

CCCLI.—*Mercury Derivatives of Acetic Acid.*

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As is well known, some metallic acetates on being heated break up into acetone and the carbonate of the metal, whilst others, such as those of copper, silver and mercury, give no acetone but pure acetic acid. At about 170—180° mercuric acetate forms a well-defined, intermediate compound which was first described, but not analysed, by F. Stromeyer in 1809 (Göttingen Comment., I, 1808–1811, "De Connubio Hydrargyri cum Acido Acetico." The short paragraph referred to was translated in Gmelin's "Handbook"). The compound has the composition represented by the formula $C_2H_2O_2Hg$ (I) (Found: Hg, 77.2; C, 9.1; H, 0.9. Calc.: Hg, 77.6; C, 9.3; H, 0.7%).

Compounds of the composition $C_2H_2O_2Hg$, and in some cases probably identical with Stromeyer's, have been obtained. Sand and Singer (*Ber.*, 1903, 36, 3707), by heating dry mercuric acetate with acetic anhydride, obtained a compound to which they gave the constitution $(C_2H_3O_2Hg)_2C \begin{smallmatrix} \text{CO} \\ \text{Hg} \end{smallmatrix} O$.

Schrauth and Schoeller (*Ber.*, 1908, 41, 2090) obtained from mercurimalonic acid a compound to which they gave the formula $CH_2 \begin{smallmatrix} \text{CO} \\ \text{Hg} \end{smallmatrix} O$ and the name "oxyquecksilber essigsäure anhydrid."

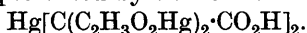
The properties of this compound as described by them differ considerably from those of Stromeyer's substance. Biilmann and Witt (*Ber.*, 1909, 42, 2067) throw doubt on the production of this substance from mercurimalonic acid.

A substituted mercuriacetic acid of a different kind, to which he gave the formula $HO \cdot Hg \cdot C(Hg) \cdot CO_2M$, was obtained by K. A. Hoffmann (*Ber.*, 1899, 32, 875) by heating mercuric oxide with sodium acetate in concentrated alkaline solution.

Stromeyer gave no name to his compound, which was probably the first organo-metallic compound to be discovered. We suggest the name *mercuretin*. We have found that mercuretin is formed in other ways than by Stromeyer's method. It gradually separates (Found: Hg, 77.4; C, 8.9; H, 0.9%) when mercuric acetate is boiled with glacial acetic acid, and it is formed completely and at once on addition of acetic anhydride to such a solution (Found: Hg, 77.2; C, 9.2; H, 0.7%). It is known that the reaction is complete when a sample dissolves completely in sodium hydroxide solution without any yellow precipitate of mercuric oxide. Mercurous acetate, which is generally present in mercuretin prepared

by either of these methods or by Stromeyer's, is easily removed by boiling water. The purified mercuretin remains white when treated with ammonia and gives a clear solution with sodium hydroxide. The formation of mercurous acetate is avoided by keeping the temperature as low as possible during the early stages of the reaction, and also when the conversion is carried out in a sealed tube at 190° ; no permanent gas is given off in the latter circumstance.

Mercuretin is not soluble in water, but it slowly dissolves with some decomposition in boiling glacial acetic acid. On cooling, crystals are obtained different from the original substance; the composition corresponds with the formula $C_{12}H_{14}O_{12}Hg_5$ (II) (Found: Hg, 74.5; C, 10.4; H, 1.0. Calc.: Hg, 74.6; C, 10.7; H, 1.0%) and the structure may be represented by the formula

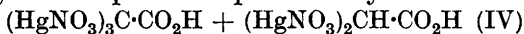


When mercuric acetate is heated with sodium acetate a different condensation occurs. The insoluble *substance*, after being washed free from sodium acetate and mercurous acetate, has the composition $C_4H_4O_5Hg_3$ (III) (Found: Hg, 81.2; C, 6.3; H, 0.5. Calc.: Hg, 82.0; C, 6.3; H, 0.5%). The formation and probable structure of this compound can be explained by supposing that the sodium acetate is attacked by the mercuric acetate with the formation of $Hg[CH(CO_2H) \cdot HgC_2H_2O_2Na]_2$ and this compound by the action of

water gives $2NaC_2H_3O_2$ and $O \begin{array}{c} \diagup Hg \cdot CH \cdot CO_2H \\ | Hg \\ \diagdown Hg \cdot CH \cdot CO_2H \end{array}$

Mercuric acetate condenses with lead acetate to give a compound completely soluble in sodium hydroxide. The condensation of the two salts may also be brought about by the addition of acetic anhydride to a boiling solution of the two salts in glacial acetic acid. The product remains dissolved in the acetic acid and is obtained by evaporation. Mercuric oxide (2 mols.) also condenses with lead acetate with elimination of water (2 mols.).

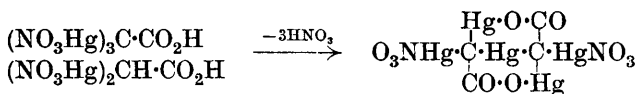
Action of Nitric Acid.—Mercuretin dissolves readily and without oxidation in warm nitric acid (*d* 1.4). Crystals are obtained on cooling which, after being washed with nitric acid and dried, have very nearly the composition represented by the mixture



(Found: Hg, 69.9; C, 3.2; H, 0.4; N, 5.3. Calc.: Hg, 70.2; C, 3.2; H, 0.2; N, 4.9%).

If the solution in nitric acid is poured into water a *substance* is precipitated which, after being washed with water and dried, has the composition represented by the formula $Hg_5(NO_3)_2C_4O_4$ (V) (Found: Hg, 80.2; C, 4.1; H, 0.3; N, 2.2. Calc.: Hg, 80.9;

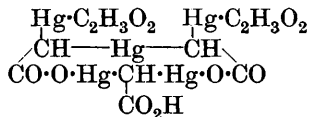
C, 3.9; N, 2.2%). The formation of this compound is readily explained by loss of nitric acid from the substances in solution :



Another nitrate was made by boiling a solution of mercuric nitrate in glacial acetic acid. The conversion was complete when a sample dissolved in excess of sodium hydroxide solution without any precipitation of mercuric oxide. The substance crystallised on cooling and had the composition represented by the formula $\text{Hg}_5(\text{NO}_3)_4\text{C}_4\text{H}_2\text{O}_4$ (VI) (Found : Hg, 73.8; C, 3.4; H, 0.3; N, 3.8. Calc. : Hg, 73.4; C, 3.5; H, 0.15; N, 4.1%). We suggest for it the structure $\text{Hg}[\text{C}(\text{HgNO}_3)_2\cdot\text{CO}_2\text{H}]_2$.

Action of Ammonia.—Mercuretin is soluble neither in ammonia nor in ammonium acetate, but it dissolves easily in a mixture of the two. On evaporation a nearly white powder is obtained which is not soluble in water but is easily dissolved by an aqueous solution of ammonium acetate and ammonia. After being washed with water and dried, the substance had the composition represented by the formula $\text{C}_6\text{H}_5\text{O}_6\text{NHg}_5$ (VII) (Found : Hg, 83.1; C, 6.0; H, 0.7; N, 1.3. Calc. : Hg, 84.0; C, 6.0; H, 0.4; N, 1.2%). This compound may be represented as formed by the replacement of two $\text{C}_2\text{H}_3\text{O}_2$ groups in $\text{Hg}_5\text{C}_{10}\text{H}_{10}\text{O}_{10}$ by the group NH.

Conclusion.—We think that Stromeier's compound, which we have called mercurerin, has the molecular formula $\text{C}_{10}\text{H}_{10}\text{O}_{10}\text{Hg}_5$. In support of this view, we have the persistence of five mercury atoms in the two nitric acid derivatives (V and VI), in the compound (II), and in the ammonia derivative (VII). The removal of some of the acetic groups by nitric acid and the easy removal of two acetic groups by the action of ammonia indicate that two of the five acetic groups are much less firmly held than the other three. Thus the formula $\text{C}_6\text{H}_4\text{O}_6\text{Hg}_3(\text{HgC}_2\text{H}_3\text{O}_2)_2$ is indicated. We suggest for mercurerin accordingly the structure



and this structure explains readily the simple relationship between mercurerin and substance II, and also its feebly acid nature.