of the sulfonic acid mixture with sodium hydroxide and the subsequent separation of these by their different solubilities in water.

On neutralization of the sulfonated mixture with lime much of the calcium salts of mono-β and 2,6 is lost in the calcium sulphate.

2,6-Sodium sulfonate of anthraquinone is very sensitive to sunlight, darkening in color from plum to almost black.

A new substance has been isolated. It has some interesting properties. When suspended in ethyl alcohol and exposed to sunlight an unstable green product results.

"Silver salt" separates best in mildly acid solution.

MIDDLETOWN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY.]

THE NEUTRAL AMMONIUM SALTS OF SOME SUBSTITUTED BENZOIC ACIDS.

[FIFTH COMMUNICATION.[1]]

BY LEROY MCMASTER AND I. H. GODLOVE.

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This work is a continuation of the preparation and investigation of the properties of the neutral ammonium salts of organic acids. This paper deals with the derivatives of benzoic acid. The salts described in the previous papers were prepared by passing dry ammonia into solutions of the organic acids in methyl alcohol, ethyl alcohol, ether, and acetone, or in mixtures of these solvents.

In the following work the neutral ammonium salts of *m*-toluic, *p*-toluic, *o*-chlorobenzoic, *m*-chlorobenzoic, *p*-chlorobenzoic, *o*-bromobenzoic, *m*-bromobenzoic, *p*-bromobenzoic, *o*-nitrobenzoic, *m*-nitrobenzoic, *p*-nitrobenzoic, 3,5-dinitrobenzoic, *o*-aminobenzoic, *m*-aminobenzoic, and *p*-aminobenzoic acids have been prepared by passing dry ammonia into solutions of the respective acids in the above anhydrous solvents, and some of their properties studied. After the salts were precipitated and tested for neutrality, they were filtered by suction on an alundum crucible and thoroughly washed with anhydrous ether. They were then put into crystallizing dishes and allowed to stand a short time in a vacuum desiccator.

Several of the salts were also prepared in pure benzene. Currie[2] states that the ammonium salts of weak organic acids can be prepared by passing dry ammonia into a benzene solution of the acids, and in this manner prepared the ammonium salts of caproic, caprylic and capric acids.

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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).

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

The analysis of the salts consisted in determining the nitrogen by either the regular or a modified Kjeldahl method. In all the salts, except those of the three amino acids, the nitrogen present as "ammonium" nitrogen was determined This is equal to the total nitrogen, except for the nitro acids For the three amino acids, total nitrogen was determined. In the case of the *m*-nitro acid, both total and ammonium nitrogen were determined.

The Toluic Acids.

Ammonium *m*-Toluate.—No record can be found of the preparation and properties of this salt. It was prepared by passing dry ammonia gas into an ether solution of *m*-toluic acid. On passing in the gas, there was first formed an amorphous powder which, after a time, became crystalline. The powder, after being filtered, washed with ether and dried, was dissolved in ethyl alcohol, from which it recrystallized in the form of long prismatic needles. It crystallizes from acetone in the same form. It is readily soluble in water, to which it imparts a neutral reaction. It is easily soluble in methyl alcohol, ethyl alcohol and acetic acid. It is also soluble in acetone but a little less so than in the last named solvents. The salt is somewhat hygroscopic, and gives off ammonia in the air. Determination of the nitrogen proved it to have the composition of the neutral salt.

Calc. for $C_8H_7O_2(NH_4)$: 9.15%. Found: 9.19% N.

Ammonium *p*-Toluate.—Noad[1] prepared this salt by neutralizing an aqueous solution of the acid and allowing the solution to evaporate. The salt crystallized out in the form of small prisms. No analysis was made of the salt. Lossen[2] found that the neutral salt could be prepared, in the form of clear, flat cubes, by cautious evaporation of a solution of the acid in ammonia water. He also obtained it in glittering leafy crystals, upon the addition of an excess of alcoholic ammonia to an alcoholic solution of the acid. If an aqueous solution of this salt were boiled and the solution allowed to cool, needle-shaped crystals of the acid salt were obtained, which crystallized from alcohol in the form of large silvery white glistening leaves.

We prepared this salt by passing dry ammonia into an ether solution of *p*-toluic acid. It precipitated as a fine, white, crystalline powder, which formed small needles when recrystallized from alcohol. The salt is soluble in water, methyl alcohol, ethyl alcohol, acetone and acetic acid. It is insoluble in ether. The aqueous solution of the salt is at first neutral, but slowly becomes acid, due to hydrolysis. The salt is only slightly hygroscopic, and gives off ammonia slowly in moist air.

Calc. for $C_8H_7O_2(NH_4)$: 9.15%. Found: 9.06 and 9.11% N.

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[1] *Ann.*, **63,** 296 (1847).

[2] *Ibid.*, **298,** 72 (1897).

The neutral ammonium salt of *o*-toluic acid has been previously prepared by one of us.[1] The neutral ammonium salts of the three toluic acids can thus be prepared in ether, but not in methyl or ethyl alcohols on account of their great solubility in these solvents. They form white, crystalline precipitates, which are all soluble in water, acetone and acetic acid. They are less soluble in acetone than in the other solvents. They are stable in dry air and give off ammonia slowly in moist air. The *o*-toluate does not deliquesce, while the *m*- and *p*-salts do so very slightly. Their aqueous solutions are neutral.

The Chlorobenzoic Acids.

Ammonium *o*-Chlorobenzoate.—Rivals[2] mentions this salt as soluble in water with the absorption of a small amount of heat, but does not describe the method of preparation, the analysis nor the properties of it. Korczynski[3] states that solid *o*-chlorobenzoic acid combines with ammonia under pressure, forming $C_6H_4ClCOONH_4$, and that a second molecule of ammonia is taken up at —15°, which is quickly given off as the temperature rises to normal.

This salt can be prepared by the method described, in an ether solution of the acid, as a fine, white powder. It is very soluble in water, methyl alcohol, ethyl alcohol, acetone and acetic acid. It is only slightly soluble in ether. A solution of the salt in water is neutral, and does not hydrolyze even on long standing. The salt is not hygroscopic, and gives off ammonia only very slowly in both dry and moist air.

Calc. for $C_7H_4O_2Cl(NH_4)$: 8.07%. Found: 8.01% N.

Ammonium *m*-Chlorobenzoate.—Gluud and Kempf[4] have prepared this salt by heating the hydroxylamine salt of the acid to 170°, treating the mixture of the salt and the free acid obtained with warm xylene to remove the acid, extracting the ammonium salt with warm acetone, and then precipitating it with petroleum ether. It crystallized in small leaflets, which melted and decomposed at 203–204° after a short sintering. It dissolved in cold water, and in some organic solvents on heating, but so readily evolved ammonia that little but the free acid itself remained in solution. An aqueous solution of the salt also gave off ammonia on heating, and the acid crystallized out on cooling. They also prepared the salt by passing ammonia into a solution of the acid in methyl alcohol, and precipitating it with ether. They thus obtained glistening scales. No analysis was made of the salts obtained. Their first method of preparation could not have given a very pure product, since it depended on the selective solubility of the free acid and the salt, and since the solutions

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[1] McMaster, THIS JOURNAL, **36**, 1924 (1914).

[2] *Ann. chim. phys.*, [7] **12**, 521 (1897).

[3] *Anz. Akad. Wissenschaften*, Krakau, 633 (1908); *Chem. Zentr.*, **2**, 2009 (1908).

[4] *J. Chem. Soc.*, **103**, 1533 (1913).

of the salt gave off ammonia on warming, even slightly so at ordinary temperatures.

This salt can easily be prepared by passing dry ammonia into an ether solution of *m*-chlorobenzoic acid. There is formed a fine, white, amorphous precipitate, which, when crystallized from alcohol, gives a crystalline powder. It is readily soluble in water, methyl alcohol and ethyl alcohol, and slowly so in acetic acid. It is insoluble in ether. The aqueous solution is at first neutral, but very slowly becomes acid. The salt does not give off ammonia in dry air, but is slightly deliquescent.

Calc. for $C_7H_4O_2Cl(NH_4)$: 8.07%. Found: 8.01% N.

Ammonium *p*-Chlorobenzoate.—This salt was also prepared by Korczynski[1] by the same method used in the preparation of the *o*-compound. It can be prepared by passing ammonia into a saturated alcoholic solution of the acid. Glistening white laminae are thus formed. Upon passing ammonia into a solution of the acid in ether, a gelatinous precipitate is formed, which soon changes to a fine, amorphous powder. This can be crystallized from acetone in the form of very fine needles. The salt is soluble in water, methyl and ethyl alcohols, and acetic acid. It is also somewhat soluble in acetone. The solution of the salt in water is at first neutral, but hydrolyzes slowly on long standing. The salt does not deliquesce, and gives off ammonia only slowly in moist air.

Calc. for $C_7H_4O_2Cl(NH_4)$: 8.07%. Prepared in ether. Found: 7.98% N.
Prepared in ethyl alcohol. Found: 8.04% N.

The three chlorobenzoates can thus be readily prepared in ether. The *p*-salt can also be prepared in a saturated alcoholic solution of the acid. They are all soluble in water, methyl and ethyl alcohols and acetic acid. They are also soluble in acetone, but to a less extent than in the alcohols and acetic acid. The *p*-salt is the least soluble of the three. The aqueous solutions of the *m*- and *p*-salts become slowly acid, but that of the *o*-salt is very stable. Only the *m*-salt is slightly hygroscopic, and all three give off ammonia very slowly in the air.

The Bromobenzoic Acids.

Ammonium *o*-Bromobenzoate.—No reference to this salt can be found in the literature. It can be prepared by passing dry ammonia into an ether solution of *o*-bromobenzoic acid. The salt at first precipitates as a slightly gelatinous mass, which soon changes to an amorphous powder. If ammonia is passed into an alcoholic solution of the acid, or into a solution of the acid in a mixture of equal volumes of ether and ethyl alcohol no precipitate is formed; but if the latter solution is allowed to evaporate in the air, the salt forms in crystalline tablets. The salt can also be prepared by passing ammonia into a solution of the acid in benzene, from which it precipitates slowly. A flocculent precipitate forms at first and

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[1] *Loc. cit.*

then changes to a fine powder. When recrystallized from benzene it forms in fan-like groups of needles.

The salt is soluble in water, methyl and ethyl alcohols and acetic acid. It is slightly soluble in acetone and insoluble in ether. The aqueous solution is neutral to sensitive litmus, there being no hydrolysis even on standing for several days. The salt is not deliquescent, is stable in dry air, and gives off ammonia very slowly in moist air. Analysis proved it to be the neutral anhydrous salt.

Calc. for $C_7H_4O_2Br(NH_4)$: 6.43%. Prepared in ether. Found: 6.41% N.
Prepared in benzene. Found: 6.38% N.

Ammonium *m*-Bromobenzoate.—As in the case of the *o*-bromobenzoate, no reference to this salt can be found in the literature. It can be readily prepared in an alcohol-ether or in an ether solution of the acid. In the former it precipitates as silky, crystalline flakes, and in the latter as a lustrous white, semicrystalline powder. It is very soluble in water, methyl alcohol, ethyl alcohol, and acetic acid. It is very slightly soluble in chloroform and appreciably so in acetone, but insoluble in ether. The salt is not at all deliquescent. It gives off ammonia very slowly in dry air, and slightly more rapidly in moist air. The salt can also be precipitated in benzene as a milky white, colloidal mass. Analysis was made of the salt prepared in ether.

Calc. for $C_7H_4O_2Br(NH_4)$: 6.43%. Found: 6.38% N.

Ammonium *p*-Bromobenzoate.—This salt has been prepared by Korczynski[1] by the method described. It was prepared by us by passing ammonia into a solution of the acid in ether, in which it formed as a white, amorphous compound. No precipitate was formed when the ammonia was passed into an alcoholic solution of the acid, but on evaporation aggregates of beautiful crystalline plates were formed. The salt is slightly soluble in cold water, but readily soluble in hot water. It is also soluble in methyl alcohol, ethyl alcohol, and acetic acid. It is slightly soluble in acetone and in chloroform. The solution in water is neutral at first, but hydrolyzes slowly and becomes acid. The salt is not deliquescent, but gives off ammonia slowly in the air.

Analysis of the salt prepared in ether proved it to have the composition of the neutral salt.

Calc. for $C_7H_4O_2Br(NH_4)$: 6.43%. Found: 6.46% N.

The neutral ammonium salts of the three bromobenzoic acids can thus be prepared in ether. The *o*-salt can also be prepared in benzene and the *m*-salt in an alcohol-ether mixture. They are soluble in water (the *p*-salt only appreciably so in hot water), methyl and ethyl alcohols, and acetic acid. They are slightly soluble in acetone and insoluble in ether. None of the salts are deliquescent.

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[1] *Loc. cit.*

The Nitrobenzoic Acids.

Ammonium *o*-Nitrobenzoate.—Korczynski[1] has also prepared this salt. It can also be prepared by conducting dry ammonia into a solution of the acid in anhydrous ether, or into a saturated solution of the acid in ethyl alcohol. It forms as a slightly yellowish white, amorphous precipitate in ether or as a white, finely crystalline compound, having a decidedly yellowish tinge, in alcohol. It is soluble in water, methyl alcohol, ethyl alcohol, and acetic acid. It is moderately soluble in acetone. The salt is only slightly hygroscopic, and imparts a neutral reaction to a water solution of it. The aqueous solution slowly hydrolyzes. The salt is fairly stable in the air, losing its ammonia but slowly in moist air.

Calc. for $C_7H_4NO_4(NH_4)$: 7.61%. Prepared in ether. Found: 7.69% ammonium N. Prepared in ethyl alcohol. Found: 7.59% ammonium N.

Ammonium *m*-Nitrobenzoate.—Beilstein mentions the acid ammonium salt, $NH_4C_7H_4(NO_2)O_2 + C_7H_5(NO_2)O_2$. Korczynski[1] says that *m*-nitrobenzoic acid takes up one molecule of ammonia at room temperature and an additional molecule at 0° to —15°.

When ammonia is passed into a solution of *m*-nitrobenzoic acid in ether, the neutral ammonium salt forms as a finely crystalline, snow-white precipitate, soluble in water, methyl alcohol, ethyl alcohol, acetone, and acetic acid. It is insoluble in ether. Its solution in water is neutral. The salt is stable in both dry and moist air. Both the ammonium nitrogen and the total nitrogen in this salt were determined.

Calc. for $C_7H_4NO_4(NH_4)$: 7.61%. Found: 7.57% ammonium N.
Calc. for $C_7H_8N_2O_4$: 15.22%. Found: 15.20% total N.

Ammonium *p*-Nitrobenzoate.—Wilbrand and Beilstein[2] prepared this salt by dissolving the acid in concentrated ammonia water, and allowing the solution to evaporate to crystallization. A hot solution of the salt produced, upon cooling, faint rose-red, much streaked, very glittering, leaf-like crystals which were very easily decomposed. Korczynski[1] also mentions this salt, but does not give its properties. We obtained this salt by our method in an ether solution as a snow-white, amorphous powder, which on analysis proved to be the neutral salt. Some of the salt was recrystallized from warm water in the form of small, transparent leaflets. This was not analyzed, but it was probably the acid salt, as the aqueous solution of the normal salt, which is neutral at first, quickly hydrolyzes and becomes acid, especially on warming. The color mentioned by Wilbrand and Beilstein must have been due to impurities.

The neutral salt is soluble in water, slowly soluble in ethyl alcohol, readily soluble in methyl alcohol and moderately soluble in acetone. It is insoluble in ether. It is not deliquescent and does not lose ammonia in the air.

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[1] *Loc. cit.*

[2] *Ann.*, **128**, 261 (1863).

Calc. for $C_7H_4NO_4(NH_4)$: 7.61%. Found: 7.58% ammonium N.

The three nitrobenzoates can thus be prepared in ether. They are soluble in water, in the common alcohols, and in acetic acid. They are less soluble in acetone than in the other solvents mentioned. Of the three, the *p*-salt is the least soluble in the organic solvents.

Ammonium 3,5-Dinitrobenzoate.—Mention is made of this salt by Korczynski.[1] Hubner[2] states that he used this salt in solution to prepare silver and copper *m*-dinitrobenzoates. He did not prepare the solid ammonium salt.

It can be prepared by passing ammonia into an ether solution of the acid as a white, amorphous powder, having a slight yellowish tinge. It is soluble in water, methyl alcohol, ethyl alcohol, acetic acid, benzene and carbon tetrachloride. It is somewhat soluble in acetone, but less so than in the other solvents mentioned. It is insoluble in ether. The salt is not deliquescent. It is stable in dry air, but loses its ammonia very slowly in moist air. Its aqueous solution is neutral, and does not hydrolyze even on standing for several days.

Calc. for $C_7H_3N_2O_6(NH_4)$: 6.12%. Found: 6.11% ammonium N.

The Aminobenzoic Acids.

Ammonium *o*-Aminobenzoate.—This salt can be prepared either in ether or in a mixture of one volume of acetone and two volumes of ether. When prepared in ether, it is a white, amorphous powder, while in the acetone-ether mixture it forms fine, white needles. It is very soluble in water, the solution being neutral at first but soon becoming acid. The salt is also very soluble in methyl and ethyl alcohols and acetic acid. It is moderately soluble in acetone, and only slightly so in ether. It is slightly deliquescent. It does not lose ammonia in dry air, and only slowly in moist air.

Calc. for $C_7H_{10}N_2O_2$: 18.18%. Found: 18.14% total N.

This analysis was made on the salt prepared in ether and proved that we had obtained the neutral ammonium salt. Although some of the salts of *o*-aminobenzoic acid have been prepared and studied, no mention of the neutral ammonium salt can be found.

Ammonium *m*-Aminobenzoate.—As in the case of the ammonium *o*-aminobenzoate, no reference to this salt can be found in the literature. It can be prepared by pouring a saturated solution of the acid into absolute ethyl alcohol, into which dry ammonia has been passed for some time, into a large amount of ether. Although the salt is only slightly soluble in ether, it cannot be prepared directly in ether since the free acid is also only slightly soluble in that solvent. While filtering off the salt, prepared as above described, it is necessary to keep the alundum crucible

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[1] *Loc. cit.*

[2] *Ann.*, **222**, 78 (1883).

filled with ether to prevent the salt going into solution on account of the alcohol present. The salt dried in a vacuum desiccator to a white, yellow-tinged, flaky, crystalline compound. The salt cannot be prepared by passing dry ammonia into a solution of the acid in methyl alcohol, ethyl alcohol, propyl alcohol, acetone, benzene, toluene, pyridine. carbon tetrachloride or carbon disulfide on account of its great solubility in these solvents. It is also soluble in acetic acid and ethyl acetate. It is only slightly deliquescent. It does not lose ammonia in dry air, but gives it off slowly in moist air.

Calc. for $C_7H_{10}N_2O_2$: 18.18%. Found: 18.12% total N.

Ammonium *p*-Aminobenzoate.—Likewise no mention of this salt can be found. When ammonia is passed into an ether solution of the acid, the salt forms as a white, amorphous precipitate. It is soluble in water, methyl alcohol, ethyl alcohol, acetic acid and acetone. It is only slightly soluble in ether. The salt is not deliquescent, and its aqueous solution is neutral to sensitive litmus paper. It is stable in dry air, and slowly loses its ammonia in moist air.

Calc. for $C_7H_{10}N_2O_2$: 18.18%. Found: 18.17% total N.

The ammonium salts of the three aminobenzoic acids can be prepared in an ether solution by the general method described, modifying the method in the case of the *m*-salt by pouring the saturated alcoholic solution into an excess of ether. The three salts are soluble in water, the alcohols, acetone and acetic acid.

Ammonium 3,5-Diaminobenzoate.—After having so easily prepared the ammonium salts of the nitrobenzoic acids, the 3,5-dinitrobenzoic acid, and the aminobenzoic acids, an attempt was made to prepare the ammonium salt of 3,5-diaminobenzoic acid by passing dry ammonia into a solution of the acid in different organic solvents. Saturated solutions of the acid in methyl alcohol, ethyl alcohol, ether, benzene and carbon tetrachloride were tried, but no precipitate formed, owing evidently to the extreme solubility of the salt in these solvents. Further attempts will be made to prepare this salt and study its properties.

This investigation is being continued with other organic acids, especially the substituted acids.

ST. LOUIS, MO.

THE VAPOR PRESSURES OF PROPANE, PROPYLENE AND NORMAL BUTANE AT LOW TEMPERATURES.[1]

BY G. A. BURRELL AND I. W. ROBERTSON.

Received July 1, 1915.

In this paper, one of a series dealing with the vapor pressures of liquid at low temperatures, are shown the vapor pressures of propane, propylene

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[1] Presented with the permission of the Director of the Bureau of Mines.