CONVERSION OF FURFURAL INTO FURAN BY VAPOUR-PHASE OXIDATIVE DECARBOXYLATION ON METAL OXIDE CATALYSTS

Preliminary Communication

By L. MÉSZÁROS

Institute of Organic Chemistry, The University, Szeged

(Received June 15, 1960)

Two catalyctic methods are known for converting furfural into furan in the vapour-phase. When furfural vapours are passed over the surface of metal turnings in the complete absence of air (1) and water at about 300—500°C, furan and CO are obtained with a low conversion. The second process (2) consists of passing furfural together with a fivefold excess of steam over a metal chromite or soda-lime catalyst, in the presence of hydrogen but carefully excluding oxygen. The products are furan, CO_2 and hydrogen. The latter type of process should be carried out between 200 and 500°C. Therefore, the employed catalysts are prepared by heating the higher oxides of metals in hydrogen atmosphere.

We have found (3) that furfural may readily be converted to furan carboxylic acid at $300-500^{\circ}$ C, on the surface of any higher oxide of heavy metals in the presence of oxygen or air, and the acid is spontaneously decarboxylated at the reaction temperature to give furan. The working hypothesis leading to this result was based mainly upon the fact that pyromucic acid decomposes at about 200°C, furthermore that even the so-called decarbonylation of furfural was presumed (4) to occur by way of pyromucic acid, and finally that furfural is easily oxidised in the vapour-phase to maleic anhydride (5) involving the formation of furan — carboxylic acid and furan, respectively MILAS and WALSH (6) and CALNIN *et al.* (7).

We succeeded in isolating this second assumed intermediate under strictly controlled experimental conditions which rendered possible to stop the oxidation at that stage.

The first precaution we have taken was diluting the oxygen by a neutral gas, *e.g.*, by using air or a mixture of CO_2 and oxygen. Useful catalysts are very simple and many, such as silver oxide, vanadium pentoxide, zinc oxide, lead oxide, tin oxide, titanium oxide, etc. All these catalysts may be employed alone or mixed or even precipitated on aluminium. The catalysts are not sensitive and they have long service lives. For example, by using a 100 cm long tube of 190 ml useful volume filled with vanadium-pentoxide on alumi-

L. MÉSZÁROS

nium and administering 5,5 g furfural at 350°C together with 0,75 mol of oxygen, 0.83 g of furfural was recovered and 3.0 g of furan (77% yield) was obtained.

Isolation of furan from the end-gases could be effected by adsorption ? towers as well as by compression and cooling to low temperatures. The / heat of reaction is at least 10:1 compared with that of converting furfural. into furan in the presence of water. In the latter method namely, the heat of decomposition of water which necessarily takes place in te first step of the process, consumes a considerable part of the energy of formation of furancarboxvlic acid.

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ДЕКАРБОКСИЛИРОВАНИЕ В ГАЗОВОЙ ФАЗЕ ФУРФУРОЛА В ФУРАН НА КАТАЛИЗАТОРЕ ОКИСИ МЕТАЛЛА

Л. Месарош

Согласно литературным данным получение фурана из фурфурола газофазным гетерогенным каталитическим путем осуществлено в условиях освобожденных ос следов кислорода. Реакция поводится автором оксидативным декарбоксилированием.