Oxidative Decarboxycondensation of Pyruvic Acid to Citraconic Anhydride

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Citraconic anhydride (Methyl maleic anhydride) was found to be produced from pyruvic acid by an oxidative decarboxy-condensation. The presence of oxygen is required to promote the reaction. The best catalyst is iron phosphate with a P/Fe atomic ratio of 1.2 and the optimum temperature is about 200 °C. The one-pass yield reaches 71 mol% at a pyruvic acid conversion of 98%. The main side-reaction is the formation of acetic acid and CO_2 by oxidative C-C bond fission.

Recently, we found that pyruvic acid, which is the simplest homologue of the α-keto acid, is obtained directly from a vapor-phase oxidative dehydrogenation of lactic acid over iron phosphate catalysts at a temperature around 230 °C.[1]

$$CH_3\text{-}CH(OH)\text{-}COOH + 0.5\ O_2 \longrightarrow CH_3\text{-}CO\text{-}COOH + H_2O.$$

In the further study on this reaction, formation of an unidentified compound was observed. From the variation in the amount owing to the variation in the extent of reaction, it was concluded that the compound is formed from pyruvic acid in parallel with acetic acid and CO_2. According to GC-mass analysis, the molecular weight was determined as 112. After NMR analyses and XRD analyses for the single crystal, the unidentified compound was decided as citraconic anhydride.

$$2\ CH_3\text{-}CO\text{-}COOH + 0.5\ O_2 \longrightarrow \begin{matrix} CH_3\text{-}C\text{-}C{=}O \\ \quad\ \| \quad\ \diagup O \\ \quad HC\text{-}C{=}O \end{matrix} + CO_2 + 2\ H_2O$$

$$CH_3\text{-}CO\text{-}COOH + 0.5\ O_2 \longrightarrow CH_3COOH + CO_2$$

Citraconic anhydride and citraconic acid are used as raw materials of various chemicals, resines, surface-active agent, and dyes, as like maleic anhydride. They are generally produced from itaconic acid which is produced by fermentation of sugar. Therefore, the price is much higher than maleic anhydride. At present, it has not yet been known that citraconic anhydride is formed from pyruvic acid by oxidative decarboxy-condensation.

An iron phosphate with a P/Fe atomic ratio of 1.2 was prepared according to the procedures described previously.[2]

The reaction of pyruvic acid was carried out with a continuous-flow system. The reactor was made of a stainless steel tube, 50 cm long and 1.8 cm i.d., mounted vertically and immersed in a lead bath. Air or a mixture of nitrogen and oxygen was fed in from the top of the reactor and an aqueous solution containing 100 g of pyruvic acid in 1000 ml was introduced into the preheating section of the reactor with an injection syringe pump. The extent of the reaction was varied by changing the amount of catalyst used from 1 to 36 g, while fixing the feed rates. The effluent gas from the reactor was led successively into four chilled scrubbers to recover the water soluble compounds. The recovered solution (about 50 ml) and the effluent gas were analyzed by four GC.

First, the reaction was done at 230 °C. The feed rates of pyruvic acid, air, and water were 10.5, 350, and 480 mmol/h, respectively. The main product were citraconic anhydride, acetic acid, and CO_2. Except for trace amounts of CO, acetone, and acetaldehyde, no other products were detected. A relatively large discrepancy was observed between the amount of consumed pyruvic acid and the sum of produced citraconic anhydride and acetic acid. This discrepancy was defined as "loss".

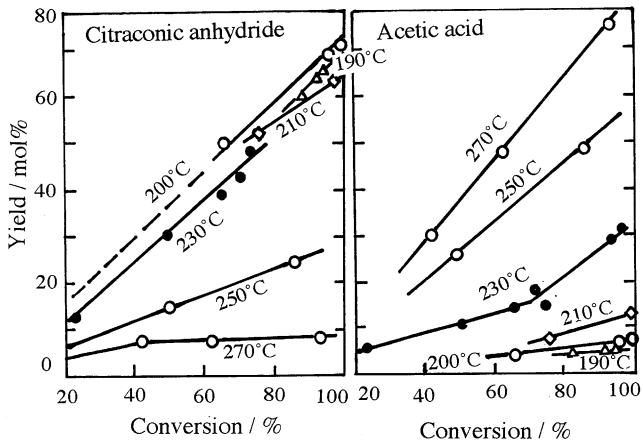

Figure 1. Effect of temperature on the product distribution.

When the amount of catalyst was 10 g (contact time = 2.6 s), the conversion of pyruvic acid reached 95%. The selectivities to citraconic anhydride, acetic acid, and loss are about 51, 29, and 20 mol%, respectively. The selectivities are almost unchanged with an increase in the conversion of pyruvic acid up to about 95%. This indicates that the produced citraconic anhydride and acetic acid are stable enough under the conditions used.

Next, the reaction was done at 230 °C by changing the feed rate of oxygen from zero to 350 mmol/h , while fixing the sum of feed rates of oxygen and nitrogen at 350 mmol/h. The yield of citracoinic anhydride at a short contact time of 0.52 s (amount of catalyst used = 2 g) increased sharply with an increase in the oxygen feed rate up to about 60 mmol/h. It is clear that the presence of oxygen is required to promote the reaction. On the other hand, the selectivity to citraconic anhydride falls a little with an increase in the oxygen feed rate.

Then, the reaction was done by changing the reaction temperature from 180 to 270 °C and the amount of catalyst used from 1 to 36 g, while fixing the feed rates of pyruvic acid, oxygen, nitrogen, and water at 10.5, 13.4, 350, and 480 mmol/h, respectively. The yields of citraconic anhydride and acetic acid obtained at different temperatures are plotted as a function of the conversion of pyruvic acid in Figure 1.

As the temperature is raised, the selectivity to citraconic anhydride markedly decreases, while that to acetic acid increases. The highest selectivity to citraconic anhydride is obtained at about 200 °C. At a temperature lower than 200°C, vaporization of pyruvic acid may become difficult under the conditions used.

At a pyruvic acid conversion of 98%, the one-pass yield of citraconic anhydride reached 71 mol% and that of acetic acid was 7 mol% (the loss was about 20 mol%).

References

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2 M. Ai, E. Muneyama, A. Kunishige, and K. Ohdan, *Bull. Chem. Soc. Jpn.*, **66**, 1542 (1994).