[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MONTANA.]

SOME SALTS OF THE HALOGENOACETIC ACIDS. II.

BY W. G. BATEMAN AND D. B. CONRAD.

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In an earlier paper[1] some salts of monochloro- and trichloroacetic acids were described. This article discusses some more compounds formed by these acids and in addition derivatives of dichloroacetic and monobromoacetic acids.

$CHCl_2CO_2NH_4$.—Ammonium dichloroacetate was prepared by passing dry ammonia into an absolute ether solution of dichloroacetic acid. The white precipitate which formed was filtered off and washed free from the acid with ether. Keiser and McMaster[2] first used this method for the preparation of neutral ammonium salts of organic acids and later McMaster[3] amplified the method and described many compounds prepared in this way. Among the solvents which may be used are alcohol, ether and acetone. We have found where the acids are fairly strong, as in the cases of dichloro- and trichloroacetic acids, that a solvent other than alcohol should be used. Both these acids formed with absolute alcohol a fair quantity of ethyl ester, the amount being increased if the solution became hot while ammonia was being absorbed. Under these conditions no precipitate was obtained. Upon evaporation of the alcohol a syrup-like liquid results, which is a solution of the ammonium salt in the ester, and from which the dry salt is obtained with some trouble. If the original solution is distilled, alcohol is first obtained, then the ester and a residue of the salt is left behind. In ether or acetone solutions these difficulties are not encountered, and not in alcohol if the acid be weak.

When prepared as above, ammonium dichloroacetate forms in white leaflets very lustrous and pearly. It is not deliquescent, has a slight halogen odor and is quite stable. When dissolved in water, in which it is very soluble, it gives first a neutral solution, but this soon becomes acid due to hydrolysis. This salt is very soluble in ethyl alcohol, another reason for not preparing it in this liquid. It dissolves readily in ethyl acetate, acetone, ethyl dichloroacetate, methyl alcohol and acetate, but not in ether or benzene and only slightly in ethyl butyrate and iso-amylbenzoate.

When heated carefully the compound volatilizes in white fumes having an odor of ammonia. Upon stronger heating it chars, while dichloroacetic acid, ammonia and carbon dioxide are evolved.

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[1] Bateman and Hoel, THIS JOURNAL, **36**, 2517 (1914).

[2] Keiser and McMaster, *Am. Chem. J.*, **49**, 84 (1913).

[3] McMaster, *Ibid.*, **49**, 294 (1913); THIS JOURNAL, **36**, 742 and 1916 (1914).

If this salt is prepared in alcohol solutions it has an odor similar to that of acetamide.

Calc. for $CHCl_2CO_2NH_4$: N, 9.60%. Found (by Kjeldahl), 9.62.

We have found no mention of this salt in the literature.

If dry hydrogen chloride is passed into an absolute ethyl acetate solution of ammonium dichloroacetate a precipitate of ammonium chloride is obtained.[1] Ammonium monochloro- and trichloroacetates act in the same way.

Water solutions of these three salts dissolve mercuric oxide readily, especially when heated. After a certain amount of the oxide has gone into solution white, amorphous substances precipitate in each case.

It is interesting to note how soluble the ammonium salts of the chloroacetic acids are in acetic ester. Naumann[1] found ammonium salts of inorganic acids to be in general insoluble in this reagent. We find ammonium acetate to be also insoluble, or only slightly so. If it is concluded that the substituted chlorine causes this effect this seems contradicted by the fact that ammonium chloride is also insoluble.

In the first paper we stated that no mention had been found regarding neutral ammonium trichloroacetate. But Malaguti (quoted in Roscoe and Schorlemmer, III, 541) obtained it in nacreous scales by cooling the melted hydrate

$CH_2BrCO_2NH_4$.—The ammonium salt of monobromoacetic acid was obtained by passing dry ammonia into an absolute ether solution of the acid. It can be prepared from alcohol as well, but is rather soluble in this solvent. It forms in glistening white leaflets which, when dry, smell faintly of bromine. Ammonium bromoacetate is not deliquescent and is stable. It is soluble in water, giving at first a neutral solution which later reacts acid. It is also soluble in ethyl acetate and in ethyl chloroacetate but not in benzene. When heated cautiously it volatilizes completely but is decomposed with charring when heated strongly.

Calc. for $CH_2BrCO_2NH_4$: N, 8.97. Found (by Kjeldahl), 9.06.

$Cu(CHCl_2CO_2)_2.4H_2O$.—This salt was prepared by adding copper carbonate in slight excess to a concentrated water solution of dichloroacetic acid. The mixture was allowed to stand for a time since action was slow. After filtering, some alcohol was added to the deep blue solution and the whole set away to crystallize. At least two different compounds were obtained. One formed in deep blue, fan-shaped clusters of needle-like crystals, another in rosets of pale blue-green small needles. The first of these, on standing or heating, passed into the second, although microcrystalline or almost amorphous in form. Both forms were very soluble in ethyl acetate, but only the green compound was left when the

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[1] Naumann, *Ber.*, 43, 313 (1910).

solvent evaporated away. This latter salt gave blue crystals when treated with a little water.

The deep blue-colored crystals are the tetrahydrate.

Calc. for $Cu(CHCl_2CO_2)_2.4H_2O$: Cu, 16.23; H_2O, 18.39. Found: Cu, 16.12; H_2O, 18.25.

The pale-colored compound is the anhydrous salt. Between these two there is another hydrate of bright green color.

The tetrahydrate recalls copper nitrate in appearance. It readily loses water in the air or in a desiccator over calcium chloride. It is very soluble in water, giving an acid solution, in ethyl acetate, in absolute alcohol, forming blue solutions. In acetone, glacial acetic acid, dichloroacetic acid and ether it gives green solutions. It is not soluble in benzene.

$Cu(CHCl_2CO_2)_2$.—The anhydrous salt gives a blue solution in water but green in other solvents. It is somewhat less soluble than the hydrate.

When heated the hydrate loses all its water at about 100° and forms the anhydrous salt. If heated above 100° the latter melts, gives off acid slowly, but at the same time increases in bulk and changes in appearance. Upon cooling the melt still appears to be copper dichloroacetate.

$Cu(CCl_3CO_2)_2.3H_2O$ was prepared in the same manner as the copper salt of dichloroacetic acid. It crystallized in fine, medium blue crystals, recalling those of copper sulfate pentahydrate. The salt is stable, but gives off the very spicy odor which we have now met with several times in connection with these copper salts. It is very soluble in water, ethyl acetate, acetone and absolute alcohol, giving blue solutions. In ether it is soluble, but gives a blue-green solution as it does in glacial acetic acid. It is not soluble in benzene.

Calc. for $Cu(CCl_3CO_2)_2.3H_2O$: Cu, 14.37; H_2O, 12.20. Found: Cu, 14.51; H_2O, 12.02.

Judson[1] has described a hexahydrate of this salt but states that it so easily loses water in the air that he took crystals from the solution and dried them merely with paper before analysis. We did not observe this compound. Judson also notes that an excess of copper carbonate decomposes trichloroacetic acid with the formation of chloroform. We have observed the same, which does not happen in cold solutions but readily in hot. If the carbonate and acid be mixed dry and gently heated, chloral is formed. Other carbonates than that of copper bring about both reactions.

$Cu(CCl_3CO_2)_2$.—When the trihydrate is heated at 103° for some hours it loses all the water and becomes a bright blue-green powder, the anhy-

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[1] Judson, *Ber.*, 3, 782 (1870).

drous salt. This is less soluble in water than the hydrate and also less soluble in absolute alcohol, with which it forms a green solution.

When a dilute solution of phenylhydrazine in absolute alcohol is added to a solution in the same reagent of the copper salt of any one of the chloroacetic acids, olive-colored substances precipitate at once. These are no doubt addition products such as phenylhydrazine forms so readily. They promptly decompose, however, with vigorous evolution of nitrogen. Next a white precipitate settles out in long needles. This is quite unstable, for when exposed to the air it turns copper-red in color, the same effect being brought about by water, only more energetically. These precipitates dissolve readily in ammonium hydroxide, but at first give colorless solutions which upon shaking with air become green and finally the deep familiar blue. Hydrochloric acid solutions quickly become colored brown.

If phenylhydrazine is used to excess and if the mixture be allowed to become hot, cuprous oxide is formed and in some cases what appeared to be free copper. Sometimes the odor of benzene is perceived.

The white precipitate is chiefly cuprous chloride, which is changed by the action of moist air or water into cuprous oxide as stated by Lescoeur[1] and Haywood.[2] It may contain, however, the salt of phenylhydrazine and the chloroacetic acid whose copper salt is used.

Still other substances are sometimes found. If the alcohol solution from the reacting mixture is diluted with water a white crystalline substance separates. This is diphenylamine, or some substitution product, since it has the agreeable odor and gives the usual test with nitric acid characteristic of this compound. Tafel,[3] and later Gatterman, Johnson and Hölzle,[4] found diphenylamine derivatives to be formed by reducing phenylhydrazines with copper acetate and decomposing the resulting compounds.

If the solution is hot and oxidation energetic, the ethyl ester of the acid is sometimes recognized by its odor. When copper monochloroacetate is concerned, the reaction mixture usually has a strong, aromatic, spicy odor. This is no doubt due to monochloroacetaldehyde, since Tafel[5] found aldehyde to be formed with copper acetate. This is all the more probable since, when copper trichloroacetate is used, the familiar, sweet, pungent odor of chloral can at times be detected. Monochloroacetaldehyde is said to have a powerful odor.

Finally chlorobenzene is formed. Gattermann and Hölzle[6] have

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[1] Lescoeur, *Ann. chim. phys.*, **7**, 97 (1894).

[2] Haywood, *J. Phys. Chem.*, **1**, 411 (1897).

[3] Tafel, *Ber.*, **25**, 413 (1892).

[4] Gatterman, Johnson and Hölzle, *Ibid.*, **25**, 1075 (1892).

[5] Tafel, *Ibid.*, **25**, 413 (1892).

[6] Gatterman and Hölzle, *Ibid.*, **25**, 1074 (1892).

shown that the monohalogen benzene compounds can be prepared by the action of copper sulfate on phenylhydrazine in the presence of hydrogen halides with the separation of cuprous chloride or metallic copper.

Comparison of Copper Acetate with the Copper Chloroacetates.

Color.—$Cu(CH_3CO_2)_2.H_2O$ has a deep green color.

$Cu(CH_2ClCO_2)_2.4H_2O$ has the same green color but lighter in shade.

$Cu(CHCl_2CO_2)_2.4H_2O$ is deep blue in color.

$Cu(CCl_3CO_2)_2.3H_2O$ is medium blue in color.

The anhydrous chloro salts all have a bright blue-green color, but $Cu(CHCl_2CO_2)$ is paler than the rest, while anhydrous copper acetate is white.

Solubility.—The salts of the substituted acids are more soluble, in general, than copper acetate. This is especially so with ethyl acetate, in which copper acetate dissolves only slightly, while the copper chloroacetates are very soluble. Copper halides are soluble as observed by Naumann.[1]

Stability and Reactivity.—Copper acetate is more stable than the copper chloro-salts but the latter are more active, especially in oxidation reactions.

$Cu(CH_2BrCO_2)_2.H_2O$.—This copper salt was prepared in the same way as the others. It crystallizes from deep green solutions in masses of small, dark green crystals similar in appearance to those of copper acetate itself and hence darker in color than those of copper chloroacetate. It is very soluble in water, alcohol, acetone and ethyl acetate, and somewhat soluble in ether and glacial acetic acid. It is insoluble in benzene.

Copper monobromoacetate reacts with phenylhydrazine in a manner analogous to the action of the chloro-salts, but slower and less vigorous. Cuprous bromide is formed which reacts with moist air or water to give metallic copper and cuprous oxide, but this action is weaker than with cuprous chloride.[2]

Calc. for $Cu(CH_2BrCO_2)_2.H_2O$: Cu, 17.78; H_2O, 5.03. Found: Cu, 17.69; H_2O, 5.14.

$Cu(CH_2BrCO_2)_2$.—The anhydrous salt has a blue-green color and is soluble in the same reagents as the hydrate, but in somewhat less degree.

If a solution of copper bromoacetate is heated for a time on the steam bath, it becomes brown in color and copper bromide separates from the cooled solution. This salt, then, is more susceptible to hydrolysis than copper chloroacetate.

$Hg(CH_2ClCO_2)_2$.—Mercury monochloroacetate was prepared by add-

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[1] Naumann, *Ber.*, **43**, 314 (1910).

[2] Bödlander and Storbeck, *Z. anorg. Chem.*, **31**, 1 and 458 (1902).

ing in small quantities at a time pure mercuric oxide to a hot water solution of the acid. The latter was kept always in excess. After a time, a white precipitate separated in shining leaflets from the hot solution. This was filtered off and the cool solutions left to crystallize. From them a white, coarsely crystalline substance was obtained having a slight tinge of yellow. Both forms are, however, the anhydrous salt.

Calc. for $Hg(CH_2ClCO_2)_2$: Hg, 52.44. Found: leaflets, Hg, 52.54;[1] crystals, 52.50.

This compound is only sparingly soluble in water, alcohol, acetone and ethyl acetate. When hydrogen sulfide is passed through the solution in ethyl acetate a bright orange precipitate is first formed but this quickly becomes black.[2] If dry ammonia be passed into the solution in the same solvent the salt is reduced with the formation of mercury. Other mercuric salts form ammonates.[3]

When mercuric monochloroacetate is heated, it begins to melt at 135° and boils at 140°. While boiling it becomes slightly pink in color. At 150° boiling ceases and the temperature rises to 185° before further action takes place. Then the residue rapidly becomes black and at 190° is mostly free mercury.

When this salt is treated with ammonium hydroxide a fine, white powder is precipitated which becomes yellow in color upon sparing washing and drying. This, if only ammonolysis[4] takes place, would be NH_2-Hg-CH_2ClCO_2 with a mercury content of 64%. If both ammonolysis and hydrolysis take place we might expect the monochloroacetate of Millon's base since, as shown by Franklin, salts of this base are usually found where ammonium hydroxide reacts with mercuric salts. The above compound contains 76% mercury. Analysis of the sample, however, gave values in the neighborhood of 85%. $HOHgNH_2$ requires about this quantity of mercury, but 2% nitrogen, while our preparation contained only 0.25% of the latter.

$Hg(CCl_3CO_2)_2$.—We tried to prepare this salt by the action of the acid on mercuric oxide since this plan succeeded with the monochloro salt. However, it did not work well in this case. Water solutions of the acid will keep on reacting with mercuric oxide long after the theoretical quantity has been used. White, amorphous substances separate out, containing varying amounts of mercury, and the solution gives forth a variety of sweet odors. If mercuric oxide in the right quantity is added, little by little, to a water solution of the acid, a beautiful, white, crystalline mass of shining needles soon collects on the top of the liquid. This apparently

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[1] This analysis was kindly made for us by Mr. A. B. Hoel.

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

[3] Neumann, *Loc. cit.;* Franklin, THIS JOURNAL, **29**, 35 (1907).

[4] Franklin, *Loc. cit.*

is the mercuric compound, but we never succeeded in getting it pure. Almost at once it falls to the bottom of the dish in the form of a white powder and this, when examined and analyzed, proves to be almost pure mercurous chloride.

Calc. for Hg_2Cl_2: Hg, 84.95. Found: 84.57.

Other attempts gave mixtures of mercurous and mercuric salts and basic salts. According to Beilstein, Clermont[1] prepared this salt in prismatic needles, but we have not seen the original paper.

$Hg_2(CCl_3CO_2)_2$.—This salt was prepared by adding a solution of trichloroacetic acid to a freshly prepared solution of mercurous nitrate. A snow-white precipitate consisting of small needles was thrown down. If this is allowed to crystallize from water, in which it is but sparingly soluble, it can be obtained in large beautiful needles.

Calc. for $Hg_2(CCl_3CO_2)_2$: Hg, 55.19. Found: 55.39.

While sparingly soluble in water, this substance is very soluble in alcohol, ethyl acetate, acetone, benzene and toluene, and somewhat so in ether. If dry hydrogen sulfide be passed through the solution in benzene a precipitate consisting of mercuric sulfide and mercury is produced. Ammonium hydroxide immediately decomposes mercurous trichloroacetate. Toward heating it is very stable and volatilizes at temperatures over 200° with very little decomposition.

$Hg_2(CH_2ClCO_2)_2$.—The mercurous salt was prepared by pouring a solution of the acid into a freshly prepared solution of mercurous nitrate containing enough nitric acid to prevent hydrolysis. A snow-white precipitate fell down which, when dry, consisted of a fluffy mass of small needles.

Calc. for $Hg_2(CH_2ClCO_2)_2$: Hg, 68.12. Found: 68.36.

This salt is but slightly soluble in water and insoluble in alcohol, ether, ethyl acetate and acetone. When treated with ammonium hydroxide it is completely decomposed in a manner analogous to other mercurous salts. When heated in the presence of water vapor it is quite unstable and darkens readily. If heated dry it does not change much below 180°, at which point it melts with some decomposition, a white powder subliming in the tube and a black residue being left.

$Hg_2(CH_2BrCO_2)_2$.—Mercurous monobromoacetate was prepared in the same way as the other mercurous salts. It is an amorphous, white powder only slightly soluble in water. In alcohol, ether, acetone, ethyl acetate and benzene it is insoluble. When heated it begins to darken at 145°, becomes yellow—due to liberated bromine—and sublimes without melting. The usual behavior of mercurous compounds with ammonia is shown by this salt.

Calc. for $Hg_2(CH_2BrCO_2)_2$: Hg, 59.18. Found: 59.42.

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[1] *Jahrsb. fort. Chem.*, **1871**, 550.

When solutions of mercurous nitrate and dichloroacetic acid are brought together no precipitation occurs; even after standing, no salt of the organic acid acid separates. This mercurous salt then, if formed, is an exception to its class in being apparently so soluble.

The same difficulty was met when the mercuric salt of dichloroacetic acid was sought by bringing the acid and mercuric oxide together as in the case of trichloroacetic acid. The compound obtained was always a mixture of mercurous and mercuric salts. The dichloro acid is, however, more stable in this respect than its trichloro relative.

Summary.

1. In the two papers of this series the preparation, analysis, description and properties of about twenty-five salts of monochloro, dichloro, trichloro and monobromo acetic acids are discussed. No, or very scanty, information concerning these appears to be in the literature.

2. The action of the copper salts of the above acids on phenylhydrazine is found to be complex, strong reduction taking place with the formation of cuprous halides, phenylhydrazine salts of the halogeno acids, cuprous salts of the same, diphenylamine derivatives, chlorobenzene and other products depending upon conditions.

3. The series of copper chloroacetates is compared with copper acetate.

4. Some of the mercury salts of the above acids are found interesting. Mercurous dichloroacetate appears to be very soluble in water while mercurous trichloroacetate is very soluble in all the ordinary organic solvents.

5. A number of reactions of some of these salts in such nonaqueous solvents as ethyl acetate and benzene are described.

MISSOULA, MONTANA.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA.]

THE ACTION OF ALUMINIUM CHLORIDE ON THE ALIPHATIC ETHERS.

BY G. B. FRANKFORTER AND E. A. DANIELS.

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It has been shown by Frankforter and Kritchevsky[1] that aluminium chloride not only acts as a catalyst according to the well-known Friedel-Crafts reaction, but also as a dehydrating reagent, removing a molecule of water according to the common condensation reaction. In a few cases, however, they found that it gave the aldol reaction when the halogen aldehydes, namely chloral and bromal, were brought in contact with other reacting constituents. Thus, when methyl phenyl ether is treated with chloral in the presence of aluminium chloride, the following almost quantitative reaction takes place if the temperature is kept low enough:

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[1] *Bull.* 2, Chemical Studies, University of Minnesota.