LVII.—*Some Reactions of Dehydracetic Acid.*

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DURING the last six months I have been working with large quantities of dehydracetic acid, and find that several important reactions of this interesting substance have hitherto escaped notice. I have therefore collected them and am induced to bring bring them before the

Society, as I think that they will be of considerable use to anyone who is working with dehydracetic acid.

Preparation.—In the preparation of dehydracetic acid, it is usually stated that when it is formed from ethylic acetoacetate, alcohol is the only other substance produced. This is quite incorrect, as the following numbers will show :—

From 1500 grams of ethylic acetoacetate, after passing through an iron tube heated to dull redness (see Oppenheim and Precht, *Ber.*, **9**, 324), I obtained:—

	Grams.
Dehydracetic acid	450
Acetone, b. p. 57—61°	150
Acetone and alcohol, b. p. 60—78°	190
Alcohol, b. p. 78—80°	160
Residue, alcohol, water, and ethylic acetoacetate, b. p. above 80°	170
Carbon dioxide, ethylene, and loss	380
Total	1500

A large quantity of ethylene dibromide (b. p. 131—132°) was obtained by passing the gases evolved during the operation through bromine. This ethylene could not have been formed by the decomposition of the alcohol, for the temperature of the iron tube was too low to effect the change; its formation must therefore be accounted for by some other reaction. I think that it may, with considerable probability, be expressed as follows:—

and the acetoacetic acid (diacetic acid), at the moment of formation, partly decomposes into acetone and carbon dioxide:—

and partly condenses to tetracetic acid and then to dehydracetic acid:—

Various trials were made to produce dehydracetic acid by other reactions. Methylic acetoacetate gives large quantities of dehydracetic acid when passed through a hot tube. Ethylic ethyl-

acetoacetate, however, does not yield a trace of dehydracetic acid, or any ethyl derivative of it, when similarly treated. Chloride of acetyl and acetic anhydride were also treated in various ways, such as passing through red-hot tubes, boiling with zinc chloride or aluminium chloride, but with negative results.

Properties.

Dehydracetic acid is volatile with steam to a considerable extent, and is also slightly decomposed with water into carbon dioxide and dimethylpyrone. In the evaporation, therefore, of a solution of the free acid, a large quantity is always lost. This conversion into dimethylpyrone is more conveniently carried out by boiling dehydracetic acid with ordinary fuming hydrochloric acid. First (*Annalen*, **257**, 272) prepares dimethylpyrone by heating dehydracetic acid in sealed tubes with ten times its weight of hydriodic acid of sp. gr. 1.5 for a day and a half at 150–160°, and states that dehydracetic acid is not attacked by sulphuric acid below 135° or by hydrochloric acid. I have shown elsewhere (p. 609) that sulphuric acid will change it into the δ -lactone of triacetic acid, and I find that if 50 grams of dehydracetic acid is boiled with strong hydrochloric acid, in about half an hour it is *totally decomposed*,

The reaction being as follows:—

In a quantitative experiment, 2 grams of acid were boiled with hydrochloric acid, and yielded, after a short time, 250 c.c. of carbon dioxide. The amount demanded by the above equation is about 260 c.c.

After boiling dehydracetic acid with hydrochloric acid, the solution, on evaporation, yields magnificent groups of tabular crystals, much resembling those of creatinine. This compound was first obtained during an attempt to reduce dehydracetic acid with tin and hydrochloric acid; after the tin chloride and excess of hydrochloric acid had been removed, the concentrated solution deposited crystals which, on analysis, gave the following numbers:—

I. 0.4035 gram substance gave 0.6950 gram CO_2 and 0.238 gram H_2O .

II. 0.3385 gram substance gave 0.2730 gram AgCl .

	Calculated for $\text{C}_7\text{H}_{11}\text{O}_3\text{Cl}$.	Found.	
		I.	II.
C	47.06	46.97	—
H	6.16	6.55	—
Cl	19.88	—	19.95

The substance was, therefore, thought to be a hydrochloride of diacetylacetone, $C_7H_{10}O_3$. It does not, however, give any reaction with ferric chloride solution, whilst diacetylacetone gives a deep cherry-red, nor can diacetylacetone be extracted from the aqueous solution by evaporation. When it is dissolved in water and treated with oxide of silver, chloride of silver is precipitated, and the solution becomes neutral, and on extraction with chloroform dimethylpyrone can be obtained (m. p. 132° , and b. p. $248-250^\circ$). When distilled, it first gives hydrochloric acid and water, and then dimethylpyrone.

It melts at $83-85^\circ$, and its solution in water is strongly acid to litmus paper. It can be produced from diacetylacetone by dissolving it in hydrochloric acid and allowing the solution to evaporate, or by concentrating over the water-bath.

Dimethylpyrone, when dissolved in hydrochloric acid, and the solution evaporated, however, does not seem to yield this compound.

Barium Salt of Dehydracetic Acid.

This salt is of interest, because it appears to be a true salt of tetracetic acid, and not of the lactone (dehydracetic acid). If a warm solution of barium hydrate be added to dehydracetic acid, the acid dissolves, but almost at once a crystalline salt begins to separate, which gave the following numbers on analysis:—

The salt was dried at 110° .

- I. 0.3720 gram salt gave 0.1680 gram $BaSO_4$. Ba = 26.55 per cent.
 II. 0.4835 gram salt gave 0.2235 gram $BaSO_4$. Ba = 27.18 per cent.

	Calculated for		Found.
	$(C_8H_7O_4)_3Ba.$	$(C_8H_9O_5)_2Ba.$	Mean.
Ba.....	29.08	27.02	26.86

On treating the substance with hydrochloric acid, dehydracetic acid is precipitated.

A Copper Compound of Dehydracetic Acid.

If dehydracetic acid is added to a solution of copper acetate in excess of strong ammonia, after standing for some time, a beautiful pink salt crystallises out in microscopic needles. This salt is very stable, not being decomposed even when boiled with sulphuretted hydrogen, but if hydrochloric acid be added, it is at once changed into ammonium chloride, copper chloride, and dehydracetic acid.

On analysis :—

- I. 0·3700 gram salt gave 22·8 c.c. of nitrogen at 16° and 768 mm.
 II. 0·499 " " 31·5 " " 15° " 763 "
 III. 0·5545 " " 0·0785 gram copper oxide.
 IV. 0·3465 " " 0·6480 gram CO₂ and 0·1470 gram H₂O.

	Calculated for C ₂₄ H ₂₅ O ₉ N ₃ Cu.	Found.			
		I.	II.	III.	IV.
C	51·24	—	—	51·00	—
H.....	4·45	—	—	4·71	—
N	7·47	7·28	7·37	—	—
Cu.....	11·21	—	—	—	11·29

The equation which accounts for the formation of the new compound would be :—

Action of Hydrocyanic Acid on Dehydracetic Acid.

These two substances seem to be without action on one another. Dehydracetic acid was warmed with a saturated alcoholic solution of hydrocyanic acid, and then allowed to stand for about three weeks; on evaporating the alcohol and hydrocyanic acid, the dehydracetic acid remained unchanged.