

General Statements.—From the data presented it is reasonably certain that the two fatty acids in largest amounts in cephalin are stearic and oleic.

The evidence for clupanodonic acid is rather conclusive though not entirely so. Other methods besides the bromination one are being tried to clear up this point.

The greatest uncertainty centers around cephalinic acid. The solubilities and appearance of the bromo derivative strongly suggest linolic acid, but the bromine value is too high. The melting point and percentage of bromine indicate an impure linolenic acid or a higher homolog. Several lines of attack are being carried on the more clearly to understand this acid.

Summary.

1. Somewhat more than one-fourth of the acids of cephalin is in the form of stearic, more than one-half oleic, one-tenth cephalinic, and one-twentieth clupanodonic.

2. From the varying amount of these acids present it is concluded that they are present in mixed cephalins, these various cephalins being closely associated.

3. There is no marked difference, either, in the kind or amount of acids in sheep and beef brain cephalins.

4. The evidence presented strongly indicates ordinary stearic and oleic acids as the principal fatty acids of cephalin.

5. The evidence for the identity of clupanodonic and cephalinic acids is not conclusive.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

THE ACTION OF ANHYDROUS ALUMINIUM CHLORIDE UPON UNSATURATED COMPOUNDS.

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Received May 10, 1916.

It is known that the product obtained by cracking petroleums with aluminium chloride under certain conditions consists very largely of saturated hydrocarbons; whereas distillation under pressure results in a large percentage of unsaturated compounds. One possible explanation of this peculiarity is that the aluminium chloride combines with any unsaturated hydrocarbons formed in the reaction and holds them back from the distillate. The simple experiment of shaking ordinary gasoline with the anhydrous chloride showed that by this treatment all of the unsaturated hydrocarbons are converted into a dark-colored sludge, and that the gasoline resulting gives no color with concentrated sulfuric acid. Petroleum ether acts in a similar way.

A careful review of the literature discloses the fact that very little work

is recorded upon the action of anhydrous aluminium chloride with unsaturated hydrocarbons. This is somewhat surprising in view of the large number of researches upon the addition products that the reagent forms with so many diverse types of organic compounds, and the rôle it plays in the Friedel-Crafts reaction. The chief researches bearing directly upon the subject are cited in the foot-note.¹ From this work it appears that various complex and ill-defined products have been described as resulting from passing vapors of unsaturated hydrocarbons over aluminium chloride heated to various temperatures; that solutions of aluminium chloride in organic solvents absorb such vapors; and that no well-defined products suitable for analysis have been obtained from these solutions.

We have undertaken a study of this field, and have secured a number of positive results. Inasmuch as it will be some time before the experiments now planned can be completed, it is thought best to publish a brief report upon the results already obtained.

The Action of Acetylene upon Anhydrous Aluminium Chloride.—Baud states that pure dry acetylene is completely absorbed by anhydrous aluminium chloride in a closed vessel, even in the cold. If heated to 70° the absorption is complete in a few minutes. A different reaction takes place when a current of acetylene is passed over the hot chloride, a reddish black sublimate forming which finally becomes black. The gas is almost all absorbed, and there is a considerable evolution of heat. At 120–130°, with a continuation of the gaseous current there is no further increase in the weight of the sublimate. To the products formed Baud assigns the formulas $(C_{20}H_{15})_7 \cdot Al_2Cl_6$ and $(C_{10}H_{15})_7 \cdot Al_2Cl_6$.

We repeated this work, generating the acetylene from calcium carbide and passing the dried gas into a closed vessel containing finely powdered, freshly prepared, anhydrous aluminium chloride. No noticeable absorption occurred within several hours. Upon heating the aluminium chloride at 60–62° a reddish brown sublimate appeared, dense vapors were produced, and the sublimate soon turned black and remained unchanged after heating to 140°. Heating to 240° yielded nothing but tar. The black substance resembled pitch, and under the microscope showed no crystalline form. It was evidently a complex mixture.

The Action of Acetylene upon Alcoholic Solutions of Aluminium Chloride.—Dry acetylene prepared from calcium carbide was passed into a solution of aluminium chloride in absolute alcohol, and after thorough

¹ Friedel and Crafts, *Compt. rend.*, **84**, 1392 (1877); *Ann. chim. phys.*, [6] **I**, 440, 446, 449, 461, 510, 518 (1884); Adrianowsky, *Ber.*, **12**, 853 (1879); Gustavson, *J. prakt. Chem.*, [2] **42**, 501 (1890); Winogradoff, *Ibid.*, **37**, 110 (1888); Baud, *Chem. News*, **81**, 286 (1900); Perrier, *Compt. rend.*, **122**, 196 (1896); *Ber.*, **33**, 815 (1900); Menschutkin, *J. Russ. Phys. Chem. Soc.*, **42**, 1310 (1910); Steele, *J. Chem. Soc.*, **83**, 1470 (1903).

saturation for several hours the solution was set aside in a desiccator charged with acetylene. After five days small, colorless, glistening, well-formed crystals appeared. These were very soluble, hygroscopic, difficult to dry, soluble in most solvents, and they decomposed with great ease. Experiments showed that this product was not merely aluminium chloride with alcohol of crystallization. When treated with acids the crystals evolved acetylene, as was shown by the precipitation of copper acetylide from ammoniacal cuprous chloride. Many difficulties were encountered in the analysis of this and similar products. The compound loses acetylene and hydrogen chloride on standing, and in the process of drying. It is exceedingly difficult to burn the carbon by ordinary combustion methods and wet methods were resorted to. Possibly aluminium carbide is formed when the compound is heated, rendering combustion difficult. The analysis, while leaving much to be desired, rather clearly indicates the composition of the product.

Calc. for $\text{AlCl}_3 \cdot 2\text{C}_2\text{H}_2 \cdot 2\text{H}_2\text{O}$: Al, 12.23; Cl, 48.03; C, 21.67; H, 3.61. Found: Al, 12.47; Cl, 45.59; C, 25.70; H, 3.97.

The presence of water in the alcohol prevents the formation of any crystalline product.

The Action of Ethylene upon Aluminium Chloride.—The action of ethylene upon aluminium chloride has been found to be closely parallel to that of acetylene. Ethylene was prepared from ethyl alcohol and sulfuric acid at 170° , dried in a train of sulfuric acid and potassium hydroxide, and passed into a closed vessel containing anhydrous aluminium chloride. No noticeable absorption occurred during several hours. Upon heating, a black tarry mass was formed containing much free carbon, and no crystalline product was obtained. A solution of aluminium chloride in absolute alcohol was then saturated with ethylene, and was allowed to stand for a week in a desiccator. A well-crystallized product was obtained closely resembling the product formed with acetylene. It was very hygroscopic, lost ethylene and hydrogen chloride in drying, and decomposed with great ease. The analysis for carbon presented the same difficulties as in the case described.

Calc. for $\text{AlCl}_3 \cdot 3\text{C}_2\text{H}_4 \cdot \text{H}_2\text{O}$: Al, 11.58; Cl, 45.15; C, 30.56; H, 5.99. Found: Al, 12.61; Cl, 44.76; C, 30.49; H, 6.45.

In addition to those described, crystalline products have been obtained with propylene, butylene, styrolene, oleic acid, and amylene. While well-crystallized, these bodies are very soluble, are difficult to crystallize, have a considerable dissociation pressure, and are, in general, very difficult to prepare for analysis. We are not at present prepared to suggest formulas for them, but shall hope to make a more complete report at some future time.