the phenylbromoacetate and phenylamidoacetate, it is slightly hygroscopic.

## The Substituted Propionic Acids.

**Ammonium α-Bromopropionate.**—Weinig[2] has investigated the properties of many of the metallic salts of α-bromopropionic acid but does not mention the ammonium salt. It can be easily prepared by treating an ether solution of the acid with ammonia. The heat of reaction is so great that, in order to prevent possible decomposition of the salt, the precipitation flask must be packed in ice. The salt separates out as a noncrystalline powder. The salt is quite soluble in ethyl alcohol, and, in order to prepare it in this medium, it is necessary to saturate the alcoholic solution of the acid with ammonia and pour it into a large amount of

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[1] McMaster, *Loc. cit.*

[2] *Ann.*, 280, 248 (1894).

ether. Under these conditions, the salt forms as large, flaky crystals instead of an amorphous powder, as is the case when it is prepared in the ether direct. The salt is also very soluble in methyl alcohol, acetic acid and water. The neutral aqueous solution slowly becomes acid. The salt is slightly deliquescent. It is stable in dry air but loses its ammonia slowly in a moist atmosphere. It is insoluble in ethyl acetate, chloroform, acetone and benzene. It does not decompose at 50° in dry air, but at 100° ammonia is given off slowly.

Calc. for $CH_3CHBrCO_2(NH_4)$: 8.23%. Found: 8.21% N (ether); 8.21% N (ethyl alcohol).

**Ammonium $\beta$-Iodopropionate.**—The literature contains no account of this salt. By our method it formed in ether in frost-like crystals, which gradually became amorphous. It can also be precipitated in the crystalline condition from a concentrated solution of the acid in ethyl alcohol. The salt is slightly deliquescent and readily soluble in water, forming a neutral solution which slowly becomes acid. It is quite soluble in methyl and ethyl alcohols, acetic acid and acetone, slightly soluble in chloroform, ether and ethyl acetate. It is insoluble in benzene. Upon standing several months, the salt became brown due to liberated iodine. A rancid odor also developed.

The salt does not lose ammonia in dry air, but does so very slowly in moist air. At 50° there is no evidence of ammonia being given off, but at 100° the salt decomposes slowly.

Calc. for $CH_2ICH_2CO_2(NH_4)$: 6.45%. Found: 6.45% N.

**Ammonium $\beta$-Chlorolactate.**—This salt can be prepared from a solution of the acid in either ethyl alcohol or ether. In the alcohol, the salt forms as small, white crystals and, in the ether, as a granular powder. It is not deliquescent, is stable in dry air, and readily gives off ammonia in moist air. It gives off ammonia slowly at 50° and somewhat more rapidly at 100°.

The salt is very soluble in acetic acid and water. The neutral aqueous solution soon becomes acid. Silver nitrate gives a white precipitate when added to an aqueous solution of this salt. The precipitate is soluble in ammonium hydroxide. The salt is very slightly soluble in methyl alcohol and ethyl alcohol, and insoluble in ether, chloroform, acetone, benzene and ethyl acetate. No mention of this salt can be found in the literature, although many of the other salts of $\beta$-chloroacetic acid have been studied.

Calc. for $CH_2ClCH(OH)CO_2(NH_4)$: 9.89% N. Found: 9.85% (ether); 9.87% (ethyl alc.).

**Comparison of Results.**—The neutral ammonium salts of propionic acid[1] and its substituted derivatives, thus far studied, can be prepared

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[1] *Am. Chem. J.*, 49, 299 (1913).

in ether from which they separate as amorphous solids. The β-iodopropionate and β-chlorolactate can be precipitated as white crystals from concentrated alcoholic solutions of the acids. The β-chlorolactate is slightly soluble in ethyl and methyl alcohols. The other ammonium propionates are readily soluble in these solvents. All of them are very soluble in water and acetic acid, and insoluble in benzene. They are unstable in moist air, losing ammonia rapidly. The β-chlorolactate is not deliquescent, while the others are.

## Some Higher Fatty Acids, Including Several Substituted Derivatives.

**Ammonium Trichlorobutyrate.**—Garzarolli-Thurnlak[1] prepared this salt by treating an ether solution of the acid with solid ammonium carbonate. The ether was evaporated from this mixture by means of a stream of dry air. The salt was then extracted from the residue by means of more ether. It crystallized out of water partly in tuft-like and partly in quartz-like crystals. The salt was found to be more readily soluble in water and alcohol than in ether.

We prepared this salt in ether by our usual method. It formed as a white amorphous solid. It is very soluble in ethyl alcohol, and on this account, the yield is small if the ammonia is conducted even into a saturated alcoholic solution of the acid. It can be prepared also by passing ammonia into a saturated solution of the acid in acetone or ethyl acetate and then adding a large amount of ether. In each solvent the precipitate formed was crystalline. It dissolved readily in water, the solution remaining neutral for at least several days. The salt is also very soluble in methyl alcohol and appreciably so in ethyl acetate and acetone, and very slightly soluble in chloroform and ether. It is insoluble in benzene. It is not hygroscopic.

At ordinary temperatures the salt is stable in dry air, but at 50° ammonia is rapidly given off. Ammonia is given off slowly in moist air at room temperature. When heated to 100°, the salt decomposes into the acid and ammonia.

Calc. for $C_3H_4Cl_3CO_2(NH_4)$: 6.73% N. Found: 6.70% (ether).

Ammonium butyrate has been described in one of the papers previously referred to. Ammonium trichlorobutyrate undergoes decomposition into ammonia and the acid salt very slowly in the air, while ammonium butyrate does so very rapidly. The aqueous solution of the latter hydrolyzes very rapidly while that of the former does so very slowly. Both the butyrate and the trichlorobutyrate are easily precipitated from ether solutions of the acids, the first one in the form of granular crystals and the second one as an amorphous powder. Both are soluble in the alcohols, acetic acid and acetone. Ammonium isobutyrate, also described

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[1] *Ann.*, 182, 185 (1876).

in a previous paper, precipitates from an ether solution of the acid as a lustrous white solid and differs from the butyrate and the trichlorobutyrate in that it has a very high vapor tension. The ammonium butyrate is deliquescent, while the isobutyrate and the trichlorobutyrate are not deliquescent. The ammonium isobutyrate resembles the other two as to solubility in the alcohols.

**Ammonium Caprylate.**—Currie[1] found that he could prepare this salt by passing dry ammonia into a benzene solution of the acid. He obtained needle-like crystals, which readily hydrolyzed in an aqueous solution, and which readily gave off the odor of caprylic acid when exposed to the air. No analysis of the salt was recorded by Currie. We have prepared the salt in ether. It dried to a cheese-like mass. It did not precipitate from ethyl alcohol, but when a mixture of equal parts of ether and alcohol were used, it precipitated as monoclinic crystals. An aqueous solution of the salt lathers freely on shaking. This solution, which is neutral at first, becomes acid on standing a very short time. The salt is slightly hygroscopic, loses ammonia very slowly in dry air and very rapidly in moist air. It is very soluble in acetic acid and ethyl alchol, and slightly soluble in methyl alcohol. It is less soluble in acetone and ethyl acetate than in methyl alcohol. It is insoluble in chloroform, ether and benzene. Analysis of the salt dried at 50° showed that there had been some decomposition.

Calc. for $C_7H_{15}CO_2(NH_4)$: 8.70% N. Found: 8.68% (ether); 8.64% (alcohol-ether mixt.).

After standing some weeks, the above salt became yellowish in color and developed the odor of caprylic acid.

**Ammonium Caprate.**—Currie[2] also describes the preparation of this salt in benzene and found that its properties are the same as those of ammonium caprylate. The salt can also be prepared in ether as a fine, white, amorphous substance, which is greasy to the touch. By conducting ammonia into a saturated alcoholic solution of the acid and then adding an excess of ether, the neutral salt precipitates as fine, white crystals. It dissolves readily in water, to which it imparts a neutral reaction. The solution quickly hydrolyzes. The salt is slightly hygroscopic. It is insoluble in benzene, slightly soluble in acetone and ether, and readily soluble in methyl alcohol, ethyl alcohol and acetic acid. It gives off ammonia slowly in dry air and rapidly in moist air. At 50° the evolution of ammonia is very rapid and is complete before the temperature reaches 100°.

Calc. for $C_9H_{19}CO_2(NH_4)$: 7.41%. Found: 7.41% N.

**Ammonium Laurate.**—Many of the salts of lauric acid have been pre-

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[1] *J. Agr. Research*, **2**, 8 (1914).

[2] *Loc. cit.*

pared by Oudemans,[1] who prepared the acid ammonium salt by neutralizing an aqueous solution of the acid with ammonium hydroxide, and evaporating to crystallization.

When the dry ammonia was passed into an ether solution of the acid, there was formed a curdy, white precipitate which soon changed to one flaky in appearance. It was also prepared by adding ether to an alcoholic ammonia solution of the acid. In this case, fine, white crystals formed. The salt is very soluble in water. This aqueous solution remains neutral for at least two days. It also lathers very freely when shaken. The salt is soluble in methyl and ethyl alcohols and acetic acid, slightly soluble in acetone, and insoluble in chloroform, ether and benzene. The salt is deliquescent. It does not lose ammonia in exposure to dry or moist air. It gives off ammonia slowly at 50° and decomposes very rapidly at 100°.

Calc. for $C_{11}H_{23}CO_2(NH_4)$: 6.45% N. Found: 6.44% (ether); 6.43% (ether-alc. mixt.).

**Ammonium Myristate.**—No record can be found of the preparation of this salt. It can be prepared by passing dry ammonia into an ether solution of myristic acid. On passing in the gas, there was formed a fine, white, noncrystalline precipitate. By dissolving this precipitate in ethyl alcohol and evaporating the solvent, the salt was obtained in the crystalline form. It is easily soluble in water, the solution remaining neutral at the end of two days. It is readily soluble in ethyl alcohol, methyl alcohol and acetic acid, and insoluble in ether, benzene, acetone and chloroform. It is not hygroscopic. At ordinary temperatures there is no evidence of decomposition in dry air, but it decomposes slowly at 50° and is completely decomposed at the temperature of boiling water. It decomposes very slowly in moist air.

Calc. for $C_{13}H_{27}CO_2(NH_4)$: 5.71%. Found: 5.70% N.

**Ammonium α-Bromopalmitate.**—We could find no record of the preparation of this salt. When prepared by passing ammonia into an ether solution of the acid, it precipitated first as a gelatinous mass, which soon changed to an amorphous powder. It could not be precipitated in alcohol, owing to its solubility in that solvent; but when a saturated alcoholic solution of the acid, into which ammonia had been passed for some time, was poured into a rather large volume of ether, the salt formed in fine, frost-like crystals.

The salt dissolves easily in water. The solution lathers copiously on shaking. We have here another example of an ammonium soap. This is true of the ammonium salts of all the higher fatty acids, such as capric acid, caprylic acid, myristic acid, etc. The neutral aqueous solution hydrolyzes very slowly. The salt is very soluble in acetic acid, methyl

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[1] *Jahresb. Fortschr. Chem.*, 1863, p. 331.

alcohol and ethyl alcohol. When the ethyl alcohol solution of the salt is warmed, there is some decomposition of the salt and an ester is formed. The salt is insoluble in ether, benzene and chloroform, and slightly soluble in acetone. It loses ammonia very slowly in dry air and rapidly in moist air. It gives off but little ammonia at 50°, but decomposition takes place rapidly at 100°. The salt is not hygroscopic.

Calc. for $C_{15}H_{30}BrCO_2(NH_4)$: 3.99% N. Found: 3.95% (ether); 3.95% (ether-alc. mixt.).

Ammonium palmitate, described in a previous paper by McMaster,[1] and ammonium bromopalmitate can both be prepared in ether. The first is soluble in acetone, while the second is only slightly soluble. Both are soluble in water, methyl alcohol and ethyl alcohol. Both lather very freely in water, indicating ammonium soaps. The aqueous solution of the palmitate hydrolyzes much more rapidly than that of the bromopalmitate. The latter decomposes in the air more slowly than the first. Neither salt is hygroscopic.

**Ammonium $\alpha$-Bromostearate.**—As in the case of the corresponding bromopalmitate, no record of this salt can be found in the literature. It was prepared in ether as a noncrystalline compound. It was also precipitated from an alcoholic ammonia solution of the acid upon the addition of ether. In this case it formed small, white crystals. The aqueous solution lathers freely on shaking and very slowly becomes acid. The salt is not deliquescent. It is stable in dry air but loses ammonia in moist air. It is soluble in methyl and ethyl alcohols, slightly soluble in cold acetone and readily soluble in hot acetone. It does not dissolve in ether, ethyl acetate, benzene or chloroform. When treated with acetic acid, $\alpha$-bromostearic acid is formed. The salt decomposes slowly with the liberation of ammonia both at 50° and 100°.

Calc. for $C_{17}H_{34}BrCO_2(NH_4)$: 3.69%. Found: 3.66% N.

The neutral ammonium salt of $\alpha$-bromostearic acid can thus be prepared in ether as well as the neutral salt of stearic acid. The preparation and properties of this latter salt have been previously described by McMaster. Both salts are soluble in water, methyl alcohol, ethyl alcohol and acetone. In the last solvent the bromostearate is less soluble than the stearate. Both salts are not hygroscopic, do not lose ammonia in dry air, but do in moist air.

**Comparison of Results.**—Including those neutral-ammonium salts described in the previous papers, there have thus far been prepared and studied twenty-two salts of the saturated monobasic acids of the aliphatic series, or derivatives of acids of that series. We have found that there is a very wide variation in many of their properties. There seems to be no uniformity in their action when exposed to the air. Some of

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[1] *Loc. cit.*

them do not deliquesce, some do so very slowly, and some very rapidly. Some of these salts lose ammonia in the air with varying degrees of rapidity, while others of them do not lose ammonia. Most of these salts hydrolyze, but not all of them. They all have the general property of being soluble in water and more or less so in the alcohols. Most of them are slightly soluble in acetone. All are insoluble in benzene and ether. A few of them have also been found to be insoluble in ethyl acetate.

## Some Monobasic Unsaturated Acids.

**Ammonium Acrylate.**—When dry ammonia was passed into an ether solution of acrylic acid, a gelatinous mass was formed. This condition did not change when the substance was dried in an atmosphere of ammonia. This same gelatinous, glue-like mass was formed also in an alcoholic solution of the acid, even when the solution was packed in ice. We also attempted to prepare the salt in acetone. On passing in the ammonia, there was formed at first a white precipitate, which very soon redissolved and formed a light brown solution. The heat of reaction was sufficient to raise the temperature almost to the boiling point of the acetone. No doubt there was formed here again some diacetoamine in which the salt, which first formed, was redissolved. The results in this case were the same as we had in the case of the glycolic acid.

The neutral ammonium acrylate was finally prepared by passing the ammonia into a benzene solution of the acid and evaporating off the benzene. Monoclinic crystals were obtained. If a solution of the acid in ethyl acetate be used, the salt separates as a fine, granular mass. The salt, prepared in either medium, is not hygroscopic, does not lose ammonia when exposed to dry or moist air, and does not decompose when warmed to 100°. After standing several months, the salt developed the odor of acrylic acid. An aqueous solution of the salt slowly hydrolyzes.

The salt is soluble in water and acetic acid, slightly soluble in methyl and ethyl alcohols, and insoluble in ether, chloroform, ethyl acetate, acetone and benzene. No previous record of this salt could be found.

Calc. for $CH_2CHCO_2(NH_4)$: 15.73%. Found: 15.69% N (benzene). Prepared in ethyl acetate. Found: 15.70% N.

**Ammonium β-Chlorocrotonate.**—Sarnow[1] prepared the ammonium salt of the α-acid by treating the acid with a saturated solution of ammonium carbonate. He found that the salt crystallized out from the solution in plate-like crystals, which sublimed at 100°. No mention is made of the ammonium salt of the β-acid.

When prepared by our method, the salt of the β-acid was precipitated from an ether solution as small, flaky crystals. The salt is very soluble in ethyl alcohol, but can be prepared by pouring a saturated, alcoholic ammonia solution of the acid into ether. It here separates out as a fine,

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[1] *Ann.*, 164, 99 (1872).

white, crystalline mass. The salt was also precipitated as fine crystals in acetone.

The salt is not hygroscopic. It is very soluble in water and forms a neutral solution, which soon hydrolyzes. The salt is stable in dry air, but loses ammonia slowly in moist air. The salt is also very soluble in methyl alcohol and acetic acid as well as in ethyl alcohol. It is only slightly soluble in acetone and ethyl acetate. It is insoluble in ether, chloroform and benzene. It can be dried at 100° without decomposition.

Calc. for $C_3H_4ClCO_2(NH_4)$: 10.18% N. Found: 10.14% (ether); 10.19% (acetone); 10.15% (ether-alc. mixt.).

Ammonium crotonate has been described by McMaster. It was prepared, as we have prepared the $\beta$-chlorocrotonate, in ether and in a saturated alcoholic solution of the acid. In the case of the $\beta$-chlorocrotonate, it was necessary to add ether to the alcoholic ammonia solution before precipitation took place. Both salts separate from ethyl alcohol in a crystalline condition, and both are readily soluble in water. The aqueous solution in each case quickly hydrolyzes. Both salts are also soluble in methyl alcohol and acetic acid, and insoluble in chloroform and ether. Neither salt is deliquescent.

**Ammonium Erucate.**—A cream-colored, amorphous precipitate of this salt formed when ammonia was passed into the ether solution of the acid. Erucic acid is only slightly soluble in ethyl alcohol, and we thus obtained a small yield of white crystals in this solvent. The solution of the salt in water also lathers freely on shaking. The aqueous solution, neutral at first, hydrolyzes. The salt does not lose ammonia in dry air, but does so very slowly in moist air. It is not hygroscopic and can be dried at 100° without decomposition.

The salt is very slightly soluble in ethyl alcohol and somewhat more soluble in methyl alcohol. It crystallizes from the latter in monoclinic crystals. The salt is sparingly soluble in acetone and insoluble in ether, ethyl acetate and benzene. It is readily soluble in acetic acid.

Calc. for $C_{21}H_{41}CO_2(NH_4)$: 3.94% N. Found: 3.91% (ether); 3.95% (ethyl alc.).

The literature makes no mention of this salt so far as we can find.

**Comparison of Results.**—The neutral ammonium salts of crotonic, oleic, and elaidic acids have been described by McMaster in previous papers. With the exception of ammonium acrylate, the salts of the unsaturated monobasic acids can be prepared in ether, from which they separate in gelatinous masses, which gradually change over to amorphous solids. Ammonium oleate can be prepared in a crystalline form if ammonia is passed in for a sufficient length of time. The acrylate can be prepared in ethyl acetate. These salts are all soluble in ethyl alcohol, methyl alcohol and water. They all separate from an alcoholic solution on evaporation as fine, white crystals. Their aqueous solutions hydrolyze. They are not deliquescent.

## The Substituted Malonic Acids.

**Ammonium Dimethylmalonate.**—There is no mention in the literature of the neutral ammonium salts of the substituted malonic acids included in this investigation. Ammonium dimethylmalonate can be prepared from a solution of the acid in ether or ethyl alcohol by our method. In ether, it is precipitated as a curdy mass, which, on washing and drying, becomes a white, amorphous powder. In alcohol, it is precipitated as crystals.

The salt forms a neutral solution in water and soon hydrolyzes. The salt is very deliquescent, and gives off ammonia slowly in dry air and very rapidly in moist air. It decomposes into ammonia and the acid when heated to 50°. The salt is readily soluble in methyl alcohol and acetic acid, slightly soluble in ethyl alcohol and ethyl acetate, and insoluble in ether, benzene, chloroform and acetone.

The neutral salt can also be prepared in ethyl acetate and acetone. From each of these solvents it readily precipitates in a crystalline form.

Calc. for $(CH_3)_2C(CO_2NH_4)_2$: 16.87% N. Found: 16.80% (ether); 16.79% (ethyl alc.); 16.81% (ethyl acetate); 16.85% (acetone).

**Ammonium Dipropylmalonate.**—This salt was prepared from solutions of the acid in ether, ethyl alcohol, ethyl acetate and acetone. From ether, it was precipitated as a gelatinous mass which changed to hard lumps. These lumps were crushed, washed and dried. From solutions of the acid in ethyl alcohol, ethyl acetate and acetone, the neutral salt precipitated as white, monoclinic crystals. It was necessary to surround the ethyl alcohol solution with ice to prevent the formation of an ester. The salt formed a solution in water which remained neutral for at least several days. It is slightly deliquescent. It does not give off ammonia in dry or moist air. There is no decomposition at 50°, but at 100° ammonia is slowly evolved.

The salt is readily soluble in acetic acid and methyl alcohol. It is slightly soluble in ethyl alcohol and ethyl acetate, and insoluble in ether, acetone, chloroform and benzene.

Calc. for $(C_3H_7)_2C(CO_2NH_4)_2$: 12.61% N. Found: 12.59% (ether); 12.58% (ethyl alc.); 12.56% (ethyl acetate); 12.62% (acetone).

**Ammonium Isopropylmalonate.**—On addition of dry ammonia to an ether solution of the acid, this salt formed as a mucilaginous precipitate which, on drying, collected in hard lumps. From ethyl alcohol, it precipitated as white crystals.

The salt is very deliquescent, and on exposure to moist air breaks up into ammonia and the acid. It is stable in dry air at ordinary temperatures. At 50° it gives off ammonia slowly. At 100° the decomposition is somewhat more rapid.

An aqueous solution of the salt remains neutral to litmus. The salt is very soluble in methyl alcohol and acetic acid. It is very slightly soluble in ethyl alcohol and benzene, and insoluble in acetone, ethyl acetate and chloroform.

Calc. for $C_3H_7CH(CO_2NH_4)_2$: 15.55% N. Found: 15.52% (ether); 15.50% (ethyl alc.).

**Ammonium Butylmalonate.**—From a solution of the acid in ether this salt precipitated in asbestos-like fibers, which dried to a hard mass. From ethyl alcohol it precipitated as rhombic crystals. In order to prevent the formation of some ester, it was necessary to keep the alcohol solution packed in ice.

The salt is slightly deliquescent, and readily dissolves in water to form a neutral solution, which soon becomes acid to sensitive litmus. The salt is stable in dry air at room temperature, but at 50° ammonia is slowly evolved. It loses ammonia rapidly in moist air or when heated to 100°. The salt is very soluble in methyl alcohol and acetic acid, slightly soluble in ethyl acetate, and insoluble in ethyl alcohol, ether, acetone, chloroform and benzene.

Calc. for $C_4H_9CH(CO_2NH_4)_2$: 14.45% N. Found: 14.40% (ether); 14.40% (ethyl alc.).

**Ammonium Allylmalonate.**—Dry ammonia precipitated this salt as a fibrous mass from an ether solution of the acid. On drying this precipitate it formed as hard lumps. It formed as a white, crystalline compound of an ethyl alcohol solution of the acid. The heat of neutralization in the ethyl alcohol was sufficient to form some ester unless the solution was packed in ice. The salt was also prepared in acetone. The crystals resembled those formed in the alcohol.

The salt is very deliquescent, and loses ammonia rapidly in both dry and moist air. It is difficult to prevent decomposition of the salt, even during the drying of it. It decomposes very rapidly at 50°, and before 100° is reached, the salt loses all its ammonia.

The aqueous solution of the salt, which is at first neutral, hydrolyzes on standing. The salt is readily soluble in methyl alcohol and acetic acid, very slightly soluble in ethyl alcohol, ethyl acetate and acetone, and insoluble in chloroform, ether and benzene.

Calc. for $C_3H_5CH(CO_2NH_4)_2$: 15.73% N. Found: 15.74% (ether); 15.70% (ethyl alc.); 15.70% (acetone).

**Ammonium Benzylmalonate.**—This salt readily precipitated in a noncrystalline condition from a solution of the acid in ether. It precipitated as hexagonal crystals from a solution of the acid in ethyl alcohol. Neither the crystalline nor the noncrystalline form was hygroscopic.

The salt does not lose ammonia in dry or moist air even at 50°, but an analysis of a sample kept at 100° for ten minutes showed that some decomposition had taken place. The salt dissolved readily in water, to which it imparted a neutral reaction. This solution remained neutral at least twenty-four hours. The salt is also very soluble in acetic acid and methyl alcohol, but only sparingly so in ethyl alcohol, ethyl acetate and chloroform. It is insoluble in ether, acetone and benzene.

Calc. for $C_6H_5CH(CO_2NH_4)_2$: 13.08% N. Found: 13.05% (ether); 13.04% (ethyl alc.).

**Comparison of Results.**—Previous papers by one of us[1] have given an account of the preparation and properties of the neutral ammonium salts of malonic acid and ethyl malonic acid. We have just described the neutral ammonium salts of six other substituted derivatives of malonic acid. All of these salts precipitate in ether as amorphous compounds, and as fine, white crystals in ethyl alcohol. They are all very soluble in water and insoluble in ether and benzene. With the exception of the allyl compound, all are insoluble in acetone. Most of them lose ammonia in moist air. The aqueous solutions of the salts of dimethyl, butyl and allylmalonic acids hydrolyze. The aqueous solutions of the others do not hydrolyze. The salts of malonic and benzylmalonic acids do not deliquesce, while all the others do. The most striking characteristics common to all these malonates is their solubility in the common alcohols. All of them are soluble in methyl alcohol and, with the exception of the butylmalonate, all are only very slightly soluble in ethyl alcohol. The butylmalonate is insoluble in this solvent.

## The Substituted Succinic Acids.

**Ammonium Monobromosuccinate.**—Meyer and Jacobson state, in their *Lehrbuch der Organischen Chemie*, that when monobromosuccinic acid is treated with a methyl alcohol solution of ammonia the $\beta$-monoamide of malic acid results. The exact conditions are not given. No mention is made of the neutral ammonium salt.

When an ether solution of the acid was treated with dry ammonia, a fibrous precipitate formed which soon changed to an amorphous powder. When an alcoholic solution of the acid was used, a crystalline precipitate formed. The salt was found to be not deliquescent, and stable in moist as well as in dry air. The salt did not decompose when heated to 50°, but at 100° there was a slight decomposition.

The salt is very soluble in water and acetic acid. The aqueous solution remained neutral for several days. The salt is slightly soluble in ethyl alcohol and much less so in methyl alcohol. It is also very sparingly soluble in ethyl acetate and chloroform, and insoluble in ether, acetone and benzene. An aqueous solution of the salt gave with silver nitrate solution a white precipitate, insoluble in dilute nitric acid. With ferric

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[1] McMaster, *Loc. cit.*

chloride solution, a yellowish brown precipitate formed, but with lead acetate solution no precipitate was formed.

Calc. for $C_2H_3Br(CO_2NH_4)_2$: 12.12% N. Found: 12.12% (ether); 12.10% (ethyl alc.).

**Ammonium Dibromosuccinate.**—Kekulé[1] prepared ammonium dibromosuccinate from an aqueous solution of the acid and found that it crystallized out of water without water of crystallization.

When ammonia was passed into an ethyl alcohol solution of the acid, the neutral salt formed as a fine, white, granular precipitate. In an ether solution, the salt first formed as a gelatinous mass, which changed to a crystalline powder. The salt is not hygroscopic. A solution of the salt in water is neutral at first but becomes slowly acid on standing. The aqueous solution gave with silver nitrate solution a white precipitate, soluble in dilute nitric acid. It also gave a yellowish brown precipitate with ferric chloride solution.

The salt is somewhat soluble in methyl alcohol. It is less soluble in ethyl alcohol than in methyl alcohol. It is soluble in acetic acid, and insoluble in ether, chloroform, ethyl acetate, acetone and benzene. The salt is stable in dry air but loses ammonia in moist air. It decomposes slowly with the evolution of ammonia at 50°. At 100° there is a rapid decomposition.

Calc. for $C_2H_2Br_2(CO_2NH_4)_2$: 9.03% N. Found: 9.00% (ether).

**Comparison of Results.**—Ammonium succinate has been described by McMaster. The neutral ammonium salts of succinic acid and its substituted bromo derivatives can be prepared in an ether or ethyl alcohol solution of the acids. In ether, the salts separate in an amorphous condition, and in ethyl alcohol in a crystalline form. All of them are easily soluble in water. The aqueous solution of the ammonium dibromosuccinate hydrolyzes very slowly. All of the salts described are only slightly soluble in ethyl alcohol. The salts of the bromo derivatives are insoluble in acetone, ether and benzene. All three salts are stable in dry air, and none of them deliquesce.

## Suberic Acid.

**Ammonium Suberate.**—Gantter and Hell[2] prepared the neutral ammonium salt of suberic acid by evaporating an ammoniacal solution of the acid in an atmosphere of ammonia and over potassium hydroxide. They obtained the salt in well-defined leaflets, which completely decomposed at 110° into ammonia and the acid.

The salt could not be prepared in ether on account of the insolubility of the acid in that medium. When dry ammonia was passed into an ethyl alcohol solution of the acid, no precipitate formed. Ether was then added to this alcoholic ammonia solution of the acid, whereupon fine,

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[1] *Ann. Spl.*, 1, 354 (1862).

[2] *Ber.*, 13, 1166 (1880).

white crystals of neutral ammonium suberate formed. A white, crystalline precipitate of the salt also formed immediately when the ammonia was passed into an ethyl acetate solution of the acid.

The salt is soluble in water and methyl alcohol, slightly soluble in acetic acid, ethyl alcohol and benzene, and insoluble in acetone, chloroform and ethyl acetate. The aqueous solution of the salt does not hydrolyze. The salt is not hygroscopic. At ordinary temperatures it does not lose ammonia in dry or moist air. At 50° it loses ammonia slowly, and at 100° the decomposition is very rapid. At 100° all the ammonia has been liberated and analysis shows that only the acid remains.

Calc. for $C_6H_{12}(CO_2NH_4)_2$: 13.46% N. Found: 13.40% (ether-alc. mixt.); 13.46% (ethyl acetate); 13.44% (benzene).

**Comparison of the Ammonium Salts of the Saturated Dibasic Acids.**—We have described in this and previous papers the preparation and properties of the neutral ammonium salts of sixteen saturated dibasic acids, or substituted derivatives of them, not including the hydroxy derivatives. While there is a rather wide variation in their general properties, they have many points of similarity. All of them can be prepared in ether, and in every case they separate as amorphous compounds. With the exception of ammonium pimelate, all of them readily precipitate in a crystalline condition from an alcoholic solution of the acid. In those salts having both carboxyl groups attached to the same carbon atom there appears to be a strong tendency to deliquesce. With the exception of the pimelate, those salts, which have the carboxyl groups attached to different carbon atoms, do not deliquesce. The aqueous solutions of the salts of the dibasic acids either do not hydrolyze at all or hydrolyze only very slowly. None of them give off ammonia in dry air, except the pimelate. Some of them give off ammonia very slowly in moist air. Unlike the salts of the saturated monobasic acids, all of them, except the pimelate, are only very slightly soluble in ethyl alcohol. The ammonium pimelate thus has different properties in general from the other saturated dibasic acids.

## Chlorofumaric Acid.

**Ammonium Chlorofumarate.**—Perkins[1] prepared this salt by allowing the acid to stand in an atmosphere of ammonia. He states that combination takes place with energy and that, if an excess of ammonia be left with the salt, there is no decomposition with removal of the chlorine. Perkins also states that, on slowly evaporating an aqueous solution of the salt, beautiful transparent crystals of the salt separate, which are moderately soluble in water and can be dried at 100° without decomposition. Mushman[2] found these crystals to be monoclinic.

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[1] *J. Chem. Soc.*, **53**, 699 (1888).

[2] *Ibid.*

By our method this salt was prepared in an ether solution of the acid. On first passing in the ammonia, a colloidal precipitate formed which passed to a gelatinous mass and then finally to a fine, white powder. In a saturated alcoholic solution of the acid, a fine, flaky, crystalline precipitate formed at once. In each case the neutral salt was formed. It is not deliquescent, and gives off ammonia very slowly in moist air. It is readily soluble in water, yielding a neutral solution which does not hydrolyze.

The salt is also soluble in acetic acid. It is very slightly soluble in methyl and ethyl alcohols, and insoluble in acetone, chloroform, ether, ethyl acetate and benzene. It can be heated to 100° without decomposition.

Calc. for $C_2HCl(CO_2NH_4)_2$: 15.17% N. Found: 15.14% (ether); 15.12% (ethyl alc.).

This salt has properties similar to ammonium fumarate previously prepared in this laboratory. Both salts readily precipitate from ethyl alcohol, the fumarate as an amorphous powder and the chlorofumarate as fine crystals. Both salts are very slightly soluble in ethyl alcohol, and neither salt deliquesces. Both salts are soluble in water forming neutral solutions, which do not hydrolyze.

This investigation is being continued with other organic acids and their substituted derivatives.

ST. LOUIS, MO.

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

# THE ACTION OF A SOLUTION OF POTASSIUM HYDROXIDE IN ALCOHOL ON OXALIC ESTERS.

BY N. C. QUA AND D. MCLAREN.

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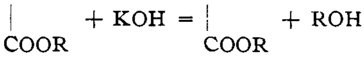
One method of preparing the monoalkyl esters of dibasic acids is by the treatment of the dialkyl esters with the calculated amount of the alcoholic solution of potassium or sodium hydroxide, the reaction being represented thus:



$$\begin{array}{c}COOR\\|\\COOR\end{array} + KOH = \begin{array}{c}COOK\\|\\COOR\end{array} + ROH$$

But it is clear that we might expect the results in some cases to be represented thus:

$$2\begin{array}{c}COOR\\|\\COOR\end{array} + 2KOH = \begin{array}{c}COOK\\|\\COOK\end{array} + \begin{array}{c}COOR\\|\\COOR\end{array} + 2ROH$$

and, in other cases, the product might contain both dipotassium salt and the potassium alkyl salt.