FROM THE HISTORY OF CARBOXYLIC ACIDS RESEARCH

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Carboxylic acids as a class of organic compounds have become well-known for people since ancient times.

The first mention of the practical usage of acetic acid, that was a product of the fermentation of wine, refers to the III century B.C. Greek scientist *Theophrastus* was the first to describe the effect of wine vinegar on metals: it was leading to the formation of some pigments for art purposes. Vinegar was also used to produce white lead and verdigris (green mixture of copper salts that contained copper acetate). In the VIII century Arab alchemist *Jabir Ibn Hayan* obtained concentrated acetic acid by distillation for the first time. But during the Renaissance for this purpose the sublimation of some metal acetates (was widely spread (copper (II) acetate was mainly used). Although chemists have wrongly considered that these two ways lead to the different substances. The identity of the obtained acids was proved only in the XVI century by the German alchemist *Andreas Libaviusom* and the French chemist *Pierre Auguste Ada.*

Medieval chemists continued studies in the carboxylic acids area. In XV-XVI century yatrochemists developed a method of crude dry distillation. Therefore tartaric acid from tartar, succinic acid from succinite (amber) and benzoic acid from benzoin (incense) were obtained.

In the XVII century there were already known such common trivial names for the simplest carboxylic acids: acetic acid, butyric acid, adipic acid, phthalic acid.

Formic acid was isolated for the first time in 1671. English naturalist *John Ray* obtained it by using red wood ants. This fact explains the compound name: Formica is a generic name for those insects. Then formic acid was also found in the needles, nettles, fruits, bee's corrosive secretions. So that was a period when carboxylic acids were mainly isolated from plants or other nature resources.

But in the middle of the XVIII century the most important organic acids (oxalic, citric, malic, gallic) were obtained by chemical synthesis. In 1762 *Andreas Sigismund Marggraf,* German chemist, described the differences between mineral and vegetable acids. Pharmacist and chemist *Carl Wilhelm Scheele* investigated tartaric, citric, oxalic, malic, lactic and uric acids during the period from 1776 to 1785.

XIX century was notable because of many significant achievements in the organic acids investigation. French chemist *Michel Eugène Chevreul* obtained butyric acid in 1817. *Edmond Frémy* discovered oleic and palmitic acids in 1840.

Next in 1838 the salicylic acid was found out. It was isolated from willow bark by Italian chemist *Raffaele Piria* and then synthesized as well. In 1846 the amino-acids was obtained by the reactions of the hydroxyacids.

Moreover, *Adolph Wilhelm Hermann Kolbe* synthesized typical carboxylic acid – acetic acid – using charcoal, sulfur, chlorine and water as starting materials (1845). Together with *Edward Frankland* he also obtained propionic acid by saponification of ethyl cyanide (1847). This research resulted in discovering one of the general methods of the carboxylic acids preparation.

Through this time next compounds were also synthesized for the first time: maleic acid by distillation of malic acid (*Lassen*, 1819), oxalic acid from cyanogen (*Friedrich Wohler*, 1824), benzyl acid (*N.N. Zinin,*1842,), formic acid from water and carbon monoxide (*Pierre-Eugene-Marcellin Berthelot,* 1855), isobutyric acid (*V.V. Markovnikov*, 1865). Markovnikov has also discovered that butyric and isobutyric acids have the same molecular formula ($C_4H_8O_2$), but different structural formulas; i.e., they are isomers.

The German chemist *Justus von Liebig* determined the structure of benzoic acid (1832). *Auguste Laurent*, a French chemist, investigated phthalic acid properties (1836). In 1879 *V.V. Markovnikov* and *G.A. Krestovnikov* synthesized the first carboxylic derivative of alicyclic hydrocarbons – cyclobutanedicarboxylic acid.

Also *Adolph Wilhelm Hermann Kolbe* synthesized salicylic acid in 1860. And then in 1861 he obtained formic acid by the reaction of carbon dioxide with the phenolates of alkali metals (Kolbe-Schmitt reaction is well-known nowadays for the salicylic acid preparation).

Then methods of carboxylic acids functional derivatives obtaining were developed. For example, the reaction of phosphorus pentachloride with carboxylic acids was investigated (*Auguste Andre Thomas Cahours,* 1846). *Alexander Williamson* studied the mechanism of esterification reactions, and in 1851 found out that sulfuric acid with ethanol gives ethylsulfuric acid, which then reacts with an alcohol with the ether formation. In 1881 *August Wilhelm Hofmann* discovered the rearrangement of acid amides to the primary amines.

Furthermore *Max Conrad* and *Carl-Gustav Bischof* developed common methods of synthesis based on natriummalonic ether (1880). Together with German chemist *Gutzeit M.* they discovered condensation reaction of substituted malonic esters with urea. All these methods are widely used in modern organic chemistry.