

Degradation of picrotin has given II (m.p. 156°, no mixed m.p. depression with an authentic sample, m.p. 156°), together with a labile acid which readily lactonizes, its properties being not inconsistent with its formulation as III. The experimental manipulation of this substance is difficult, and a pure specimen has not yet been obtained.

The general assumption that two lactone systems are present in the picrotoxin series is based, we believe, upon unwarranted interpretations of the experimental evidence cited. On the other hand, published evidence with an important bearing on this fundamental problem has not yet been assessed, and it is apparently not realized that *reversible* opening of the lactone systems in this series is quite common. For example, dihydropicrotoxinin is recovered unchanged by acidification of its solution in cold dilute aqueous sodium hydroxide. These and other points will be described and discussed more fully elsewhere.

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¹ Slater, *J. Chem. Soc.*, 806 (1949).

² *Helv. Chim. Acta*, 32, 1855 (1949).

Reactions of Formic Acid and its Salts

MOST text-books of organic chemistry contain the statement that formic acid and formates owe their reducing character to the presence of an aldehyde group in their molecule, quoting in support of this their ability to reduce ammoniacal silver nitrate to the metal; while this reaction certainly is given by aldehydes, it is not specific for this class of compound since many other acids, such as tartaric or citric, similarly reduce silver nitrate. The reduction of mercuric chloride to mercurous chloride by formates likewise offers no support for the aldehyde theory, since aldehydes in general, including formaldehyde, cannot effect this change. Actually, formates give none of the reactions which characterize an aldehyde; thus they fail to restore the colour to Schiff's reagent, produce no reaction with 2,4 dinitrophenylhydrazine hydrochloride, and above all do not reduce Fehling's solution, which is probably the most specific of all aldehyde reagents.

In view of the above facts, it appears more likely that the reduction of silver nitrate or mercuric chloride by formates is not an aldehyde reaction at all; but is due to the breakdown of silver or mercury formates produced by double decomposition.

It was shown by Liebig in 1832 that these salts readily decompose on heating as follows:

- (1) $2\text{HCOOAg} = 2\text{Ag} + \text{HCOOH} + \text{CO}_2$.
- (2) $2(\text{HCOO})_2\text{Hg} = (\text{HCOO})_2\text{Hg}_2 + \text{HCOOH} + \text{CO}_2$.
- (3) $(\text{HCOO})_2\text{Hg}_2 = 2\text{Hg} + \text{HCOOH} + \text{CO}_2$.

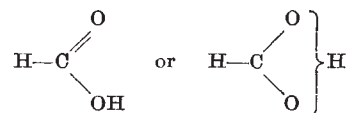
It follows from this that when silver nitrate is added to a formate, the silver formate produced by

double decomposition gives rise on heating to silver according to equation (1). Similarly, when mercuric chloride is added to a formate, the resulting mercuric formate undergoes spontaneous decomposition according to equation (2) to mercurous formate, which immediately reacts with the chloride ions present giving a precipitate of mercurous chloride. The assertion that the mercurous chloride so formed may be further reduced to mercury has no foundation in fact, since prolonged boiling of this salt with sodium formate produces no reduction whatever. On the other hand, if mercuric acetate is substituted for mercuric chloride, no immediate change is observed on adding sodium formate, but on gentle warming, bubbles of carbon dioxide begin to escape from the solution, and on cooling, a feathery mass of crystals of mercurous formate separates out; on heating, the crystals dissolve and decompose with formation of mercury according to equation (3).

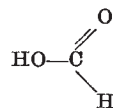
If to a solution of mercurous formate, prepared as above, there is added a quantity of sodium chloride insufficient to precipitate all the mercurous ions as chloride, the remaining mercurous formate will, on heating, decompose, depositing mercury on the white precipitate of mercurous chloride, thus creating the erroneous impression that the latter has been further reduced.

The formates of lead and copper (both cupric and cuprous), being stable, do not undergo reduction when they are heated; thus no reduction occurs when lead nitrate is heated with sodium formate, but if silver nitrate is heated with lead formate it is reduced to silver.

From the evidence submitted it must be concluded that formic acid reacts essentially as a carboxylic acid and that, as the lowest member of the fatty acid series, its constitution is correctly represented by the formula



and further that, in the absence of any positive evidence for aldehyde character, no significance attaches to the fortuitous occurrence of a potential aldehyde group, as suggested by the alternative presentation



It is to be hoped that the constantly repeated misstatement regarding the aldehyde character of formic acid may, in time, disappear from the text-books.

The rejection of the aldehyde theory raises the question of the reason for the marked reducing character of formates towards oxidizing agents; possibly this may be connected with the comparative ease with which formic acid parts with its two hydrogen atoms, according to the equation $\text{HCOOH} = \text{H}_2 + \text{CO}_2$, when brought into contact with finely divided rhodium, ruthenium or iridium, or with which sodium formate liberates hydrogen to give sodium oxalate.

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