

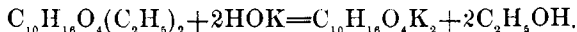
HEPTYLMALONIC AND HEPTYLACETIC ACIDS.

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A brief mention of the preparation of these two acids has already been made (Ber. XIII, 1657). I have since utilized the small amount of the acids which I had on hand in the preparation of some new salts, and will give a description of them, as they serve to characterize these acids more fully than was done in the previous notice.

HEPTYLMALONIC ACID $C_{10}H_{16}O_4$.

This acid belongs to the oxalic acid series and is an isomer of sebaccic acid. It can be prepared from heptylmalonic ether. The simplest decomposition of this ether by means of an alkali is of course the breaking up into alcohol and heptylmalonic acid. We can look upon the reaction as taking place in accordance with the following formula :



An alcoholic solution of potassium hydroxide was used. A small portion of the ether and four times the theoretical amount of potassium hydroxide were heated four to six hours in a small flask upon the water bath. At the close of the reaction water was added, and then hydrochloric acid, and the whole gently heated. The heptylmalonic acid separated as a brown-colored oil on the surface of the water. This was then shaken with ether, allowed to stand for evaporation of the ether and the residue placed in a desiccator over sulphuric acid. The mass solidified, but was still a yellow color, and after drying gave the melting point at 90–93° C. In order to free the acid from all impurities it was washed well with petroleum ether. It proved almost insoluble in this liquid, and was left as a white crystalline mass, melting by 97–98° C. (uncorrected). It is but slightly soluble in water, but easily so in alcohol, chloroform and ether. The solution has a strongly acid reaction. Analyses were made as follows :

I. 0.1432 grm. of acid taken	% C=59.76	% H=9.01.
II. 0.1557 grm. of acid taken	% C=59.59	% H=9.04.
Calculated for $C_{10}H_{16}O_4$	% C=59.41	% H=8.91, % O=31.98.

The acid is dibasic and capable of substituting carbonic acid in the cold. Heated to 130–160° C. it breaks up into heptylacetic

acid and carbon dioxide. The salts crystallize very indistinctly, if at all, and are easily soluble only in the case of the alkalis.

SILVER HEPTYLMALONATE.

An aqueous solution of ammonia was added to the acid until nearly neutralized, and the ammonium heptylmalonate formed in this way was added to a solution of silver nitrate, causing a white precipitate of silver heptylmalonate. The precipitate is heavy and white, seemingly composed of minute, indistinct crystals, and is quite insoluble in water, whether cold or hot. Alcohol also fails to dissolve it appreciably. It was dried in a steam-bath to a constant weight. Only after long keeping does it change to a reddish brown. The melting point, as determined with a portion only slightly changed in color, was 244° C. Two determinations of silver were made.

- I. 0.4330 grm. silver salt taken, % Ag=51.34.
 II. 0.3904 grm. silver salt taken, % Ag=51.56.
 Calculated for $C_{10}H_{16}O_4Ag_2$. % Ag=51.92.

BARIUM HEPTYLMALONATE.

As in the case of the silver salt, this was obtained as a precipitate from barium chloride by means of ammonium heptylmalonate. It is a white amorphous powder, insoluble in water and alcohol. The salt was dried at 100° C. and analyzed. It can be heated to 160° C. without suffering decomposition.

- I. 0.3002 grm. barium salt taken, found % Ba=40.19.
 II. 0.5133 grm. taken, found % Ba=40.45.
 Calculated for $C_{10}H_{16}O_4Ba$. % Ba=40.65.

COPPER HEPTYLMALONATE.

The ammonium salt was not used in the preparation of this compound, but the acid itself (slightly impure) dissolved in water and added to a concentrated solution of pure cupric sulphate. The impure acid was used because the traces of impurity made it much more soluble in water, and the nature of the impurity did not seem to interfere with the formation of the cupric salt. The addition of the acid caused a light-blue precipitate, which was washed well with water. As it was somewhat soluble in water, an excessive use of this had to be avoided. It is more soluble in alcohol, and on evaporation is left behind as an indistinctly crystalline mass. On standing several days over sulphuric acid it becomes almost dry

and loses at 100° C. the last traces of water. On further heating it suffers no loss in weight, until at quite a high temperature it begins to turn brown and decompose. It seems therefore to contain no water of crystallization.

Analysis :

0.3253 grm. taken, found % Cu=23.80.

Calculated for $C_{10}H_{16}O_4Cu$. % Cu=24.04.

LEAD HEPTYLMALONATE.

Alcoholic solutions of heptylmalonic acid and lead acetate were made, and on mixing them a heavy white precipitate formed. This precipitate was repeatedly washed with water, and some of the last washings were evaporated, yielding scarcely any residue, thus showing the almost entire insolubility of the lead heptylmalonate in that solvent. In alcohol it is slightly soluble. After thorough washing, the precipitate was dried in the steam-bath; drying at 110° C. caused no further loss in weight. A portion of the dried salt was taken for a determination of the melting point; melting at 235° C. The remainder of the precipitate, amounting to nearly 0.2 grms., was taken for analysis. It was dissolved in dilute nitric acid and the lead determined by evaporation with sulphuric acid.

Analysis :

found, % Pb=50.49.

Calculated for $C_{10}H_{16}O_4Pb$, % Pb=50.89.

ZINC HEPTYLMALONATE.

On adding an alcoholic solution of the acid to one of zinc acetate the whole mass gelatinized, very much like silicic acid. It is stiff and can be cut or broken up with the stirring rod. This jelly-like mass was first washed with alcohol and then boiled with water, becoming compacted, white and flaky and easy to wash. It is somewhat soluble in water when in this form, more so in hot than in cold, separating from a hot solution on cooling in minute crystals. Some of these crystals dried on filter paper were found to melt at 247° C. The rest of the precipitate was collected in a crucible, dried on water-bath and weighed. On heating at a higher temperature, 140°-170° C., slight loss in weight was noticed. This loss was continuous, and resulted from commencing decomposition. The exact temperature at which the decomposition commenced was not determined. The salt is also easily soluble in ammonium hydrate.

The zinc was determined by dissolving in dilute hydrochloric acid and precipitation as carbonate.

Analysis :

- I. 0.1298 grm. salt taken, found % Zn=24.49.
 II. 0.0411 grm. salt taken, found % Zn=24.33.
 Calculated for $C_{10}H_{16}O_4Zn$ % Zn=24.52.

HEPTYLACETIC ACID, $C_8H_{16}O_2$.

According to the researches of Wisliceus (Annalen, 190.267), ethers of the aceto-acetic series can undergo two different decompositions on treatment with alkalis—one resulting in the formation of alcohol, potassium carbonate and a ketone, the second in the formation of alcohol, potassium acetate and a mono-basic acid. In preparing heptylacetic acid from the heptylaceto acetic ether the methods of Wisliceus were closely followed, yet it was found impossible to bring about any one decomposition unaccompanied by a partial decomposition in accordance with the second formula. In preparing the acid then, traces of methylactyl ketone were formed at the same time. The mode of preparation was as follows. Four times the theoretical amount of a concentrated alcoholic solution of potassium hydroxide was added to the heptylaceto-acetic ether placed in a flask connected with an inclined condenser, and the mixture heated six hours upon the water bath. The main portion of the alcohol was then distilled off, dilute hydrochloric acid added to the solution left behind, and the heptylacetic acid separated immediately as a brownish thick oil on the surface of the liquid. This oil was washed with water and dried over calcium chloride. As the heptylacetic ether could be procured with difficulty, and the product of acid from its decomposition was very unsatisfactory, it was found more convenient to prepare the acid from the heptylmalonic acid already mentioned.

As is well known, all diatomic, dibasic fatty acids, which have the two carboxyles joined to the same carbon atom, fall on heating into carbon dioxide and a monatomic, monobasic acid. Thus oxalic acid (where the two carboxyls are united to one another) yields on rapid heating carbon dioxide and formic acid. Malonic acid yields carbon dioxide and acetic acid. Heptylmalonic acid, then, should yield carbon dioxide and heptylacetic acid. The heating was done in a small flask with condenser inclined and its open end connected with a pipette which just dipped beneath the surface of some water

in a beaker. In this way the evolution of carbon dioxide, and hence the progress of the reaction, could be watched. The flask was heated in a bath of paraffine. The heptylmalonic acid first melted, then at about 130° C the evolution of carbon dioxide commenced, at 150° C the evolution was quite rapid. The temperature was finally raised to 170° C to complete the reaction, the condenser was then inverted and the dark oily fluid left in the flask fractionated. Up to 220° C nothing, distilled over, then a few drops to 228° C, and the greater part of the acid came over at 232–233° C. The pure acid was found to boil at 233° C. It is a colorless, oily liquid, with somewhat of the characteristic smell of the acetic ethers, though not so pleasant. It is nearly insoluble in water, but easily soluble in alcohol and ether. Cooled to 23° C, it becomes viscous, but does not solidify. Analyses were made as follows:

Analyses :

I. 0.2033 grm. acid taken, found	% C = 67.97 ;	% H = 11.64.
II. 0.1116 grm. acid taken, found	% C = 68.11 ;	% H = 11.70.
Calculated for $C_7H_{12}O_2$ acid taken	% C = 68.35 ;	% H = 11.40.

This acid is an isomer of pelargonic acid, and is monobasic. Towards litmus its reaction is faintly acid, and only by aid of heat is it capable of decomposing carbonates. With the metals it forms salts which are, as a rule, non-crystalline and difficultly soluble in water. They are fairly stable when heated, decomposition not taking place generally until a temperature considerably above 100° C. has been reached.

CALCIUM HEPTYLACETATE.

It was found best to make this salt first and use it in preparing others which were deemed of value in characterizing the acid. Heptylacetic acid was suspended in water and boiled with an excess of calcium carbonate. Bubbles of carbon dioxide were noticed, but the action was slow. The filtered solution, smelling strongly still of the acid, was placed over sulphuric acid in a desiccator. After some days a crust formed over the surface, but no crystals were observed. By further evaporation a white powder was obtained if a good deal of the salt was present, otherwise a dry transparent crust. This was thoroughly dried at 100° C. The salt is not very soluble in water, nor in alcohol. Hydrochloric acid dissolves it with the separation of the acid. The analysis was carried out by simple ignition.

Analysis :

0.1181 grm. salt taken ; found	% Ca = 11.38.
Calculated for $(C_9H_{17}O_2)_2Ca$	% Ca = 11.29.

SILVER HEPTYLACETATE

was gotten as a heavy white precipitate by adding silver nitrate to the aqueous solution of the calcium salt. This was filtered off and washed well with water, alcohol, and finally ether, and dried in the steam-bath. It is nearly insoluble in cold water, very slightly more soluble in hot, and not perceptibly soluble in either alcohol or ether. There was no loss in weight nor change of color from heating in the steam-bath, nor in the air-bath as high as 130° C. Between 200° and 220° C complete decomposition takes place. Long continued exposure to the light changes the color, though not very deeply.

Analysis :

I. 0.3065 grm. salt taken ; found	% Ag = 40.88.
II. 0.2910 grm. salt taken ; found	% Ag = 40.65.
Calculated for $C_9H_{17}O_2 Ag$	% Ag = 40.76.

BARIUM HEPTYLACETATE.

This salt was gotten by the direct action of the acid, suspended in water, on barium carbonate. It is somewhat soluble in water and rather more soluble in alcohol. A saturated aqueous solution remained some days over sulphuric acid in a desiccator from which most of the air had been withdrawn, but no crystals were obtained.

The solution was then evaporated to dryness, and the white powder left heated in an air bath to 150° C. without loss of weight. In determining the barium the salt was slowly and carefully tested till the residue was nearly white, ammonium carbonate was then added and the whole again heated until a constant weight was obtained.

Analyses :

I. 0.3042 grm. salt taken ; found	% Ba. = 30.13.
II. 0.1970 grm. salt taken ; found	% Ba. = 29.55.
Calculated for $(C_9H_{17}O_2)_2Ba$.	% Ba. = 30.38.

COPPER HEPTYLACETATE.

To prepare this ammonium heptylacetate was first made by treating the acid with an aqueous solution of ammonia. The solution of this was then added to a cupric sulphate solution and the greenish-

blue precipitate, gotten in this way, washed well with water. It was then dissolved in alcohol and after slow evaporation of the alcohol there was left instead of crystals a few deep green oily drops on the bottom of the dish. Minute crystals could be gotten however, in the form of a precipitate by slowly adding water to the alcoholic solution. An analysis showed the purity of the compound.

Analysis :

0.2262 grm. salt taken ; found % Cu = 16.53.

Calculated for $(C_7H_{17}O_2)_2Cu$. % Cu = 16.78.

ZINC HEPTYLACETATE.

The first mode of preparation attempted was by adding a solution of calcium heptylacetate to one of zinc acetate. This gave a white cloudy precipitate which settled slowly. It was washed with water and then with alcohol. It seemed somewhat more soluble in alcohol than water, though not very soluble in either. On drying in the steam-bath after washing with alcohol, a white sticky mass was left, continued drying at 100° C. however, caused no further loss in weight. The analysis made of this precipitate showed only an approximate purity, the percentage of zinc being too high. A different mode of preparation was then tried. The acid, suspended in water, was boiled with freshly precipitated zinc carbonate. A slight solution of carbon dioxide was noticed, an excess of acid was added and the boiling was long continued. Analysis of the product finally showed by the high percentage of zinc, that much of the zinc carbonate remained unacted upon. A last attempt with the small remaining portion of the acid was made by dissolving it in alcohol and adding to it an alcoholic solution of zinc acetate. This caused a slight turbidity only, as both the acetate and the heptylacetate of zinc are soluble in alcohol. The acetate, however, is more soluble in water than in alcohol, just the reverse being true, apparently, for the heptylacetate. On adding water, then, to this solution of the two in alcohol, a cloudy white, slowly settling precipitate was gotten. The amount however was too minute for any reliance to be placed upon an analysis, hence none was attempted.

The ammonium salt and the potassium salt of this acid was made incidentally for the preparation of other compounds by saturating the acid with solutions of ammonium and potassium hydroxide respectively. They seemed easily soluble in water and in alcohol, but gave no good crystals and were not analyzed.