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.

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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.

$$2C_6H_5OCH_3 + OCH - CCl_3 + AlCl_3 = (C_6H_4OCH_3)_2CHCCl_3 + H_2O + AlCl_3;$$

but, when anthracene is treated with chloral in the presence of aluminium chloride, the aldol reaction takes place according to the following equation:

$$C_{14}H_{10} + CHO - CCl_3 + AlCl_3 = C_{14}H_9CHOH - CCl_3 + AlCl_3$$

In a very few cases aluminium chloride was found to combine directly with the reacting components forming unstable compounds.

Following out the line of work mentioned above as well as the work of Frankforter and Poppe,[1] the aliphatic ethers were treated with chloral in the presence of aluminium chloride and finally with the chloride alone. It was soon found that the reaction with the aliphatic ethers does not proceed along the same lines as observed in the aromatic ethers. However, the reaction proved to be of considerable interest, although it was extremely complex.

The first experiments were tried with common ethyl ether and chloral in the presence of aluminium chloride. Although the conditions were widely varied, the reaction seemed extremely complex in each case and no compounds analogous to those obtained from the aromatic ethers were formed, but when commercial ether was used, a heavy, white, flocculent precipitate was formed. The formation of this precipitate which was subsequently found to be due to moisture in the ether was used as a basis for a qualitative test for water in ether.

It was thought that the complex reaction was due, partly at least, to reactions between two of the constituents, namely, aluminium chloride and chloral, or aluminium chloride and ether. Thus Combes[2] found that chloral and aluminium chloride react on each other, forming tetrachlorethylene and a polymerized form of chloral which he called perchloral. We were unable to obtain this compound. In fact, we were unable to identify any of the compounds formed in this experiment.

The experiments which follow were carried out with perfectly dry ether, inasmuch as we found that water in the ether completely changed the reaction. In order to eliminate any possibility of moisture during the reaction, a flask was fitted with a two-hole stopper, one hole connected with a calcium chloride drying tube and the other carrying a thermometer in order to observe the temperature. The mixture of ether and chloral was placed in the flask and cooled down to 0°, then powdered aluminium chloride was added in 5 g. portions. A large amount of heat was generated notwithstanding the fact that the flask was kept in ice-water. At the same time a small amount of hydrochloric acid was liberated and

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[1] *8th Intern. Congr. Appl. Chem.*, **25**, 363 (1910).

[2] *Ann. Chem.*, [6] **12**, 3, 199 (1887).

escaped through the drying tube. Aluminium chloride was added until the ether was saturated and a small quantity of solid chloride was left in the bottom of the flask. We were unable to prove that the hydrochloric acid gas liberated was not due to the action of moisture on the chloride.

It required about an hour to add the chloride. At the end of that time the solution had changed from a perfectly colorless to a straw yellow. After standing in ice-water for two hours, the flask was removed and the temperature allowed to slowly rise to room temperature. The color changed with the rise in temperature until at 22° it was a reddish brown. The mixture was then allowed to stand over night at a temperature of 0°. In the morning the whole mass had changed to a light brown jelly. It turned darker on standing at room temperature. Treated with water a large amount of heat was liberated and the substance separated out as a thick, dark brown mass. This was subjected to steam distillation when several substances were obtained, but the quantities were too small to permit a careful examination. During the distillation, there was a distinct odor of ether. The viscous insoluble material remaining in the flask after the steam distillation was filtered off and examined. It was dissolved in ether and filtered. There remained an undissolved gelatinous substance which subsequently was found to be a simple aluminium compound.

The ether extract, which carried practically all of the organic substance, left upon evaporation a dark brown resinous mass. It was distilled under diminished pressure. At 52° and 22 mm. pressure, crystals formed in the condenser, evidently chloral hydrate; at 62–80° and the same pressure, a small amount of liquid passed over, then the temperature rapidly rose to 125°, when a very small quantity of a liquid passed over, but the quantity was too small for exhaustive examination. The résidue left in the flask was of a dark brown color and appeared charred. With the hope of obtaining more satisfactory results, the above experiment was repeated, except that the temperature was kept at —8° instead of 0°. The same reaction seemed to take place although the results obtained by distillation *in vacuo* were somewhat different. A small quantity of liquid passed over at 100°, together with a large amount of hydrochloric acid. The oil was found to react vigorously with water, and is evidently an organic compound of aluminium chloride. Crystals passed off between 110 and 135°. They were removed, pressed between filter paper and finally dried in a desiccator over sulfuric acid. They melted at 22–24° and were readily decomposed in the air, changing to a liquid. The quantity of substance, however, was not sufficient for an exhaustive examination. They were doubtless the compound of aluminium chloride and ether to be described later. The residue left in the flask was insoluble in ether.

It was partially soluble in water with evolution of heat and a peculiar disagreeable odor. An exhaustive examination of the residue failed to yield a definite compound.

The Action of Aluminium Chloride on Ether.—It was observed early in the above experiments that aluminium chloride combined readily with ether, producing a well crystallized compound. Absolute ether was therefore treated with equal weight of anhydrous aluminium chloride at a low temperature. The solution immediately changed to a dark purple and much heat was liberated. The mixture was kept at —15° over night. In the morning the whole was a solid mass of well defined crystals. These crystals were found to dissolve when the room temperature was reached, but reformed on cooling. They were found to react violently with water.

In going over the literature it was found that various salts of ether had been prepared. Thus titanium chloride[1] was found to combine with ether and to form a double salt. Tin, bismuth, zinc, arsenic and antimony chlorides and bromides[2] form double salts with ether, representing the general formula,

$$SnCl_4.C_4H_{10}O \quad \text{and} \quad SbBr_3.C_4H_{10}O.$$

Boeseken,[3] in his work on aluminium chloride, prepared an acetyl double salt by treating acetyl chloride dissolved in carbon disulfide with aluminium chloride, to which he gave the formula

$$AlCl_3.CH_3COCl.$$

Plotnikov[4] described a double salt of ether and aluminium bromide to which he gave the formula

$$AlBr_3.(C_4H_{10}O)$$

and Walker and Spencer[5] in a study of the action of aluminium chloride on organic compounds containing oxygen incidentally studied the reaction between ethyl ether and aluminium chloride. They dissolved the organic substance in carbon disulfide and then added the aluminium chloride. Evaporating off the solvent by a current of dry air, they obtained large brown plates. They obtained by analysis 13.93% of Al for the compound to which they ascribed the formula

$$Al_2Cl_6.2C_4H_{10}O.$$

The theoretical for Al is 13.01%.

Inasmuch as the reaction between ether and aluminium chloride, and especially the compound mentioned above, has not been carefully studied,

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[1] *Bull. soc. chim.*, **33**, 566 (1880).

[2] *J. Pharm.*, [3] **26**, 161 and *J. prakt. chem.*, **83**, 259 (1861).

[3] *Rec. trav. chim.*, **20**, 102 (1901).

[4] *Z. anorg. Chem.*, **56**, 53 (1907).

[5] *J. Chem. Soc.*, **85**, 1106 (1904).

we have given the reaction further consideration, feeling that there was still much to be learned.

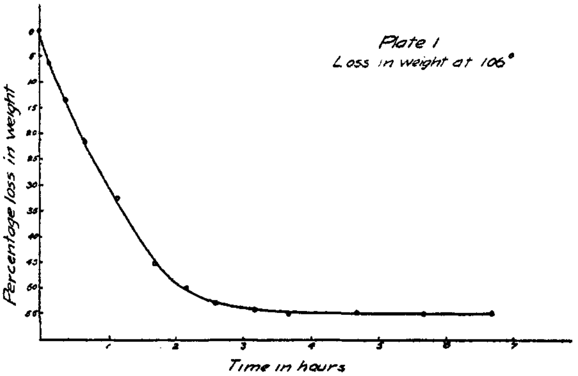
Best results were obtained by using pure, dry ether without a diluent and keeping the temperature fairly constant at 15° until the first few portions of the chloride had been added. After this the reaction seemed to proceed best between 35 and 50° with frequent shaking. It was also found that good, fresh aluminium chloride in pieces about the size of a pea gave better results than the powdered chloride, which reacts too vigorously, resulting in more or less decomposition. The chloride dissolves slowly, forming a syrupy solution after about one and one-half times the weight of the ether has been added. On cooling the thoroughly saturated ether solution, a large amount of beautiful, transparent crystals in the form of large plates separated out from an almost colorless mother liquor. They were recrystallized from absolutely dry ether several times and allowed to dry in a desiccator over concentrated sulfuric acid.

The freshly prepared crystals have a melting point of 33–35°, a little lower than the corresponding bromide. The average of several analyses for aluminium was 14.9% and for chloride 50.8%. The theory for the compound $Al_2Cl_6.2C_4H_{10}O$ is Al 13.01%, Cl 51.3%. That the results for aluminium were higher than the theory is very easily explained by the fact that these crystals are not stable and a slight loss of ether would make an appreciable increase in the percentage of aluminium. After standing for some time, over sulfuric acid in a desiccator, the crystals were found to contain a higher percentage of aluminium (15.16%) and a lower per cent. of chlorine (50.4%). They were found to be fairly stable in a desiccator over sulfuric acid, although there was a gradual loss in weight, due not only to loss of ether, but also hydrochloric acid gas. Thus, in 6 days, a loss of 2.7% and in 38 days 6.1% loss was found. The compound is doubtless stable in perfectly dry air, and the loss of both ether and hydrochloric acid is due to partial hydrolysis forming basic aluminium chloride, thus liberating the ether. The odor of hydrochloric acid is noticeable if the salt is brought in contact with moist air; dissolved in water, both hydrochloric acid and ether are liberated. On evaporating this water solution to dryness and drying at 106°, the substance on analysis showed 32% of aluminium and 16% of chlorine.

It is interesting to note, as is shown by the curve (Plate 1) that the original crystals when heated to constant weight at 106° showed a loss in weight of 55%, and the residue when analyzed gave practically the same percentage (32.85% Al, 17.27% Cl) of aluminium and chlorine as that obtained from the water-soluble residue. It is evident, therefore, that a basic aluminium salt is formed, probably a mixture of the approximate formula.

$$3Al(OH)_3.2Al(OH)_2Cl.$$

On exposure to the air the crystals changed first to a liquid, then a scum formed on the surface, later the whole mass became a solid of a slightly yellow color. The material gains in weight gradually, then loses, and finally the weight fluctuates with atmospheric conditions. Thus in one case a maximum increase in weight of 17.9% was noted after exposure to the air for 12 days. This then gradually lost in weight until after 28 days, an increase of only 7.3% of the original was noted. If the crystals are exposed to moist air over water in a desiccator a very rapid increase in weight took place. Thus, in one instance the crystals gained 11.6% in weight in 8 hours, 38.1% in 29 hours and 238% in 15 days. The water absorbed caused a loss of hydrochloric acid and probably of ether. Chlorine was determined and a loss of about 5% was found.



Normal propyl ether was substituted for ethyl ether and the properties of the additive compound studied. This compound is apparently a liquid, red in color and not as reactive toward water as the ethyl ether addition product. The excess of propyl ether was evaporated from it by a current of dry air and the aluminium and chlorine determined. The percentages found were 15.73% Al and 42.61% Cl. The theory for the compound $Al_2Cl_6.2C_6H_{14}O$ is 11.5% Al and 45.16% Cl. Our analyses correspond closely enough with the theory considering the properties of the compound, to assume this formula. Further work on this and other aliphatic ethers is being continued in the laboratory.

Qualitative Test for Water in Ether.—In the early part of our research it was found that any solvent not entirely free from water, added to the solution of aluminium chloride in ether, would give a distinct cloudiness or precipitate. We base our test for water in ether on the fact that anhydrous aluminium chloride will dissolve in absolutely dry ether, the solution remaining clear all the time. But, if there is present a trace of water, the solution of the chloride is accompanied by the formation of a cloud or a precipitate. We assumed that the aluminium chloride is hydrolyzed by the water forming a basic aluminium chloride which is insoluble in ether.

A thorough search of the literature shows that aluminium chloride has never before been used, so far as we have been able to find, for the detection of water in ether, and that the test which we propose is by far the most delicate, convenient, and practical of any now in use.

The procedure found to be best is given below. Five to ten cubic centimeters of the ether to be tested are placed in a dry test tube and the tube closed with a rubber stopper. This is then cooled to about 10° by ice or running water, a piece of fresh anhydrous aluminium chloride of the size of a kernel of wheat dropped in, the tube again stoppered and observed with a black background. As the ether warms to room temperature, a reaction takes place, evidenced by the formation of small bubbles which rise to the top of the liquid carrying with them, in the presence of water, a delicate white cloud which, if present in large enough amount, will spread out as a milky layer near the top of the ether.

The density of the cloud, of course, depends upon the amount of water present. If there is an appreciable amount present, the precipitate remains permanent on shaking. This cloud, if present in small amount, is soluble or coagulated if too much aluminium chloride is present, if the solution is agitated, and thirdly, if the reaction is allowed to proceed at too rapid a rate.

The test is rendered obscure by the presence of alcohol in comparatively large amounts; thus, 7% of absolute alcohol will cover up the tests entirely, while 5% does not. Alcohol present in ether in this amount can readily be detected by the hydrogen evolved upon the addition of metallic sodium. Moisture of the air does not affect it, as the exposure to air is very short. Ether, direct from chemical houses, in every case shows a positive test. Ether dried over calcium chloride always gives a positive test. Ether which had been allowed to stand over metallic sodium, refluxed and distilled until moisture was proven absent by the above test, was placed in a glass stoppered bottle which was opened only occasionally and allowed to stand for several weeks. It gave at the end of this time a positive test. This proves that anhydrous ether like practically every other absolutely dry substance is hygroscopic.

The test is intended to prove the complete dehydration of ether by sodium and has been found delicate enough to detect one drop of water in 500 cc. of ether which had been freshly distilled over sodium.

Conclusions.

1. No definite products could be isolated from the reaction between chloral and ether in the presence of aluminium chloride.

2. The compound, $Al_2Cl_6.2C_4H_{10}O$, an addition product of ethyl ether and aluminium chloride, has been prepared and its physical and chemical properties studied.

3. The addition product of aluminium chloride and normal propyl ether, analogous to the ethyl ether compound, has been prepared and described for the first time.

4. A new qualitative test for water in ether has been proposed and is thought to be very satisfactory and quickly made.

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VERATRINE AND SOME OF ITS DERIVATIVES. II.

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The alkaloid known as veratrine, or cevadine, as it has recently been named, has been studied by one of us several years ago.[1] A number of derivatives were studied in order to determine the constitution of the alkaloid.

Among other derivatives, a chloralhydro-veratrine was prepared from chloral and veratrine. As chloral and veratrine are of great importance physiologically, it was thought that a condensation product of the two substances might be interesting pharmacologically. We therefore decided to take up the study of that compound again in order to determine the true nature of the chemical reaction between the two substances. It was obvious that if the reaction is a true condensation reaction, the new compound formed would possess properties entirely different from either of the components. It would therefore quite likely have different physiological properties. If, on the contrary, the substance proved to be an additive product, then its physiological properties would be the result of one or both of the reacting constituents.

Compounds of cevadine and cevine with chloral and bromal were therefore prepared by the following general method:

The alkaloid was dissolved in carbon disulfide and the necessary amount of chloral added. A precipitate formed at once and the reacting mixture became warm. After the reaction had ceased and the solution cooled to room temperature, cold ether was added and the precipitate filtered off. It was washed with ether several times, dried and analyzed. Neither the analysis nor the molecular weight determination proves conclusively that the new compound formed was either a condensation or an additive product. When heated in a drying oven at a temperature of 130–140° for several hours it was found that the compounds lost weight and did not contain either chlorine or bromine. A qualitative study proved that the loss was equal to the percentage of the aldehyde originally present. This shows conclusively that the new compounds are simple additive products. We have not been able to find any definite ratio between the chloral and the alkaloid. We found that by varying the conditions, namely, the quantity of aldehyde, we were able to change the ratio between the reacting components which enter the new molecule.

[1] *Am. Chem. J.*, **20**, 358.