Calculated for $(C_8H_{11}O_4S)_2Pb.6H_2O$: Pb, 27.72; H_2O, 14.48.
Found: Pb, 27.76, 27.57; H_2O, 14.53, 14.69.

All of the above salts have a much stronger crystallizing force and are much less soluble in water than the corresponding salts of paramethoxymetatoluenesulfonic acid prepared and described by Alleman.[1]

We are indebted to Mr. R. L. Hill, of this laboratory, for assistance in connection with the purification and analysis of the lead and copper salts.

The evidence showing that the sulfonic acid entered in the meta position will be presented in a subsequent paper.

SWARTHMORE, PA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

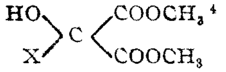
CONDENSATIONS IN THE MESOXALIC ESTER SERIES.

BY RICHARD SYDNEY CURTISS AND EARLE K. STRACHAM.

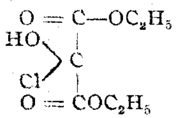
Received January 19, 1911.

The methods hitherto used for making ethyl oxomalonate, $O = C = (CO_2C_2H_5)_2$, have given a product which is a mixture of this substance with ethyl dihydroxymalonate. To produce the former substance in a state of purity it is necessary to distil ethyl dihydroxymalonate with phosphorus pentoxide.[2] Thus we have prepared this substance, a very reactive green oil, and have studied its carbonyl reactions, following them by the interesting, and more or less rapid change of color.[3]

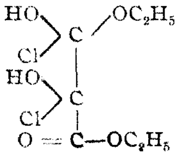
We have first investigated the action of dry hydrochloric and hydrobromic acid gases on ethyl oxomalonate. These substances react readily at a low temperature, giving colorless, crystallin products. This keto ester differs from the methyl ester which gave well defined, but very unstable crystallin addition products of the haloid acids on the ketone double bond, thus:



in that it appears to be more reactive and to yield a mixture of the mono-, di- and trihaloid acid addition products. These are probably correctly represented by the following typical formulas:

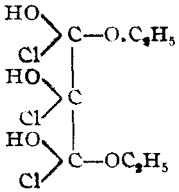


I.



II.

and



III.

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[1] *Am. Chem. J.*, **31**, 24 (1904).

[2] See Curtiss and Spencer, THIS JOURNAL, **31**, 1054.

[3] *Ibid.*

[4] *Ibid.*, **31**, 1055.

Our reasons for assigning this structure in Formula I, as opposed to that of an oxonium salt on the α-carbonyl oxygen, were briefly discussed in the paper referred to above. That the second and third molecules of acid may add on the carboxyl oxygen as oxonium salts, we are not prepared to deny. The addition products herein described are very unstable and experiments have shown that the haloid acid slowly dissociates from them even at the low termperature of an ether-carbon-dioxide freezing mixture (about —60 to —70°). When melted, they form thick, colorless liquids, which then give off the acid gas rapidly below zero, while the green color of the original keto ester returns. These compounds are to be utilized in organic syntheses.

Further, we have studied the action of some acid amides on this ketone ester. Urethan and urea react vigorously and yield colorless, crystallin products. The analysis of the ethylurethan derivative shows that the intermediate addition product on the carbonyl double bond was formed, $C_2H_5O.CO.\underset{H}{N}.C.(OH) : (COOC_2H_5)_2$. This compound gives a disodium salt when treated with metallic sodium. An attempt was made to remove the elements of water from this addition compound to produce the $N = C<$ double bond and chromophore group. A crystallin compound was formed which melted at 121.5°. It was, however, colorless.

The analysis of the condensation product of urea with ethyl oxomalonate shows that an unstable addition compound is apparently formed:

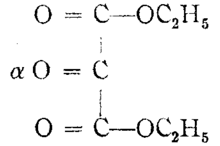
$$NH_2.CO.NH.C.(OH) : (COOC_2H_5)_2$$

with one of the amine groups.

Experimental.

Ethyl Oxomalonate.—Twenty-five grams of ethyl dihydroxymalonate were mixed with 23 grams (1.25 molecules) of phosphorus pentoxide in a distilling flask. After fifteen minutes a green oil appeared. At the end of three hours the mixture was distilled under reduced pressure. It boiled quite constantly at about 122° at 40 mm. (uncor.); yield, 21.1 grams or 90.5 per cent. A larger yield, 94 per cent., was obtained when the ketone ester was extracted from the reaction mixture by sodium-dry ether before distilling. The ester boiled at 117° under 31 mm.

Ethyl oxomalonate is a green oil, slightly more yellow than the corresponding methyl compound. Its density at 20°/20° is 1.119. When chilled in a mixture of solid carbon dioxide and ether, it crystallizes completely in balls of colorless radiating plates. The crystals melt below —30°.

Action of Hydrochloric Acid Gas on Ethyl Oxomalonate.—One gram of ethyl oxomalonate was placed in a well stoppered flask provided with a calcium chloride tube, and cooled to —60° to —70°. Dry hydrochloric acid gas was passed into the flask. The green color of the ester soon disappeared and a thick colorless syrup resulted. The loss of color indicated saturation of the α carbonyl double bond, which plays its part as a chromophore in  $\begin{array}{l} O = C\text{—}OC_2H_5 \\ \quad\;\; | \\ \alpha\, O = C \\ \quad\;\; | \\ O = C\text{—}OC_2H_5 \end{array}$, and, as shown in the reaction with the methyl ester,[1] is the first point of attack by the acid. The viscous syrup soon solidified to a white crystallin mass, which slowly melted between —29° and —10°, with the evolution of hydrochloric acid.

For analysis, 1.0250 grams of ethyl oxomalonate were exposed to a stream of the acid gas for half an hour, during which time the colorless, crystallin product was thoroughly ground until it formed a fine, dry powder, by means of a glass rod which had previously been fitted to the rubber stopper of the flask.

The combined hydrochloric acid was determined by inverting the flask in a beaker of water, removing the stopper, and allowing the water to enter the flask. Water instantly decomposes the product. The solution was titrated with standard alkali. Correction was made for the gaseous hydrochloric acid in the flask.

1.0250 g. gave 0.4984 g. HCl, equivalent to 2.32 molecules.
1.2152 g. gave 0.6091 g. HCl, equivalent to 2.39 molecules.

The fact that hydrochloric acid readily dissociates from these compounds even at —60° is shown by the following experiments. Dry carbon dioxide gas was passed for fifteen minutes through the apparatus containing the dry powdered hydrochloride made as above described. An analysis was then made of the product, and showed the following results:

1. 1.0759 g. gave 0.3430 g. HCl, equivalent to 1.52 molecules.
2. 1.1110 g. gave 0.3963 g. HCl, equivalent to 1.70 molecules.
3. 1.1238 g. gave 0.4125 g. HCl. equivalent to 1.67 molecules.

A second experiment conducted as above, but in which the hydrochloric acid was passed for an excessively long time (2 hours), and then carbon dioxide for five hours, showed on analysis but 0.68 molecule of hydrochloric acid remaining in combination.

0.8864 g. gave 0.1260 g. HCl, equivalent to 0.68 molecule.

In like manner ethyl oxomalonate was saturated with dry hydrobromic acid gas. A crystallin product was obtained which melted in the flask between —21° and —15°. The analysis showed that 2.52 molecules of acid were added.

1.0522 g. gave 1.2760 g. HBr, equivalent to 2.52 molecules.

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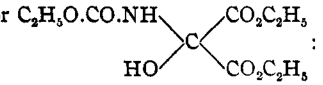
[1] Curtiss and Spencer, THIS JOURNAL, 31, 1054.

In three other experiments in which dry carbon dioxide was passed for fifteen minutes through the flask, the analyses showed

1. 1.0692 g. gave 0.9251 g. HBr, equivalent to 1.90 molecules.
2. 0.9937 g. gave 0.9187 g. HBr, equivalent to 1.92 molecules.
3. 1.2723 g. gave 1.0980 g. HBr, equivalent to 1.80 molecules.

Hydrobromic acid, therefore, behaves very similarly to hydrochloric acid under like conditions in these experiments. The additive power of ethyl oxomalonate is shown to be much greater for these acids, than is that of the methyl ester.

Action of Ethylurethan on Ethyl Oxomalonate.—18.5 grams of ethyloxomalonate were mixed with a molecular amount (9.46 grams) of urethan. The urethan dissolved slowly in the oxomalonate with a lowering in temperature of 3°. When all was in solution, the temperature rose 25° in ten minutes. As the mixture cooled, the green color of the oxomalonate faded rapidly at first, and in twenty-four hours it had disappeared completely. The viscous, colorless syrup so obtained was crystallized from a mixture of ether and petroleum ether. The crystals melted at 32° to 33° and gave the following figures when analyzed:

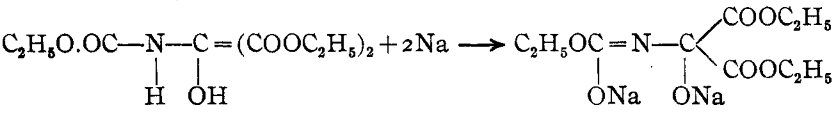
Calculated for 
$\begin{matrix}\mathrm{C_2H_5O.CO.NH}\\ \mathrm{HO}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{CO_2C_2H_5}\\ \mathrm{CO_2C_2H_5}\end{matrix}$: C, 45.60; H, 6.46; N, 5.32.
Found: C, 45.66, 45.61; H, 6.52; N, 5.46.

Ethyl carbethoxyaminotartronate is easily soluble in alcohol, ether, benzene, and toluene, and slightly soluble in ligroin. It reacts with sodium and yields a disodium salt.

1.25 grams of sodium (1.2 molecules) were added to 5 grams of ethyl carbethoxyaminotartronate dissolved in 15 cc. of sodium-dry ether. The solution became green at once and evolved hydrogen rapidly. Gradually the gas was given off more slowly, and the liquid became darker in color. In three hours the liquid was decidedly brown, and a nearly white salt had separated. This was filtered out, and was washed with dry ether. Yield, 4.91 grams; theory, 5.85 grams. When analyzed the following figures were obtained:

Calculated for $C_{10}H_{15}O_7NNa_2$: Na, 14.98.
Found: Na, 14.80, 14.88, 14.97.

The substance is probably a salt of the enol form of ethyl carbethoxyaminotartronate, and tautomeric in its reactions.



$$\mathrm{C_2H_5O.OC{-}\underset{H}{N}{-}\underset{OH}{C}=(COOC_2H_5)_2+2Na}\longrightarrow\mathrm{C_2H_5O\underset{ONa}{C}=N{-}\underset{ONa}{C}}\!<\!\begin{matrix}\mathrm{COOC_2H_5}\\ \mathrm{COOC_2H_5}\end{matrix}$$

It is easily soluble in water and alcohol, soluble with difficulty in ether, and insoluble in benzene and ligroin. On standing in the air, it becomes pasty, and absorbs carbon dioxide.

Action of Phosphorus Pentoxide on Ethyl Carbethoxyaminotartronate.—8.5 grams ethyl carbethoxyaminotartronate were mixed with 1.8 grams (1.1 mols.) of phosphorus pentoxide and placed in a tightly stoppered flask and allowed to stand at room temperature for twenty-four hours. The reaction was indicated by a darkening of color of the solution and the formation of a gummy mass. This was filtered, washed with ether, and recrystallized from alcohol. It melted at 121.5°, was colorless, and contained no phosphorus. It was analyzed.

Found: C, 46.97, 47.09; H, 6.53, 6.79; N, 8.62, 8.49.

Neither the analysis nor the lack of color corresponds to ethyl carbethoxyiminomalonate, $C_2H_5O_2C—N = C = (CO_2C_2H_5)_2$, the simple product which might be formed by loss of the elements of one molecule of water. A more complex reaction takes place, and will be further studied.

Action of Urea on Ethyl Oxomalonate.—1.72 grams finely powdered urea were added to 5 grams (1 molecule) of ethyl oxomalonate. The temperature rose quite rapidly to about 60°, and the green color of the keto ester disappeared. The mixture soon solidified. A constant melting point was not obtained, even after repeated recrystallization from ether and alcohol. The substance melted constantly at 132–133° after being three times recrystallized from hot chloroform. But even here as the following analyses show, decomposition apparently takes place during the process of crystallization from hot solutions.

Calculated for $NH_2CO.NH.C.(OH) : (COOC_2H_5)_2$: C, 41.03; H, 5.98; N, 11.96.
Found: C, 40.3, 40.2, 40.7; H, 6.0, 6.1, 5.8; N, 13.8, 13.8.

The figures correspond very closely to those of the primary addition product of urea on the keto ester, containing 5 per cent. of urea. Apparently this addition product, like most of the others we have hitherto made in the mesoxalic ester series, dissociates, when heated, into its constituent parts.[1]

URBANA, ILL.,
January 18, 1911.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

KETO ESTER ADDITION PRODUCTS WITH ARYL AMINES AND ALCOHOLS.

BY RICHARD SYDNEY CURTISS, HARRY S. HILL AND R. H LEWIS.

Received January 23, 1911.

In continuing this line of investigation, which was first worked out on methyl oxomalonate,[2] we have studied the behavior of the three toluidines, aniline, and benzylamine on ethyl oxomalonate, with intent of obtaining

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[1] THIS JOURNAL, 31, 1054.

[1] Curtiss and Spencer, *Ibid.*, 31, 1053.