30. *Catalytic Reduction by Formic Acid under Pressure. Part I. The Preparation of Aldehydes from Carboxylic Acids with Titanium Dioxide as Catalyst.*

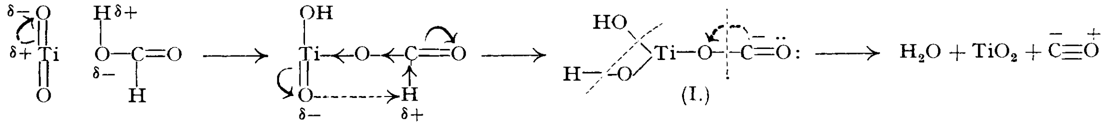
By R. Ronald Davies and Herbert H. Hodgson.

An apparatus is described in which reduction by formic acid in the presence of catalysts has been effected under pressure and at comparatively low temperatures. With titanium dioxide as catalyst, nonoic, undecenoic, and lauric acids have been converted into their respective aldehydes, whereas butyric, heptoic (trace), and phenylacetic acids failed to react. Benzoic, salicylic, *p*-sulphobenzoic, and *p*-chlorobenzoic acids also gave good yields of aldehydes, but *p*-nitrobenzoic acid was mainly reduced to nitrobenzene.

According to the conditions and catalyst employed, formic acid may decompose to give : (1) carbon monoxide, $H\cdot CO_2H \longrightarrow CO + H_2O$; (2) nascent hydrogen, $H\cdot CO_2H \longrightarrow 2H + CO_2$; or (3) formaldehyde, $2H\cdot CO_2H \longrightarrow H\cdot CHO + CO_2 + H_2O$. When reactions (2) and (3) coexist, methyl alcohol will be produced : $H\cdot CHO + 2H \longrightarrow CH_3\cdot OH$. Sabatier and Mailhe (*Compt. rend.*, 1911, **152**, 1212) state that reaction (2) predominates at relatively low temperatures when finely divided metals (*e.g.*, nickel) are used as catalysts, although reactions (1) and (3) are not excluded; that titanium dioxide and the blue oxide of tungsten, however, promote reaction (1) exclusively at temperatures above 170°, whereas thoria, lime, and other metallic oxides promote all three reactions simultaneously.

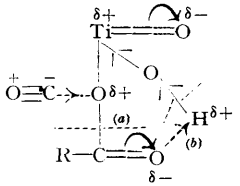
Reaction (1) was used by Sabatier and Mailhe (*ibid.*, 1912, **154**, 561) for the catalytic preparation of aldehydes, by passing the vapours of the corresponding carboxylic acid and formic acid over titanium dioxide at 300°. We now find that this reaction can be made to proceed more smoothly if the reactants and catalyst are heated together under pressure, although the special technique now described had to be devised to render the method safe in small-scale operation. Moreover, the reaction may be performed at lower temperatures, *e.g.*, 250—260°, than those employed by Sabatier and Mailhe, and the process possesses the obvious advantage that the relative volatility of the reactants has not to be considered. Further advantages are the availability of the reaction for non-volatile carboxylic acids, and its ready applicability to micro-scale work.

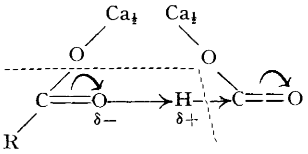
In the present investigation, aldehydes have been prepared from aromatic carboxylic acids in which chlorine or the hydroxyl group, when substituted in the *o*- or *p*-position, appears to improve the yields. As an exception, *p*-nitrobenzoic acid was reduced mainly to nitrobenzene. With aliphatic carboxylic acids, reaction only occurred when more than seven carbon atoms were present, the yields increasing with rise of molecular weight.



The following mechanisms are suggested for the reactions involved : (a) *Decomposition of formic acid into carbon monoxide and water.* The initial stage will be the formation of a complex (I) between the titanium dioxide and formic acid, which then decomposes as at the dotted lines. (b) *Aldehyde formation.* The fatty (or aromatic) acid forms a similar complex (II), in which a 6-membered ring is produced by hydrogen bonding, wherein the oxygen atom labelled (*a*) tends to become positively charged, and is thereby in a condition ripe for attack by the dipolar carbon monoxide, $\overset{-}{C}\equiv\overset{+}{O}$. The resulting rearrangement, with breaks at the dotted lines, liberates the titanium and carbon dioxides, together with the ephemeral compound, $R-\overset{-}{C}=\overset{+}{O}\leftarrow\overset{\delta+}{H}$, which spontaneously rearranges to the isomeric aldehyde, R—CH=O.

(II.)





(III.)

To explain the facts of ready reaction with aromatic acids, but interaction only with aliphatic acids of relatively high molecular weight, the reasonable assumption is made that reactivity is dependent mainly on two factors : (1) facility of hydrogen bonding at (*b*), and (2) the positivity of oxygen atom (*a*). With the fatty acids, where R exerts an electron-repelling effect, (*b*) is apparently not possible until C_7 is reached, the carbonyl oxygen then being sufficiently anionoid to form the bond. When R is normally electron-attracting, as in benzoic and salicylic acids, oxygen (*a*) will become very positive and will react with $\overset{-}{C}\equiv\overset{+}{O}$ immediately bond (*b*) is formed; although R apparently tends to prevent bond (*b*) being formed, there will be resonance phases in which the carbonyl oxygen becomes sufficiently negative to attract the hydrogen. Resonance does not occur in the fatty acids, and the long chain appears to be necessary for the required anionoid activity of the carbonyl group at (*b*).

In the usual method of heating a mixture of calcium salts of the fatty acids with calcium formate to obtain aldehydes, bonding between the carbonyl oxygen of the fatty acid and the hydrogen of the formate will occur, and scission of calcium carbonate will leave the ephemeral compound, $R-\overset{-}{C}=\overset{+}{O}-H$, which will immediately change into the aldehyde, R·CHO (see III). This pyrolytic reaction, however, is only one of several proceeding simultaneously, *e.g.* formation of ketones from the calcium salts of the fatty acids, carbon monoxide from the calcium formate, and by-products due to the interaction of the primaries. Since a less crude aldehyde is obtained with the barium salts of the acids, it would appear that the hydrogen bonding will then ensue more readily, and this may be expected, since barium is more electropositive than calcium, and in consequence the carbonyl oxygen will be more anionoid in the barium salt. It is noteworthy that if calcium or barium oxide is used instead of titanium dioxide with formic acid under pressure, then hydrogen and formaldehyde are liberated as well as carbon monoxide and water. These oxides are therefore inferior to titanium dioxide for aldehyde production.

It was found expedient to employ a slight excess of formic acid, and since with lauric acid, the typical example described, a 10% excess gave the optimum yield, this excess has been adopted throughout the investigation. In like manner, the optimum temperature range for maximum conversion appeared to be 250—260°, even though aldehyde was formed below 200°, whereas heating to 300° brought about no appreciable increase in yield although considerably increasing the danger of bursting the container. Prolonged heating at any particular temperature did not appear to alter the equilibrium mixture at that temperature.

At first the catalyst was prepared by precipitating it as titanium hydroxide on pumice, but equally good results were later obtained with finely ground commercial titanium dioxide.

EXPERIMENTAL.

Apparatus.—A mild-steel tube A, 2 ft. 4 in. long and of 1½ in. internal and 2 in. external diameter, is fixed concentrically inside a mild-steel tube B, 2 ft., and of 2½ in. internal and 3 in. external diameter, by means of female joints which are each connected to the ends of A and B by 12 screw threads, into which in turn screw 2 plugs C. The annular space between tubes A and B is filled with a low-melting fusible alloy, and tube B contains a circular aperture of ½ in. diameter to which is cemented a short ring, 1 in. deep and of ½ in. internal and 1 in. external diameter, which is filled with the alloy of the annular space; this outlet serves as a thermometer pocket, and as an overflow outlet when expansion occurs. The apparatus is arranged lengthwise on a wooden stand, and tilted at an angle of *ca.* 20°; it is heated from below by two batswing Bunsen burners.

Method of Working.—The sealed Carius glass tube, charged with the reactants, was inserted in the inner tube A by means of a short wooden stick, and the plugs C screwed into position. Heat was then applied, and alloy abstracted or added *via* the outlet as occasion required, and when the reaction was completed, the apparatus was allowed to cool, plugs C were removed, the glass Carius tube was pushed so that one end just protruded from the upper end of A, the lower end being first packed with cotton waste or similar material, and then secured again to absorb the shock due to recoil after the tube had been opened in the usual manner.

The following example is typical of the general procedure employed, and the results for 11 carboxylic acids are included in the table below.

Preparation of Lauric Aldehyde.—Lauric acid (0·1 g.-mol.), 95% formic acid (0·11 g.-mol.), and titanium dioxide (0·5 g.) were charged into a Carius tube of *ca.* 15 in. in length and 1 in. internal diameter, which was inserted in the above apparatus, heated to 260° during 3 hours, and maintained at 250—260° for 2 hours. After cooling (generally by keeping overnight) to room temperature, the residual pressure was released, and the contents of the tube removed by ether extraction (*ca.* 50 c.c.). The ethereal extract was filtered from titanium dioxide, washed with N-sodium hydroxide to remove unchanged carboxylic acid, then with water, dried (calcium chloride), filtered, and the ether removed; the residue (6·5 g.) was a colourless oil. Estimation of the aldehyde content by the hydroxylamine method (Stillmann and Reed, *Perfume and Essential Oil Record*, 1932, 279) indicated 5·7 g. of lauric aldehyde. The crude oil above was purified *via* its bisulphite compound in the usual manner, and then had m. p. 38—39·5°, b. p. 238°, $d_{4^\circ}^{15^\circ}$ 0·9213. The alkaline filtrate above, when acidified and extracted with ether, afforded 13·1 g. of unchanged lauric acid. The conversion was therefore 31%, *i.e.*, a yield of 90% on the lauric acid consumed.

All the yields recorded in the table have been calculated as above. The following carboxylic acids have been reduced by the above procedure: undecenoic, nonoic, heptoic, butyric, phenylacetic, benzoic, salicylic, and *p*-chloro-, *p*-nitro-, and *p*-sulpho-benzoic. The last acid was estimated by dissolving the initial reaction product in 5% aqueous sodium carbonate (100 c.c.), filtering the solution, and obtaining the aldehyde content in the solution.

Carboxylic acid.	Yield of aldehyde, %.	Recovered acid, %.	Yield of aldehyde on actual acid reduced, %.	Carboxylic acid.	Yield of aldehyde, %.	Recovered acid, %.	Yield of aldehyde on actual acid reduced, %.
Butyric	Nil	—	— *	Benzoic	37	92	92·8 †
Heptoic	<5	—	—	Salicylic	92	—	92 ‡
Nonoic	22	92	78 †	*p*-Chlorobenzoic	41	83	89
Undecenoic	25	87	79·5 †	*p*-Nitrobenzoic	8	—	— §
Lauric	31	95	90	*p*-Sulphobenzoic	22	—	—
Phenylacetic	Nil	—	— *				

* No reaction. † No by-products. ‡ A little phenol formed. § Mainly nitrobenzene.

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TECHNICAL COLLEGE, HUDDERSFIELD.

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