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The Action of Aluminium Chloride on Ethers.

Part I. Aliphatic Ethers.

A Thesis submitted to the Faculty  
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## Theoretical Part.

It has been shown in this laboratory by Frankforter working with Kritchevsky and Poppe that Chloral under the influence of aluminium chloride combines with many organic substances. The normal course of the reaction is the splitting out of molecules of water and the formation of a condensation product, when the substances are brought together under the proper conditions. The aluminium chloride acts as a very strong catalytic and dehydrating agent.

Frankforter and Kritchevsky (1) have shown that this new reaction proceeds very nicely with the aromatic ethers and well defined crystalline compounds were obtained. A specific example taken from their work is as follows: Anisol and chloral were mixed and cooled in ice water. Small portions of aluminium chloride <sup>were</sup> added with constant agitation. The reaction mixture becomes dark colored and much hydrochloric acid is given off. After one molecular <sup>of aluminium chloride</sup> equivalent is added the reaction mixture is allowed to stand in the cooling bath for a few hours, then at room temperature for one to three days. The reaction mixture is then decomposed with water and distilled with steam. The crude product remaining undistilled is dissolved in ether, the ether solution washed with water, dried over calcium chloride, and allowed to evaporate. Colorless crystals separated out, possessing the composition as represented by the formula,  $\text{CCl}_3\text{CH}(\text{C}_6\text{H}_4\text{OCH}_3)_2$ .

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Many other authors have sought to use aluminium chloride as a catalytic in reactions of both organic and inorganic chemistry. Playfair was probably the first to state that an aluminium salt could act as a catalytic agent. In his experiments he observed that the blue indigo color disappeared when the dyed calico was dipped in nitric acid, if there was present in the latter an aluminium salt.

Friedel and Craft (2) first describe their well known reaction in which it is thought that the function of the aluminium chloride is entirely catalytic. They found that small quantities of anhydrous aluminium chloride added to amyl chloride caused a vigorous reaction to take place, liberating hydrochloric acid and at the same time forming hydrocarbons which do not absorb bromine. These authors also added benzene to their reaction mixture and obtained the condensation product. They then substituted other alkyl halide compounds for amyl chloride.

Gustavson (3) explained the catalysis by saying that an organic aluminium compound was formed which immediately breaks down liberating condensed hydrocarbons with the re-formation of aluminium chloride. To verify his conclusion, he cited compounds known to be formed such as  $\text{AlCl}_3 \cdot (\text{C}_6\text{H}_6)_3$  and  $\text{AlBr}_3 \cdot (\text{C}_4\text{H}_8)$ . However there was not given enough data to prove the formation of these compounds.

A.G. Paye (4) says that aluminium chloride possesses the power of transporting chlorine to organic compounds. He synthesizes anthraquinone from phthalic anhydride and benzene by means of aluminium chloride and sulphuric acid. The dehydration is accomplished by the sulphuric acid.

Otto Ruff (5) describes an inorganic reaction in which aluminium chloride acts as a catalytic. Sulphur crystallizes unchanged from sulphuryl chloride when the two are heated together at 130° and subsequently cooled. Chlorination of the sulphur takes place at about 200°. At a temperature 30-70° the reaction,  $\text{SO}_2\text{Cl}_2 + 2\text{S} = \text{S}_2\text{Cl}_2 + \text{SO}_2$ , takes place quantitatively in the presence of aluminium chloride. With less sulphur present as well as aluminium chloride the following reaction takes place quantitatively at 40°,  $\text{SO}_2\text{Cl}_2 + \overset{\text{S}}{\text{S}} = \text{SCl}_2 + \text{SO}_2$ . Cinnabar does not act on sulphuryl chloride alone but in the presence of aluminium chloride, mercuric chloride is formed. Other catalytic reactions of a similar type were described.

Stokes (6) says that aluminium chloride acts as a catalytic on ethyl trichlor silicate with the formation of ethyl chloride and probably silicon dioxide and oxychlorides of silicon.

Boedtker (7) described a new catalytic reaction of aluminium chloride. Chlorpicrin submitted to Friedel-Crafts reaction gave triphenylcarbinol and some triphenylmethane. Ethyl nitrate and benzene in the presence of aluminum chloride gives nitrobenzene. Homologues were prepared in the same way.

Roland (8) gives a general discussion of both organic and inorganic synthesis by means of aluminium chloride.

The object of the authors when beginning this research was to investigate the action of chloral on the aliphatic ethers in the presence of aluminium chloride.

It was found that there is a reaction between ethyl ether, chloral, and aluminium chloride but the products of the reaction are very hard if not impossible to isolate and identify. The proportions used were approximately equimolecular amounts of chloral and ether, and a little more than an equivalent amount of aluminium chloride. The chloral and ether were mixed and well cooled to  $0^{\circ}$ , then aluminum chloride was added in small amounts. After mixing thoroughly and allowing to stand at a low temperature for some time, the reaction was allowed to proceed at room temperature for several days. The color of the mass changed from yellow to red, then to deep brown or almost black. No definite reaction product could be obtained by treating the mixture with the numerous organic solvents and with water. The material would not <sup>undecomposed</sup> distill at low pressures. The reaction is without doubt very complicated and the products formed are unstable. It is thought that by using a higher aliphatic ether, the reaction will proceed in such a way that satisfactory results may be obtained.

While working with the above it was thought that aluminium chloride may combine with chloral or with ether forming compounds, which might interfere with the proper understanding of the reaction when they are present at the same time.

Combes (9) describes a reaction between chloral and aluminium chloride when these are heated to  $70^{\circ}$ . The reaction mixture was precipitated by water and the oil separating out distilled. A small amount boiling about  $130^{\circ}$  was found to be tetrachlorethylene. The greater part boiled about  $239^{\circ}$  and consisted of a polymer of chloral, called by him parachloral. Boeseken says that chloral decomposes by gentle warming with aluminium chloride according to the equation,  $\text{CCl}_3\text{CHO} = \text{CCl}_2 + \text{HCl} + \text{CO}$ . The  $\text{CCl}_2$  polymerizes immediately to  $\text{CCl}_4$ . A side reaction proceeding at the same time is:  $\text{CCl}_3\text{CHO} = \text{CO} + \text{CHCl}_3$  from which carbenyl chloride and chloralid is formed. The products obtained by the above authors did not correspond to any substances obtained by us.

The reaction between aluminium chloride and ether was next investigated. An experiment was tried in which no chloral was used. The aluminium chloride was added in small portions to ether until it no longer dissolved. The temperature was kept about  $0^{\circ}$  and after standing over night at a temperature below freezing, colorless plates separated out in the violet colored liquid. This showed that there is a reaction between these substances and we felt that we should

investigate this reaction so that we could more easily explain the results with the chloral condensation.

At this time the literature was very carefully gone through to find what metallic halides combine with or form addition products with ethers and the properties and methods of preparation of these resulting compounds. The compounds formed when aluminium chloride reacts with numerous organic compounds were also noted at the same time. Those, that have a direct bearing on the present research, are given below.

Titanium chloride forms a <sup>crystalline</sup> yellow substance with anhydrous ether, probably consisting of a double compound of the two. This was prepared by Bertrand (10) and again by Ellis (11). The latter man distilled the compound and obtained four fractions, three of which solidified. The substance decomposed with an evolution of hydrochloric acid and ethyl chloride.

Robiquet (12) describes a compound of stannic chloride and ether, the composition of which is probably  $\text{SnCl}_4 \cdot \text{C}_4\text{H}_{10}\text{O}$ . Kuhlman has also prepared this compound.

J. Nicklis (13) describes several compounds that he made from bismuth, antimony, and arsenic bromides and chlorides and ether. In some cases two compounds were formed, one of which had two molecules, the other four molecules of ether to one of the metallic halide. The iodides do not form such compounds. The products were liquid bodies, slightly

soluble in ether. Bismuth bromide does not form the compound directly except by heating to  $100^{\circ}$  in a closed tube or by the action of metallic bismuth on an ether solution of bromine. The formula given for the bismuth compound is:  $\text{BiBr}_3 + 2\text{C}_4\text{H}_5\text{O} + 4\text{HO}$ . It crystallized in vacuo over sulphuric acid. The antimony compounds were thought to possess the formulae:  $\text{SbBr}_3 + 4\text{C}_4\text{H}_5\text{O}$  and  $\text{SbBr}_3 + 2\text{C}_4\text{H}_5\text{O}$ . The antimony compounds decompose only partially on distillation. The properties of the arsenic bromide addition product with ether are similar to these given above. Later the same author (14) describes other metallic bromide addition products with ether. Aluminium bromide ether addition product was the only one which was volatile without decomposition. Its composition was given as  $\text{Al}_2\text{Br}_3 \cdot 2\text{C}_4\text{H}_5\text{O}$ . The aluminium iodide ether compound was one of the few iodide compounds which can be made. Tin bromide, aluminium bromide, cadmium bromide, and zinc bromide-ether addition products were made by the action of the metal on the bromine ether mixture. The mercury bromide compound was represented by the formula,  $\text{HgBr}_2 \cdot 3\text{C}_4\text{H}_5\text{O}$ . Thallium and chlorine and ether gave a compound represented by the formula,  $\text{Cl}_3\text{Tl}_2(\text{C}_4\text{H}_5\text{O})\text{ClH} + 2\text{HO}$ . The bromine compound was similar. It must be remembered that this work was done before the new system of atomic weights and valences was adopted.

Bedson (15) prepared an addition product of vanadium oxychloride and ether of the composition,  $\text{VOCl}_3 \cdot \text{C}_4\text{H}_{10}\text{O}$ . The melting point was given as under  $20^\circ$ . The titanium chloride ether addition product was also prepared by him.

Carlton-Williams (16) made the compound  $\text{SbCl}_5 \cdot \text{C}_4\text{H}_{10}\text{O}$ .

Gasselin (17) described a compound  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  which was formed as one product of the action of boron trifluoride on ethyl alcohol.

Uranium chloride forms a compound,  $\text{UO}_2\text{Cl}_2 \cdot 2\text{C}_4\text{H}_{10}\text{O}$ , with ether. The crystals lost their ether upon standing in a vacuum or in a warm stream of air. Dry ammonia gas passed into the solution caused the precipitation of a compound to which the formula,  $\text{UO}_2(\text{NH}_3\text{Cl})_2 \cdot \text{C}_4\text{H}_{10}\text{O}$ , was applied. The author of this work was Regelsberger(18).

Hoffmann and Sand (19) describe compounds made from ethylene and the water solution of the mercury salt. These appear to have the general formula,  $\text{XHgCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{HgX}$ , showing an ether structure. Although they were not made from ether and the mercury salt, it is interesting to note their structure in this connection.

Blasse (20) describes a compound of magnesium iodide and ether to which he ascribes the formula:



It is prepared by the reaction between metallic magnesium

and iodine in the presence of anhydrous ether. It is crystalline and melts at 52-53°. Other ethers were also used and similar results were obtained. It is interesting to note here that some of the higher ethers did not form crystalline compounds. The oxygen is thought to possess a valence of four. The basic character of the quadravalent oxygen atom increases with the complexity of the alkyl group. The author offers evidence to show that the above structure is correct.

Manchot and Haas (21) describe an ether addition product of ferrous chloride and ascribe to it the formula,  $C_2H_4 \cdot FeCl_2 \cdot 2H_2O$ . This compound was not made from ferrous chloride and ether but by heating an ether solution of ferric chloride in a closed tube for a few hours with the addition of a small amount of a carbon disulphide solution of phosphorus. The substance had the form of grey crystals, unstable in the air. They decomposed at 100° on the water bath with the evolution of ether. By heating them over a free flame ethyl chloride is formed. The bromide of the above compound was prepared by Chojnacki (22).

Weinland and Binder (23) prepared a compound possessing the formula,  $FeCl_2(OC_6H_5OH) \cdot C_4H_{10}O$ , by the action of an ether solution of ferric chloride on an ether solution of pyro-  
*Catechin.*  
~~gallio acid.~~

Aluminium bromide and chloride have been known to form addition products with many compounds. Gustavson (24) prepared the compounds,  $\text{Al}_2\text{Cl}_6 \cdot 6\text{C}_6\text{H}_6$  and  $\text{Al}_2\text{Cl}_6 \cdot \text{C}_7\text{H}_8$  by passing dry hydrochloric acid gas into a mixture of aluminium chloride and the hydrocarbon. He was of the opinion that Friedel-Crafts' synthesis is caused by the formation of these compounds and the conversion of anhydrides to chlorides which react with benzene splitting out hydrochloric acid. He also prepared the addition product with cymene (25).

Band (26) prepared from acetylene and aluminium chloride the compounds to which he attributes the formulae,  $7(\text{C}_{10}\text{H}_{15.6}) \cdot 2\text{Al}_2\text{Cl}_6$  and  $7(\text{C}_{20}\text{H}_{15}) \cdot \text{Al}_2\text{Cl}_6$ . The same author (27) described the preparation of an addition product,  $2\text{AlCl}_3 \cdot 5\text{COCl}_2$  from carbonyl chloride and aluminium chloride. Other compounds possessing a different proportion of the constituents were also formed.

Otto Ruff (28) forms the compound,  $\text{AlCl}_3 \cdot \text{SO}_2$ , from liquid sulphur dioxide and aluminium chloride. It can also be obtained from aluminium chloride and sulphuryl chloride. The same author (5) describes a compound,  $\text{AlCl}_3 \cdot \text{SCl}_4$ , obtained by the action of sulphur tetra chloride on aluminium chloride dissolved in sulphuryl chloride.

Boeseken (29) prepared the compound,  $\text{AlCl}_3 \cdot \text{CH}_3\text{COCl}$ , by the action of acetyl chloride on aluminium chloride at  $10^\circ$  below freezing, using carbon disulphide as a solvent.

It was unstable but by allowing it to react with benzene the compound,  $C_6H_5COCH_3 \cdot AlCl_3$  was isolated. Upon treating this compound with water acetophenone was liberated. The same author later (30) described an additive compound of aluminum chloride and chloroform, also other additive compounds of benzene and benzene acid chlorides. Boeseken and Clemen (31) describes a compound of acetic anhydride and aluminium chloride. Acetyl chloride distills over and the heavy residue diluted with anhydrous ether and allowed to stand. Large limpid crystals were formed which were not easily soluble in water and smell of ether. The compound is  $(C_2H_5)_2O \cdot 2AlCl(OCOCH_3)_2$ .

Kronberg (32) prepared additive compounds of benzoyl chloride and aluminium chloride to which he attributes the formula,  $C_6H_5CCl_2 \cdot OAlCl_2$ . This reacts with benzene to form the compound formulated as, ~~XXXX~~  $C(C_6H_5)_2OAlCl_2$ , which is decomposed by water into benzophenone and aluminium<sup>oxy</sup> chloride.

Kablukov and Khanov (33) say that aluminium bromide does not form additive compounds with benzene, toluene, xylene, naphthalene, diphenylmethane, methylene bromide, phenyl bromide, or dibrombenzene. He obtained addition products with aluminium bromide and aniline and derivatives, benzonitrile, pyridine and nitrobenzene. They say that alcohols, aldehydes, ketones, organic acids, and esters react readily with

aluminium bromide at ordinary temperatures but the resulting products are less stable than those of organic nitrogen compounds.

Menschutkin (34) described aluminium chloride addition products with nitrobenzene and its derivatives. The aluminium chloride is present in the proportion of one molecule to one, and to two molecules of the nitro body. These compounds are, on the whole, hygroscopic crystals, though some crystallize with difficulty. The melting points vary—some being as low as  $25.5^{\circ}$  and others as high as  $145^{\circ}$ . The same author as above (35), prepared aluminium chloride addition products with acetophenone and benzophenone. He says that aluminium chloride addition products are much more stable than the corresponding aluminium bromide compounds.

Perrier and Pouget (36) prepared an alcohol aluminium chloride addition product in which one molecule of aluminium chloride was present to eight molecules of ethyl alcohol. He also described substitution products, like  $Al_2Cl_3(C_2H_5O)_3$ . The compounds were prepared by allowing the constituents to react upon each other and the product obtained depended upon the temperature at which the combination took place. He used beside ethyl alcohol, methyl, butyl, normal propyl, and isoamyl alcohols.

Plotnikov (37) prepared and described the compound,  $AlBr_3 \cdot (C_2H_5)_2O$ . It melted at  $46^{\circ}$  in a closed capillary.

It was deliquescent and upon exposure to the air or to a trace of moisture, it decomposed. Heating above the melting point gave ethyl bromide as the chief product. It is soluble in most organic solvents. It was prepared by the direct action of the aluminium bromide on ether. He may not have obtained the same product as did Nicklis (13).

Kohler (38) studied the action of aluminium chloride on many organic substances containing oxygen. He says " The aluminium halogen compounds of the aliphatic ethers are either liquids or finely divided solids, hard to wash and purify without serious decomposition", therefore their properties were not studied. He obtained additive compounds of aluminium chloride with many aromatic esters, ketones and ethers. He states that the compounds have double the molecular weight usually assigned to them. He found that addition products with substances that contain one atom of oxygen to the molecule, invariably contain two molecules of the oxygen compound to one double molecule aluminium halide while the addition products obtained from substances that have two atoms of oxygen, generally contain only one molecule of the organic compound to one double molecule of aluminium halide.

Walker and Spencer (39) prepared the Aluminum chloride addition product with ethyl ether and other substances. They say that aluminium chloride combines directly with many substances containing oxygen. The general method of procedure

used by them is as follows: The excess of the organic compound is dissolved in carbon disulphide and the aluminium chloride added. Then the upper layer was removed, the excess of solvent evaporated in a current of dry air. In the case of the ether compound it separated out as a yellow oil on the surface of the carbon disulphide and when the excess of solvent was evaporated it crystallized in large brown plates. An analysis of Aluminium was made and the percentage found was 13.92% and 13.94%. The theory for the addition product of the composition,  $\text{Al}_2\text{Cl}_6 \cdot 2\text{C}_4\text{H}_{10}\text{O}$ , is 13.01% Al. Anisol, ethyl benzoate, methyl mandelate, ethyl oxalate, ethyl malonate, acetic acid, orthonitrotoluene, and metadinitrobenzene all gave addition products when treated in this way.

In summing up the work of others on the addition products of aluminium chloride and organic compounds, it is well to note; (1) these compounds are usually crystalline solids of low melting point, (2) they usually decompose in the air and with water, (3) most have been described as possessing the double molecular weight formula.

The crystals which we obtained appeared to be pure white and we were anxious to find out if they were identical with those obtained by Walker and Spencer. The physical and chemical properties of this body were not described. In our present research we have tried to find out what we could concerning these.

Our crystals were found to have a melting point of 33-35°. This is a little lower than the corresponding aluminum bromide compound. They were found to be fairly stable in a dessicator over concentrated sulphuric acid, although they showed a gradual and slow loss of hydrochloric acid and ether. It is thought that moisture of the air, coming in contact with the compound, hydrolyses it, forming a basic aluminum chloride and liberating ether and hydrochloric acid. Upon exposing the compound to an atmosphere saturated with water vapor, there is found to be a small loss of hydrochloric acid. The water solution of the crystals smells of ether if the hydrochloric acid odor is not too strong to obscure it. Upon evaporation of this solution to dryness and heating to constant weight at 106°, a residue containing about <sup>32%</sup> ~~IX~~% aluminium and 16% of chlorine remained. This would correspond to a mixture of aluminium hydroxide and basic aluminium chloride containing a larger proportion of the former constituent.

If the crystals are heated directly to constant weight at 106°, the loss in weight is about 55% and the residue obtained has about the composition of the one described above. This one analyzed 32.85% aluminium and 17.2% chlorine.

If the crystals are heated to constant weight at 50°, the loss in weight is not so great. The percentage of aluminium in this residue was found to be lower and that of chlorine

higher than that in the above.

When the crystals were exposed to the air at room temperature, they showed a gradual loss in weight at first, then a gain and finally the weight fluctuated with the humidity of the air.

All of the analyses for aluminium were much too high for the theory for  $\text{Al}_2\text{Cl}_6 \cdot \text{C}_4\text{H}_{10}\text{O}$ , which is 13.01% Al. Our analyses averaged about 14.9% Al and showed a slight increase after the crystals were allowed to stand in the dessicator over concentrated sulphuric acid. It is thought that this variation from the theory is not excessive as the compound is not very stable and a slight loss of ether would make a very appreciable increase in the percentage of aluminium.

The chlorine on the first sample analyzed, checked higher than the theory for the above compound which is 51.3% Cl. This is explained by the fact that the air above the crystals in the dessicator was pretty well saturated with hydrochloric acid gas. Some of this was probably in the weighing bottle when it was weighed. The later analyses for chlorine showed a gradual decrease in chlorine content, through the loss of hydrochloric acid gas. The gradual loss of ether would tend to increase the percentage of chlorine in the remaining compound, if it were not for the evolution of hydrochloric acid gas. The loss of ether probably has the effect of holding

the percentage of chlorine nearly constant for the month or so that intervened between the first and last analyses.

In one case it was found that upon cooling the ether solution of the crystals below zero for some time the liquid became dark brown in color and the crystals took on the same color. This is thought to be the reason for Walker and Spencer thinking that the compound had a brown color. Another factor to consider here is the influence of the solvent, carbon disulphide, which he thought necessary as the initial reaction between aluminium chloride and ether is rather vigorous.

In the preparation of this compound, it has been found that the ether should be cooled under the tap for the first few additions of aluminium chloride. After these the reaction proceeds most favorably at temperatures between 35 and 50°. It is much better to use fresh pieces of aluminium chloride about the size of a pea, and to shake gently until they are dissolved. If pulverized material is used the reaction is so vigorous that much of the ether is boiled off. It is thought best not to allow the temperature to rise above sixty degrees as decomposition of the product is liable to result. The aluminium chloride dissolves slowly after about one and one half times the weight of the ether has been added. Upon cooling the solution under the tap, a large amount of the crystals separate out. They are found to be soluble in practically all organic solvents. In some cases there is probably decomposition as well as solution.

Aluminum chloride and propyl ether combine to form a liquid compound, probably of the composition as represented by the formula,  ~~$(Al_2Cl_6 \cdot 2(CH_3CH_2CH_2)_2O)$~~   $Al_2Cl_6 \cdot 2(CH_3CH_2CH_2)_2O$ .

It is also not stable in the air. It does not act so readily with water as the ethyl ether compound. It was prepared by the action of Aluminium chloride on normal propyl ether at room temperature. After standing for some time the liquid will separate into two layers, if the proportions are approximately one part of aluminium chloride to five parts of propyl ether. The lower layer is dark red in color and contains the addition product. The solubility of this compound in ether is greatly affected by a change of temperature and at this concentration is more soluble with a rise of temperature. The excess of solvent was evaporated from the lower layer and the remaining compound analyzed. The analysis showed too much aluminium and too small an amount of chlorine. This would be the natural result if the compound decomposed as did the ethyl ether addition product.

In the early part of our research it was found that, should we add any solvent, not entirely free from water, to the solution of aluminium chloride in ether, there would be a distinct precipitate or a cloudiness formed. It was also noticed that if the ether ~~x~~ used was not freshly distilled over sodium, there would be a cloudiness upon the first addition of aluminium chloride. This is the principle upon which we base our qualitative test for water in ether. It is thought that the water hydrolyzes the aluminium chloride forming a basic aluminium chloride which is insoluble in ether.

The methods used by other authors to determine the presence of amount of water in ether were carefully examined in the literature on the subject. In no place was mention found of the application of aluminium chloride to this test.

Merck (40) gives as the test for water in ether the following: Shake 20 cc. of ether in a closed vessel with one gram of dehydrated copper sulphate. If the latter is colored green or blue, water is present. From our experience it has been found that ~~this~~ test is not as delicate as required in most cases.

V. Wartha (41) applies the well known test for water in ether with carbon disulphide. The carbon disulphide is purified by distillation over silver amalgam. An equal volume is added to the liquid to be tested. The presence of water is shown by the formation of turbidity. This test is not delicate.

Gorgew (42) uses turpentine in exactly the same manner as the above. The limit is three or four thousandths.

L. Crismer (43) says that the liquid paraffin of the German pharmacopoeia, possessing a boiling point of 215-242° under 6mm. pressure, will form a clear solution with alcohol, ether or chloroform if these solvents are perfectly free from moisture. With a minute quantity of water present, the solutions are turbid.

Squibb (44) mentions that the use of an equal volume of oil of copiaba or of carbon disulphide is not sensitive to one tenth of one percent of watery alcohol in ether and is not reliable. He proposes the test dependent upon the fact that rosaniline colors the solution pink if a trace of alcohol and water are present in ether. The acetate is very hygroscopic and the test must be performed with great care. Most any ether will give a slight test for water. The presence of 0.2% of alcohol will not alter the test.

Schoras (45) describes a method of testing for the presence of water, which depends upon the fact that filter paper dipped in calcium platinum cyanide and dried is strongly colored canary yellow and becomes colorless by gentle warming. It immediately absorbs moisture and becomes yellow.

Blitz (46) gives a very delicate reaction for the detection of water in ether. He prepared test paper of

colorless potassium lead iodide. The paper is practically colorless and will turn to a distinct yellow color, if placed in liquids containing moisture. His procedure is as follows: A filtered warm solution of four grams of lead nitrate in 15 cc. of water is mixed with a warm solution of 15.g. of potassium iodide in 15 cc. of water. Lead iodide is precipitated. By cooling the yellow precipitate disappears and the whole solidifies to a straw colored mass. This is quickly sucked dry and is dissolved in 15-20 cc. of acetone. If the anhydrous powder is wished, the substance is precipitated from the acetone solution by adding a double volume of ether and is dried in a vacuum dessicator. The acetone solution should be filtered. When ready to make the test, one places a piece of filter paper, recently dried at  $110^{\circ}$ , in an erlenmeyer flask, fitted with two dropping funnels and a gas inlet and outlet. A few drops of the acetone solution of the reagent is dropped on the filter paper. Air, dried by passing through concentrated sulphuric acid, is passed into the flask until the whole is free from acetone. Now through the other funnel, the liquid to be tested is allowed to run into the flask. It is shaken with the paper and then allowed to stand. Ether which had stood over sodium for eight days caused the paper to become yellow in three hours.

C. Mann (47) gives a test for water as follows: Mix two parts of citric acid and one part of molybdic acid, heat to incipient fusion and dissolve in 40 parts of water. Warm and filter. Filter paper dipped in this solution and dried at 100° is blue. If this is immersed in alcohol or ether which is perfectly free from water the color remains unchanged, but if water is present the paper will lose its color, especially if warmed.

Parenti (48) gives a test depending upon the fact that the rose color, formed by the action of sulphocyanic acid on filter paper, is not changed by water free ether, alcohol, benzol, carbon disulphide, or chloroform. Moist ether changes the rose color on evaporation to a bright green, which later disappears.

Ad. Claus (49) describes a test for water in ether as follows: In a test tube are placed a few flakes of sublimed anthraquinone with some sodium amalgam and flow over the whole absolute, alcohol free, ether. The whole is shaken and the finely divided quinone crystals change to dark brown crystal plates. If one lets a drop of water fall on the ether there appears after easily moving the cylinder, a red solution around the amalgam. This red solution disappears when shaken with air above the ether and appears anew after a short time.

Tyer (50) describes a method for the quantitative estimation of water in ether, dependent upon the fact that cadmium iodide is practically insoluble in absolutely dry ether. The solubility of this salt increases with the amount of water present. Tables are given showing the solubility when the ether contains a varying amount of water. This is said to be accurate to 0.001%.

We feel quite sure that the test that we propose has not been described in any literature before this. Our method depends upon the fact that absolutely dry ether will dissolve anhydrous aluminium chloride-- the solution remaining clear all of the time. If there is present a trace of water, the solution of the aluminium chloride is accompanied by the formation of a white cloud. This cloud forms at the top of the ether and 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 procedure found to best is given below. Five to ten cubic centimeters of the ether to be tested is placed in a dry test tube and the tube corked with a rubber stopper. The lower part of the test tube is then held under the tap and thus cooled to probably 10°. A piece of fresh aluminium chloride of the size of a kernel of wheat or a little larger is dropped in and the tube again corked. Then without agitating the liquid, the ~~liquid~~ tube is viewed with a black

black background. The reaction between ether and aluminium chloride is slow at temperatures 10° and below while at room temperature the reaction is quite vigorous. The reaction should proceed slowly - small bubbles will rise from the aluminium chloride thus slightly agitating the liquid. The bubbles will carry up with them, if there is a trace of water present in the ether, a delicate white cloud. This cloud spreads out in the upper part of the tube. The time required for the test is not over a minute. The cloud should form immediately upon the commencement of the reaction, evinced by the evolution of a few bubbles of gas.

It has been found that the presence of a large percentage (7%) of absolute alcohol will cover up the test. One would not have occasion to test for water in ether containing this large percentage of alcohol. The test is intended, especially, to determine whether the sodium has completely dehydrated the ether when the latter has been distilled over the metal.

The test has been found to give satisfactory results when water is present to the extent of one drop in 500cc. of ether. It is thought that the real sensitivity is far below this point. The test does not seem to be affected by the moisture of the air. If there is any doubt on this question a blank may be run along side of the ether to be tested, using in this blank ~~an~~ ether which shows very little or no cloudiness with aluminium chloride. Ether, which has stood for a week or more after distillation over sodium, will give a faint cloudiness by this method.

### Experimental Part.

#### Experiments with chloral, ether, and aluminium chloride.

It was found at the beginning of this research that upon adding aluminium chloride to commercial ether a heavy, white, flocculent precipitate is formed. By using ether which had been freshly distilled over sodium, there was no precipitate formed and the aluminium chloride dissolved to a perfectly clear solution. This fact was later made use of by us in a qualitative test for water in ether. In all of the following experiments, perfectly dry ether was used.

An experiment was tried in which the proportion of the constituents were as follows:

80.g. of dry ether

100.g. of chloral

100.g. of aluminium chloride.

The ether and chloral were mixed in a flask fitted with a two hole stopper-- one carrying a thermometer, the bulb of which was immersed in the liquid; the other hole connected with a calcium chloride tube, thus protecting the reaction mixture from the moisture of the air and at the same time allowing the escape of gases formed in the flask.

The mixture was cooled to zero, then the pulverized aluminium chloride was added in five gram portions. The flask was kept in ice water, except when it was necessary to shake the mixture or read the thermometer. There was a great deal of heat given off at each addition and the temperature was kept below ten degrees. The aluminium chloride dissolved almost completely after each addition, except at last when quite a little remained undissolved. Fumes of hydrochloric acid appeared to be given off, but it is not known for certain whether these came from the reaction mixture or from the aluminium chloride adhering to the neck of the flask as it reacted with the moisture of the air.

This process of adding the aluminium chloride in small portions required about an hour. At the end of this time, the solution was rather dark straw colored and slightly turbid. After standing in the ice water for two hours, the flask was removed and the temperature allowed to rise slowly from 10° to 22° (room temperature), during which time the color gradually changed to red brown. The reaction mixture was kept at a temperature a little below freezing over night. The next morning the mass had a consistency like jelly. The color of the mixture changed

to dark brown by allowing it to stand at room temperature for a few hours.

The reaction mixture was treated with several organic solvents, with the result that none of these caused a separation of the main product of the reaction.

Some of the above reaction mixture was poured slowly into ice water. Much heat was given off and a thick dark mass separated out on the bottom. This mass was separated as well as possible from the water above-- more water was added and then it was subjected to steam distillation. The dark masses collected in balls of pasty consistency. In the distillate from the above, there separated out on the bottom a very small amount of a liquid yellow in color, and possessing a boiling point of approximately 175°. The amount was so small that the thermometer was much overheated. A slight scum, which was probably another liquid, was seen floating on the top of the steam distillate. The odor of ether was noticed in the first portion. The liquid, remaining in the flask after steam distillation, was filtered and extracted with ~~water~~ ether. This ether extraction after evaporation deposited crystals which have the odor of chloral hydrate.

The dark viscous masses were dissolved in ether and the ether solution filtered. A gelatinous substance remained insoluble and after drying was found to be aluminium hydroxide or a very insoluble basic aluminium compound, occluding some organic matter. The ether extraction was very dark brown in color and upon evaporation left a viscous, brown, resinous mass. This was distilled under a reduced pressure. At 52°, pressure 22 mm., crystals formed in the condenser. These are thought to be chloral hydrate. At 62-80°, pressure 22 mm., a liquid appears to come over but is very small in amount. The temperature then rose rather rapidly to 125° when about ten drops of a liquid came over. The material left in the flask was dark brown and appeared charred. During the distillation much frothing was observed and it is thought that gases, especially hydrochloric acid gas was given off.

In another experiment the following proportions were used:

Ether	130.cc.	100.g.
Chloral	135.cc.	200.g.
Aluminium Chloride		225.g.

The aluminium chloride was added in exactly the same manner as in the previous experiment. This time the

mixture was kept at a temperature always below 0° by means of a salt and ice mixture. The temperature range was — 8° to 0°. The reaction mixture was kept at a temperature below freezing for two days at the end of which time the mass was jelly-like in consistency and light brown in color. This was allowed to stand at room temperature for four days. The color became dark brown-- almost black.

Some of this material was distilled in vacuo at a pressure of 22 mm. It began to bump at room temperature, caused by the ether which it contained. The first distillate came over at 35-42° and was thought to be chloral. Between the temperatures 66° and 75°, the material in the flask frothed very much. Hydrochloric acid was known to be given off in large quantities during the whole process, especially when the flask was heated strongly locally. Very little if any liquid came over at these temperatures. The temperature rose slowly upon more strongly heating to 100°. A small amount of liquid came over in the distillate. This liquid reacts vigorously with water and all of the reaction products appear to be soluble in water. It contains aluminium and chlorine and is thought to be a compound or solution of aluminium chloride with ether or possibly chloral. Between the temperatures 110-135°, colorless

crystals form in the cold part of the condenser.. These crystals were removed and pressed out on filter paper and dried on a porous plate in a dessicator over sulphuric acid, They appeared to decompose readily in the air and change to a liquid. In a sealed capillary tube, the melting point obtained was 22-24°. They are thought to be indetical with the crystals obtained from aluminium chloride and ether. They reacted very vigorously with water or with moist air with the evolution of hydrochloric acid and ether. An analysis was not made as the amount of crystals obtained was very small.

The residue left in the flask was insoluble in ether. It appeared to dissolve in part in water with the evolution of heat and a peculiar, rather disagreeable odor. It dissolved partially in alcohol to a red solution showing that there was some organic material left in the flask.

It will be noticed from the preceeding experiments that the reaction between aluminium chloride and chloral and ether is very deep seated. Probably many changes occur and organic aluminium compounds are formed, which are impossible to separate from the other reaction products.

Experiments with ether and aluminium chloride.

Absolute ether was treated with an equal weight of aluminium chloride. The addition was made rather rapidly and the highest temperature (estimated) was  $20^{\circ}$ . The solution became very dark purple color upon the first addition and much heat was given off. The reaction mixture was kept at a temperature of about  $-15^{\circ}$  and over-night a mass of crystals, equalling about half the bulk of the solution, separated out. These were found to dissolve when the temperature was allowed to rise to room temperature, but again crystallized out on cooling the solution. These crystals reacted very violently with water. A scum appeared on top of the liquid when the surface was exposed to moist air. This scum dissolves if an excess of water is added. Much heat is given off when the crystals react with water.

The colored ether solution was treated with bone charcoal but it had no appreciable effect of decolorizing.

Some of the colored liquid, having the crystals in solution, was distilled at atmospheric pressure. The ~~thermometer~~ temperature rose gradually from  $35^{\circ}$  to  $135^{\circ}$ . A small amount of ether came over, probably carrying other material. At  $135^{\circ}$  the mass foams very much and hydrochloric

acid gas in large amount was given off, and a liquid small in amount came over. This liquid became solid immediately upon breathing on it and did not crystallize after standing for half an hour at  $0^{\circ}$ . This liquid was probably some of the ether aluminium chloride addition product which remained undecomposed by distillation or was carried over mechanically by the gases. Some addition products of aluminium chloride under certain conditions crystallize with difficulty. The material in the flask foamed very much and appeared to decompose at this higher temperature.

It was thought that the reaction could be made to proceed without the formation of a colored solution by keeping the temperature, during the addition of the aluminium chloride, very much lower than in the preceding experiment.

In a new experiment we used equal parts of aluminium chloride and ether and kept the temperature always below  $-8^{\circ}$ . Half of the aluminium chloride was added and the mixture was allowed to stand over night at a temperature of  $-15^{\circ}$ . The next morning the other half of the aluminium chloride was added. The color of the liquid turned yellow, then red after the addition of a small amount of aluminium chloride. It changed finally to violet.

The aluminium chloride dissolved completely except the last few portions. Upon standing at about  $-5^{\circ}$ , the liquid began to deposit crystals shortly after the last addition.

The above process was repeated at room temperature or above. The ether boiled at first but did not change in color to the deep purple as in the preceding experiment. Upon the addition of 170.g. of aluminium chloride to 100.g. of ether by the last method, the color changed to a very light green. The solution became viscous after most of the aluminium chloride had been added. During the process the temperature rose to  $50^{\circ}$  and upon cooling the whole mass crystallized. If these crystals are allowed to form slowly they take on the form of plates.

Some of the liquid holding the crystals in solution was distilled under a pressure of about 25.mm. It was found to decompose very readily. After the excess of ether was driven off, the material in the flask foamed very much. Hydrochloric acid was known to be given off and it was thought that ethyl chloride was given off also. A liquid appeared to drip off the thermometer and a very little came over, which solidified in the receiver. This liquid reacted very violently with water, contained aluminium and

chlorine. The receiver and tubes were covered on the inside with a fine white powder. This was soluble in water, did not change on ignition and was thought to be aluminium chloride, which is known to be volatile under reduced pressure.

Upon cooling a solution of the crystals to  $0^{\circ}$ , a part of the crystals separated out and the remainder of the liquid changed to a dark brown color.

The solution of the crystals was warmed and filtered, then cooled and the crystals filtered off by suction, washed with dry ether, and sucked ~~as~~ dry as quickly as possible. They were recrystallised from ether once more, then placed in a dessicator over sulphuric acid.

After drying a few days in a dessicator, the crystals appeared to be colorless plates. They decompose slowly even when standing in the dessicator over concentrated sulphuric acid. Hydrochloric acid and ether are known to be given off.

The melting point of the crystals was found to be  $33-35^{\circ}$ . A sealed capillary and a standard thermometer were used.

A weighed amount of the aluminium chloride ether addition product was exposed to the air and the change in weight noted. This is given in the table below.

Experiment #	I	II	III
Weight of crystals	2.2280 g.	1.1196 g.	.6008 g.
Weight after 3hrs.	2.2090	1.0948	.6092
1 da.	2.0562	1.0764	.5908
2 days.	2.0000	1.0778	.5908
4 "	1.9297	1.0119	.5635
6 "	1.9375	1.0083	.5497
7 "	1.8994	.9919	.5332
9 "	1.8546	.9660	.5701
12 "	1.8301	1.0015	.5664
14 "	1.8628	<sup>.0375</sup> <del>1.0015</del>	.5458
19 "	1.9170	1.0207	.5571
28 "	1.9050	.9833	.5354
38 "	1.9747	.8782	.5318
58 "	2.0660	1.1770	.3914

The material 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 above weighings show that the material absorbs moisture--loses hydrochloric acid and ether, and after a time the weight varies with the humidity of the surrounding air.

The analyses for aluminium and chlorine on the crystals are given below.

(1)	.5234 g. gave	.0801 g. $\text{Al}_2\text{O}_3$	8.12% Al.
(2)	.6705 g. "	.1880 g. "	14.87% Al.
(3)	.8205 g. "	.2291 g. "	14.80% Al.
(4)	.5393 g. "	.1496 g. "	14.90% Al.
(5)	.2312 g. "	.0661 g. "	15.16% Al.
(6)	<del>.6686</del> g. "	.1910 g. "	15.15% Al.
(7)	.1865 g. "	.3955 g. $\text{AgCl}$	52.51% Cl.
(8)	.1380 g. "	.2833 g. "	50.80% Cl.
(9)	.6686 g. "	1.3665 g. "	50.43% Cl.

Assuming that the correct formula for the addition product is  $\text{Al}_2\text{Cl}_6 \cdot 2\text{C}_4\text{H}_{10}\text{O}$ , we may tabulate the results as follows:

Calculated for	Found								
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
$\text{Al}_2\text{Cl}_6 \cdot 2\text{C}_4\text{H}_{10}\text{O}$									
Cl	51.3%							52.51	50.8
Al	13.01%	---	14.87	14.8	14.9	15.16	15.15%		50.43%

In the above analyses (1) was made by direct ignition of the crystals and is discarded as it is considered too low.

Numbers (2) and (3) were made by ignition of the crystals with sulphuric acid to constant weight. Numbers (4), (5), and (6) were made by the ignition of the aluminium hydroxide precipitated by ammonia. In (7) and (8) the silver chloride was ignited in a porcelain crucible. In (9) a gooch crucible was used.

The later analyses show that the crystals lose chlorine in the form of hydrochloric acid, as well as ether. That this loss is slow and gradual is shown by the following experiment. A weighing bottle containing a weighed amount of the crystals was exposed to the air in the same dessicator with the crystals and the loss in weight was noted. The weighings are given below:

Weight of sample	.5097 g.
Weight after 24 hrs.	.5027 g.
" " 2 days	.5000 g.
" " 6 "	.4958 g.
" " 15 "	.4921 g.
" " 38 "	.4781 g.

The odor of hydrochloric acid is very strong in the dessicator.

A sample was placed in a closed vessel over water and the change in weight noted.

Weight of sample	.5780 g.
Weight after 1.5 hrs.	.5819 g.
" " 3 "	.5931 g.
" " 4.5 "	.6111 g.
" " 6 "	.6301 g.
" " 8 "	.6694 g.
" " 29 "	.7986 g.
" " 6 da.5 hrs.	1.3062 g.
" " 15 da.5 hrs.	1.9671 g.

These weighings show that the crystals absorb moisture from the air. The odor of hydrochloric acid was noticed at the time of the third weighing. It was thought that it would be interesting to know how much chlorine would be lost by the crystals under these conditions. After the last weighing the material was dissolved in an excess of water to which a little nitric acid had been added, to make sure to get in solution all of the aluminium. This was then diluted to 250 cc., and 100 cc. was taken and the aluminium and chlorine determined directly. The results were:

Weight of original sample	.5780 g.	
Weight of sample for analysis	2/5 of the above	.2312 g.
.2312 g. gave	.0661 g. $Al_2O_3$ ( $Al(OH)_3$ ignition)	15.16% Al.
.2312 g. "	.4256 g. AgCl (gooch)	45.56% Cl.

The above results were calculated on the original sample and show a loss in this case of about 5% chlorine.

Another 100 cc. of the above solution was evaporated to dryness and heated at  $106^\circ$  to constant weight.

.2312 g. after drying weighed	.1074 g.	Loss of 53.55%
.1074 g. gave	.0634 g. $Al_2O_3$ ( $Al(OH)_3$ ignition)	31.29% Al.
.1074 g. "	.0698 g. AgCl (gooch)	16.08% Cl.

The composition of this residue corresponds to a mixture of aluminium chloride and aluminium hydroxide, containing a ~~large~~ <sup>smaller</sup> ~~substantial~~ proportion of the former constituent.

In another experiment the crystals were heated in an oven at 106° to constant weight. The results are given below.

Weight of sample	.5393 g.
" after 10 min.	.5044 g.
" " 25 "	.4654 g.
" " 40 "	.4192 g.
" " 70 "	.3635 g.
" " 1 hr. 40 min.	.2963 g.
" " 2 hrs. 10 "	.2694 g.
" " 2 " 35 "	.2513 g.
" " 3 <sup>b</sup> " 10 "	.2456 g.
" " 3 " 40 "	.2415 g.
" " 4 " 40 "	.2432 g.
" " 5 " 40 "	.2408 g.
" " 6 " 40 "	.2410 g.

.5393 g. after heating at 106° weighed .2415 g. Loss = 55.21%

.2415 g. gave .1496 g.  $\text{Al}_2\text{O}_3$  ( $\text{Al}(\text{OH})_3$  ignition) 32.85% Al.

.2415 g. " .1686 g.  $\text{AgCl}$  (goosh) 17.2% Cl.

The composition of this residue is very approximately the same as the one obtained in the previous experiment. It consists of a mixture of Aluminium hydroxide and aluminium chloride or a basic aluminium chloride.

The previous experiment was repeated in all details with the one exception that the temperature was kept at 50°.

Weight of sample		.4847 g.
"	after 16 hrs.	.3070 g.
"	" 20 hrs,	.3038 g.
"	" 26 hrs.	.2928 g.
"	" 29 hrs.	.2960 g.
"	" 31 hrs.	.2953 g.

.4847 g. after heating at 50° weighed .2953 g. Loss 39.1%.  
 .2953 g. gave .1280 g.  $\text{Al}_2\text{O}_3$  ( $\text{Al}(\text{OH})_3$  ignition) 22.98% Al.  
 .2953 g. gave .2459 g. AgCl (gooch) 20.6 % Cl.

This shows that the compound does not lose as much chlorine nor as much in weight when it is desiccated at 50° as it does when dried at 106°.

Experiments on the Qualitative Test  
for Water in Ether.

The test that we propose for water in ether should be carried out as follows: Place 5-10 cc. of the ether to be tested in a dry test tube. Cork with a rubber stopper and cool under the tap to about  $10^{\circ}$ , then hold against a black back-ground and drop into the test tube a piece of fresh anhydrous aluminium chloride about the size of a kernel of wheat. The action of the aluminium chloride on the ether is much moderated by cooling the ether to this temperature. As the ether warms up the aluminium chloride acts on it, causing a circulation of the liquid. If there is a trace of water in the ether, there is seen a white cloud, rising from the aluminium chloride and spreading out in the upper part of the ether. This cloud disappears upon shaking the test tube or upon the addition of more of the aluminium chloride. 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. The moisture of the air does not seem to affect this test, but to make sure of the presence of water when the ether contains a very small amount, a blank should be carried along beside the test. Freshly distilled ether should be used for this blank.

Experiments were tried for the purpose of determining the approximate sensitiveness of the test. Ether freshly distilled over sodium does not give any cloudiness when treated in this way. Ether distilled over sodium and allowed to stand in a glass stoppered bottle for two weeks gave a faint test. When allowed to stand six weeks there was a distinct cloud formed. Five hundred cubic centimeters of ether freshly distilled over sodium gave no cloud with aluminium chloride when treated by this method. Then one drop of water was carefully added, the whole shaken thoroughly and allowed to stand for some time for the water to dissolve. Then a portion of this was taken and compared with the original ether by this method as given. The ether, which contained approximately .014% of water gave a very distinct cloud. In every trial there was no question which contained the most moisture.

It was later found that alcohol interfered with the test. One hundred cubic centimeters of the above ether containing one drop of water in 500cc., was taken and 5 cc. of absolute alcohol added. It still gave a very distinct test. Upon the addition of another 5 cc. of alcohol the test was obscured. If it is thought that there is sufficient alcohol in the ether to cover up this test for water, its presence can be readily detected by the addition of a small piece of sodium, which would cause an evolution of hydrogen.

Water added to the ether to saturation did not have any effect of diminishing, but rather intensified the test. Ether direct from the chemical supply houses in every case showed a positive test. Ether dried over calcium chloride always gives a positive test.

The aluminium chloride should act very slowly on the ether to be tested. If there is too rapid action, the mixing of the solution, caused thereby, obscures the test. There should not be too much aluminium chloride added as an excess of this appears to dissolve or coagulate the precipitate formed. The aluminium chloride must be fresh and in one small piece. Pulverized aluminium chloride acts too rapidly and is more liable to contain partially hydrated material.

#### Experiments with Propyl Ether and Aluminium Chloride.

The material used was Kahlbaum's chemically pure product, labeled "Dipropyl ether". The boiling point of this substance is usually given as  $90.7^{\circ}$ . The ether was distilled at atmospheric pressure. It began to boil at  $86.5^{\circ}$  and the temperature rose slowly to  $87.5^{\circ}$ , then more slowly to  $89.5^{\circ}$ . Between these two latter temperatures, the most of the product distilled. Thinking that we had an impure product we sought to purify it by allowing it to stand over sodium wire and then distilling. This did not change the boiling point appreciably. The sodium caused a voluminous white precipitate to settle out and was itself coated with green substance. The ether was then heated on the reflux for 15 hours over fresh sodium. It was then distilled. The boiling started at  $86^{\circ}$  and the temperature rose rapidly to  $87.7^{\circ}$ . Most of the product came over between  $87.7^{\circ}$  and  $89^{\circ}$ . Although the boiling point does not correspond to that usually given, we assume that we have a pure product. The specific gravity was .7444 which corresponds very well with that usually given for this product.

When aluminium chloride is added to this substance, a slight precipitate is formed at first, later this dissolves and the solution turns dark red.

This red color is also produced by aluminium chloride which has been freshly distilled with the addition of metallic aluminium.

To five grams of the propyl ether was added one gram of aluminium chloride in small portions with four days intervening. At the end of this time a small red layer separated out on the bottom. This layer disappeared by gentle warming. More aluminium chloride was added and the liquid would not separate in two layers. After cooling in a salt and ice mixture, it would not separate, but after standing another two days, two layers were formed upon cooling. These remained permanent at room temperature. In no case could the separation into two layers be obtained at the same time the aluminium was added to the ether.

This lower layer is the aluminium propyl ether addition product. The excess of the solvent was evaporated from it by a current of dry air and the resulting liquid analyzed for aluminium and chlorine.

.7256 g. gave .2151 g.  $\text{Al}_2\text{O}_3$  ( $\text{Al}(\text{OH})_3$  ignition) 15.73% Al.

.7256 g. gave 1.2534 g AgCl (gooch) 42.61% Cl.

Calculated for the compound,  $\text{Al}_2\text{Cl}_6\text{C}_6\text{H}_{14}\text{O}$ , the percentage of aluminium is 11.5% and of chlorine 45.16%. The analogy is sufficient to assume this the formula of the compound.

## Experiments with Zinc Chloride.

Sticks of anhydrous zinc chloride were heated in a porcelain crucible to quiet fusion. This was then poured carefully into dry ether. The zinc chloride dissolved quite readily and formed a heavy, viscous layer separating out on the bottom of the ether. If these constituents are present in the right proportion there is two layers at room temperature and by cooling in salt and ice, the mass becomes homogeneous.

Zinc chloride can not be used for the test for water in ether as the cloudiness which is formed is not distinct enough to detect traces of water in ether.

Zinc chloride and propyl ether form two layers at room temperature. The ~~zinc~~<sup>zinc</sup> chloride does not dissolve very readily in the propyl ether.

### Conclusions.

There was found to be a reaction between chloral, ether and aluminium chloride but the products of the reaction were impossible to isolate and identify.

In this research the compound,  $\text{Al}_2\text{Cl}_6 \cdot 2\text{C}_4\text{H}_{10}\text{O}$ , has been made by a method, which has not been described before. It has been analyzed, both for aluminium and chlorine. Its physical and chemical properties have been studied.

A new qualitative test for water in ether has been proposed, and is thought to be very satisfactory and rapid. The materials used are found in practically all organic laboratories. It is delicate enough for all practical purposes.

The addition product of normal propyl ether and aluminium chloride is a liquid and has the composition as represented by the formula,  $\text{Al}_2\text{Cl}_6 \cdot 2\text{C}_3\text{H}_7\text{O}$ . Its properties were similar to the one described above.

This research was done under the direction of Professor Frankforter and it is with pleasure that I acknowledge the care and enthusiasm with which he has followed and directed the work. I wish to express to him my appreciation for all he has helped me to accomplish.

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