contain the impurities mentioned above, the following procedure is recommended. Make up an approximately fifth molar solution of the salt, let it stand in a flask, sealed to prevent excessive loss of water, for twenty-four hours on a water-bath at 75–85°. Then filter through a very retentive paper or asbestos filter and recrystallize by the usual methods the residue left on evaporation. By this means a salt of higher purity can be obtained in one recrystallization than can be obtained by the three recrystallizations from water recommended by Clark.[2] In place of evaporation to complete dryness, the salt may be precipitated from a cold saturated solution (obtained by partially evaporating and cooling the filtered solution) to which is added an equal amount of cold 95% ethyl alcohol. This gives very small crystals which may be used as such or which may be further recrystallized from water.

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CATALYTIC OXIDATION OF FURFURAL IN THE VAPOR PHASE

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Introduction

During the course of recent investigations upon the catalytic oxidation of furfural in aqueous solutions,[1] it was found that by use of various metallic oxide catalysts, different products could be obtained. Among these products were fumaric acid, mesotartaric acid and oxalic acid. The purpose of the present investigation was to determine what products are formed when furfural is oxidized in the vapor state with a similar catalyst.

Experimental Part

To prepare the catalyst, vanadic acid was precipitated upon asbestos by adding hydrochloric acid to a solution of ammonium vanadate, the asbestos filtered, washed, dried and ignited to free it from ammonium chloride and to convert the vanadic acid into vanadium pentoxide.

The catalytic mass showed a tendency to become less active during the course of the experiments, undoubtedly due to some form of poisoning. For regeneration, it was necessary only to redissolve the vanadium pentoxide in ammonia and reprecipitate with hydrochloric acid.

The furfural used in these experiments was the ordinary commercial article, which is dark colored and contains about 1% of water. It was employed without redistillation.

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[2] Clark, "The Determination of Hydrogen Ions," 2nd ed., Williams and Wilkins, Baltimore, Md., **1922**, p. 100.

[1] Milas, THIS JOURNAL, **49**, 2005 (1927).

The furfural was placed in a 300cc. distilling flask to which was fitted a right angled tube with a flare at the end projecting into the liquid. This served to break up the air current. A soda lime drying tube was connected to the other end to absorb any atmospheric carbon dioxide. The flask rested in a water-bath which could be maintained at an even temperature by an electric hot-plate. The side arm of the distilling flask extended into a Pyrex catalysis tube through a two-holed cork stopper, a 500° thermometer projecting through the other hole and extending into the middle of the asbestos. This served to indicate the temperature of the contact mass. The catalysis tube was heated by an electric furnace whose temperature was controlled by variable resistances. To the tube was fitted a long Pyrex adapter for the condensation of the oxidation products. An additional receiver was furnished by a water cooled flask. In series with this flask was a spiral condenser to condense any possible low boiling products. To the top of the condenser was fitted a gas washing bottle containing a solution of sodium hydroxide free from carbonate. A stream of air was drawn through the whole apparatus by means of a water pump attached to the bottle.

The velocity of the vapors through the system could be controlled by means of the water pump and the ratio of furfural to oxygen in the vapors by varying the temperature of the water-bath around the flask containing the furfural. For each run, the loss in weight of this flask was taken as the weight of furfural sent through the reaction tube. Conditions of temperature were varied in the several runs in order to find those necessary for the best yield.

Unchanged furfural was identified in the end products by its color reactions with resorcinol or phloroglucinol and sometimes by its boiling point and odor. Formaldehyde was identified by its odor and color reaction with resorcinol, wherein it differs from furfural. Water was sometimes present in sufficient quantity for identification by its boiling point; otherwise the blue color imparted to anhydrous copper sulfate showed its presence. Carbon dioxide was always to be found in the alkaline solution in the wash bottle. Maleic anhydride formed in the receivers as long white needles melting at 53°. Maleic acid was also present as clear, prismatic crystals melting at 138.5–140° (corrected). On recrystallization from water, the crystals melted at 138–139° (corrected). When recrystallized from an alcohol–benzene mixture, the melting point decreased with successive crystallizations until it became constant at 130–131°, which is the temperature generally given in the literature. The product was further identified as maleic acid by titration with tenth normal sodium hydroxide and also by carbon and hydrogen analysis, showing 3.57% H and 41.08% C against a calculated percentage of 3.47% H and 41.38% C.

A number of runs were made under various conditions of temperature, time and rate of flow of the air–furfural vapors over the catalyst. The best conditions seemed to be to keep the catalyst at temperatures from 200–300° and the furfural at a temperature of 45–50° while the air was passing through it. This represents a concentration of approximately one part of furfural to twelve of oxygen. Too rich a mixture gives unoxidized furfural in the product. In any case the yields were very poor, the best being 5.5 g. of maleic acid from 38 g. of furfural. Too low a temperature of the catalyst results in little or no oxidation; too high a temperature yields only carbon dioxide and water. The latter also is true when oxygen is used instead of air. Removing the product from the catalyst at a more rapid rate, obtained by increasing the rate of vapor flow, effected no marked increase in yield.

As to the mechanism of the reaction which takes place, it seems probable that at the temperature of the catalyst, maleic anhydride is formed according to the equation

$$C_4H_3OCHO + 2O_2 \longrightarrow C_4H_2O_3 + CO_2 + H_2O$$

but as maleic anhydride is readily converted to the acid in the presence of water, and water is one of the oxidation products, maleic acid is also found in the receivers. No fumaric acid could be isolated either from the end-products or the mother liquors. The formaldehyde is assumed to be a product of the further oxidation of the maleic anhydride, as whenever maleic acid was found in the receivers, formaldehyde as well as carbon dioxide and water could be identified.

It was observed that a solid phase separated in the distilling flask containing the furfural after air had been drawn through for some time. This material was somewhat rubbery in nature, but when dried and the occluded furfural removed with alcohol, it proved to be a rather granular solid, dark brown in color and quite insoluble in organic and inorganic reagents. It had no apparent melting point, merely charring.

Conclusion

When furfural is oxidized with air at temperatures from 200–300° in the presence of vanadium pentoxide as a catalyst, small amounts of maleic acid and maleic anhydride are formed, as well as formaldehyde, carbon dioxide and water.

The maleic acid formed is evidently quite pure and has a melting point of 138.5–140°.[2]

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[2] This value has been observed by Rinckes, *Rec. trav. chim.*, **45**, 822 (1926), and in 1922 Dr. H. T. Clarke of the Eastman Kodak Co. prepared some melting at 142–143°.