of the nature of oxonium salts. This reaction is *ionic* and *instantaneous*. The addition compounds obtained are possibly—but not necessarily—real intermediate products in the formation of sulfonic acids.

It will be obvious that similar reactions, such as nitration, may be considered to follow an exactly similar course.

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SOME SALTS OF THE CHLOROACETIC ACIDS.

BY W. G. BATEMAN AND A. B. HOEL.

Received October 9, 1914.

While looking up constants in connection with the regular work in the organic laboratory, we noted the paucity of information in the literature relating to the derivatives of the chloroacetic acids. The work described in this paper was then undertaken to fill up some of the gaps encountered.

$CH_2Cl.CO_2NH_4$.—The difficulty of obtaining neutral ammonium salts of organic acids from water solutions has many times been mentioned. In the case of chloroacetic acid this difficulty is increased by the fact that both ammonium hydroxide and carbonate increase in aqueous solutions the hydrolysis of the acid into glycollic acid and hydrogen chloride. It was decided, therefore, to prepare this salt by passing ammonia into an absolute alcohol solution of the acid. This method is the same as that employed by Keiser and McMaster[1] who prepared many neutral ammonium salts by this method, but whose papers did not come to our notice until this work was practically finished.

Ammonia, made by heating the concentrated hydroxide and dried by passing through a high soda lime tower, was passed into a solution of monochloroacetic acid in absolute alcohol. In a few minutes a heavy, white precipitate fell down which was filtered off, washed with alcohol, in which it was sparingly soluble and dried in a current of air. The product was snow white and beautifully crystalline. It is readily soluble in water, to which at first it imparts a neutral reaction, which, in a few minutes, becomes acid, due to hydrolysis. The salt is also soluble in methyl alcohol, but insoluble in ether, benzene or chloroform.

When heated in an open dish ammonium chloroacetate volatilizes completely without charring, and giving off dense fumes like those of ammonium chloride.

The only mention we find of this salt is in Beilstein[2] who quotes Rival[3] as saying the salt is "unbeständig." Our product seemed quite stable,

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[1] *Am. Chem. J.*, 49, 84 (1913); THIS JOURNAL, 36, 742 (1914).

[2] *Beilstein, Ergänzb.*, I, 167.

[3] Rival, *Ann.*, 12, 504

no changes being observed after several months' standing. It is not deliquescent. In a few samples a slight but unmistakable odor like that of impure acetamide was perceived. Chloroacetamide with its unknown odorous companion might here be formed in two ways: by a slight amount of chloroacetic ester being formed and reacting with the ammonia, or by a slight decomposition of the ammonium salt itself.

Calc. for $NH_4CH_2ClCO_2$: N, 12.55; found (by Kjeldahl), 12.51.

$CCl_3CO_2NH_4$.—This salt was prepared like the above, by passing dry ammonia into an absolute alcohol solution of trichloroacetic acid. No precipitate was formed; the solution gave out so much heat that it was cooled in ice water. After passing the gas for some minutes, the solution became very viscous. The addition of ether gave no precipitate, but after standing some days a skim of crystals collected on the top. The alcohol evaporated away very slowly, suggesting the possibility of some combination involving it. At the same time the solution gave off a most agreeable odor which was found to be due to trichloroacetic ester. Upon gentle heating the alcohol was given off slowly, leaving behind a thick, odorless syrup. When this was stirred and briskly beaten it solidified into a mass of slightly moist white crystals, which were dried in a desiccator. The product gave a neutral reaction to water solutions, which quickly became strongly acid. It was soluble in alcohol, ether and ethyl acetate. Careful heating in an open dish caused complete volatilization, without charring, in white fumes having the odor of the acid. Upon stronger heating the compound decomposes, gives off ammonium chloride, irritating vapors of carbonyl chloride and, in addition, carbon monoxide. No mention of this salt was found, but Rival[1] describes the dihydrate and several acid compounds.

Calc. for $NH_4CCl_3CO_2$: N, 7.75; found (by Kjeldahl), 7.63.

$Cu(CH_2ClCO_2)_2.4H_2O$.—This compound was formed by adding a slight excess of copper carbonate to a water and alcohol solution of chloroacetic acid. After filtering, the deep blue solution was set aside to crystallize. Beautiful, deep green crystals formed, less dark in hue than those of copper acetate. These are soluble in strong alcohol, forming a bright green solution.

Calc. for $Cu(CH_2ClCO_2)_2.4H_2O$ Cu, ——; found, 19.71, 19.84; 0.2261 g. heated at 102–105° for some hours lost 0.0495 g.; water calculated for above, 22.30%; found, 21.91%.

$Cu(CH_2ClCO_2)_2$ was prepared by dehydrating the tetrahydrate, the product being a bright blue-green powder. This dissolves in absolute alcohol, not so readily as the hydrate, giving a greenish blue solution. The anhydrous salt is also less soluble in water, with which it forms a slight, white precipitate, probably a basic salt. Some of this compound

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[1] *Loc. cit.*

was dissolved in alcohol and dry ammonia passed in. In addition to some of the white ammonium salt, a considerable amount of a deep blue crystalline substance was formed. This was judged to be $Cu(NH_3)_4(CH_2ClCO_2)_2$ by its resemblance to analogous compounds, but the sample was lost during analysis.

Calc. for $Cu(CH_2Cl.CO_2)_2$: Cu, 25.37; found, 25.46.

In an attempt to prepare an addition product of copper chloroacetate and phenylhydrazine, the two were brought together in alcohol. A very vigorous reaction occurred in the cold. Cuprous oxide was precipitated and nitrogen evolved in large quantities. At the same time, a substance having a most agreeable spicy odor was formed. Copper acetate is reduced in hot solutions by hydrazines in a similar fashion,[1] but the halogen substituted salt is much more energetic. We hope to investigate this reaction further.

$Zn(CH_2ClCO_2)_2.2H_2O$.—Prepared in the same way as the preceding. This compound formed in fan shaped clusters of large almost transparent crystals. These were very deliquescent, being wet after standing over concentrated sulfuric acid. During this drying the crystals changed form and appearance, becoming smaller and white. Analysis of the higher hydrate were unsatisfactory, but indicated the tetrahydrate.

Calc. for $Zn(CH_2ClCO_2)_2.2H_2O$: Zn, 22.66; found, 23.

$Pb(CH_2ClCO_2)_2$.—Prepared by heating together equivalent quantities of pure litharge and the acid in water solution. Upon cooling the solution the salt crystallized out in fine, white, prismatic plates. Both salt and solutions have a sweet taste. The salt is sparingly soluble in cold water, much more soluble in hot.

Calc.: Pb, 52.55; found, 52.73.

$Mn(CH_2ClCO_2)_2CH_2ClCO_2H.4H_2O$.—When water solutions of monochloroacetic acid were treated with manganese carbonate, it was found impossible to neutralize the solution. Even when cold some black, hydrated manganese dioxide always formed, the quantity of which was increased by heating. Both hot and cold solutions after filtering and evaporating gave crops of transparent crystals having no trace of color. Upon drying these became pure white and microcrystalline. Solutions of this were rather strongly acid, and even the moist salt had an acid odor.

Calc.: Mn, 13.46; found, 13.51.

Slightly soluble in cold alcohol and ether. Soluble in acetic ester.

$Mn(CH_2ClCO_2)_2CH_2ClCO_2H.2H_2O$.—When the tetrahydrate was heated for some time below 105° it readily lost two molecules of water, became somewhat more bulky and rather fluffy in appearance. A very little

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[1] Tafel, *Ber.*, **25**, 413 (1892); Gatterman, Johnson and Hölzle, *Ibid.*, **25**, 1075 (1892).

acid was given off during the heating and the faintest tinge of pink color was noted.

Calc.: H_2O, 8.81; Mn, 15.51; found, 8.05, 15.32.

When the dihydrate or tetrahydrate were heated much above 105° water was given off very slowly, but the amount of acid volatilized was much increased. The residue acquired the familiar pink color of normal manganous salts. Neither the anhydrous acid nor the normal salt could be secured in this way, since decomposition occurred on stronger heating with the darkening of the residue due to the formation of manganese dioxide.

When the acid tetrahydrate is dissolved in hot alcohol, there is precipitated, upon cooling, a very bulky white crystalline mass, which is freed from the solvent with considerable difficulty. As the alcohol evaporates away the compound shrinks in bulk, and has the same appearance when dry as the hydrate described above, looking much like purified cellulose. Analysis showed it to be the same compound.

Calc.: Mn, 15.51; found, 15.17.

The compound lost water and acid by prolonged drying or gentle heating.

$Ni(CH_2ClCO_2)_2.3H_2O$.—Obtained by treating water solutions of the acid with nickel carbonate. The deep green solutions upon evaporation gave only thick, green syrups, which did not crystallize upon seeding with a crystal of nickel acetate, or by treating with alcohol or ether. Finally, heated on the water bath, both solutions became very viscous, and, after standing some time in a desiccator, gave apple-green crystals.

Calc.: Ni, 19.61; found, 19.37.

$C_6H_5.NHNH_2(CH_2ClCO_2H)_2$.—Formed by bringing together the proper quantities of phenylhydrazine and acid in absolute alcohol. The compound formed in heavy, white, needle-like crystals, which were filtered, washed with alcohol and dried. They had a faint odor of the hydrazine, which increased on standing showing the salt to be unstable. Soluble in water.

Calc.: N, 9.43; found, 9.50.

In the same way finely crystalline salts of this acid with aniline and *p*-toluidine were obtained, but not with methyl and ethyl substituted aniline, diphenylamine or salts of hydroxylamine. When methylbenzyl aniline was treated with chloroacetic acid, benzaldehyde was formed.

$CO(NH_2)_2CH_2ClCO_2H.C_2H_5OH$.—Equivalent quantities of pure urea and monochloroacetic acid were brought together in absolute alcohol. Upon evaporation very large, leafy, transparent crystals were formed having a high luster. These upon standing constantly smelled of alcohol, which was given off until the crystals fell into a fine, white crystalline powder, evidently the anhydrous salt. Both crystals and powder are very soluble in water, which, however, hydrolyzes the combination to some extent, since urea crystals form before the salt itself separates out.

Calc.: N, 13.67; found, 13.60.

Basic Iron and Chromium Compounds.—No definite compounds were obtained by treating ferric and chromic hydroxides with water solutions of chloroacetic acid. The normal ferric salt appears to hydrolyze very easily, since even in cold solutions the iron is practically all removed by precipitating as a mixture of the basic salts. A solution containing the chromic salt was strongly dichromatic, green and purple; upon evaporation crystals of pure monochloroacetic acid were deposited. Later a pale green crystalline substance separated out and appeared to be a hydrate of $Cr(CH_2ClCO)_2OH$ mixed with a small amount of some salt more basic.

All of these salts, when treated in solution with silver nitrate, in no case gave more than a very slight opalescence.

None of the above salts are found mentioned in available literature.

A number of other compounds have been prepared and work is in progress upon still others.

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[CONTRIBUTION FROM THE ESSENTIAL OILS LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE RESOLUTION OF ASCARIDOLIC ACID.

BY E. K. NELSON.

Received October 13, 1914.

Ascaridolic acid,[1] possessing the structure of a 1,4-cineolic acid, should, like ordinary $d + l$ cineolic acid, be a racemic compound.

Attempts to effect its resolution by means of its brucine or strychnine salt resulted in failure. With the cinchonidine salt, however, little difficulty was experienced.

Twenty grams of ascaridolic acid were dissolved in 2500 cc. of hot water and 27 g. of powdered cinchonidine were gradually added while boiling and stirring. On cooling, a salt separated in the form of fine, silky needles, which, filtered, washed with a little water and dried, weighed 19 g., corresponding to 8 g. of the original acid. The mother liquors and washings were concentrated at a low temperature (not over 40°) and the salt separated was fractionally crystallized until it was fairly free from the difficultly soluble salt.

The cinchonidine salt of the acid was thus separated into a slightly soluble and a readily soluble salt. These salts, dissolved in warm water and decomposed with an excess of dilute hydrochloric acid, yielded the corresponding acids, both of which, after purifying by repeated crystallization, were obtained in well formed prisms.

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[1] E. K. Nelson, THIS JOURNAL, **33**, 1410 (1911), **35**, 89 (1913).