

# ALIEN PROPERTY CUSTODIAN

## PRODUCTION OF ALIPHATIC DICARBOXYLIC ACIDS

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The present invention relates to the production of aliphatic dicarboxylic acids, more particularly it relates to an improved process of preparing adipic acid and its higher homologues by the catalytic oxidation of cyclohexanone and its homologues.

In the preparation of dicarboxylic acids by oxidizing alicyclic ketones in the liquid phase by means of gaseous oxygen in the presence of oxidation catalysts, it has been found suitable to carry out the oxidation in the presence of a substantial amount of acetic acid which acts as a solvent. By this method of carrying out the preparation of adipic acids, which expression includes adipic acid itself and its higher homologues, generally part of the cyclohexanone which expression includes cyclohexanone and its homologues is decomposed to lower homologues of adipic acid, in particular to glutaric and succinic acid.

I have now found that the formation of lower homologues of adipic acid may be suppressed to a considerable extent, thereby increasing the yield of adipic acids, by carrying out the oxidation in a liquid containing from about 10 to about 40 per cent, preferably about 25 per cent of acetic acid. It is understood that the acetic acid content of the reaction mixture should not exceed 40 per cent and should not be below 10 per cent at any stage of the oxidation, i. e. at any stage of the process during which gaseous oxygen is allowed to pass through the reaction liquid.

The oxidation is carried out under conditions usually employed in the catalytic oxidation of ketones to carboxylic acids. Generally speaking, the temperature is kept within the range from about 40 to about 120° C. As catalysts there may be used, for example, copper, manganese, cobalt or vanadium and their salts, e. g. the acetates or nitrates. As oxidizing gases there may be used oxygen alone or air or oxygen in admixture with other inert gases different from nitrogen.

The oxidation may be carried out continuously, for example, by charging a tower with a mixture of acetic acid and cyclohexanone in the ratio 25 to 75 containing 0.1 per cent of a catalyst, e. g. manganese acetate, and passing a current of oxygen or air at 80° C through a porous filter plate at the bottom of the tower. Depending on the rate of the conversion of cyclohexanone into adipic acid, cyclohexanone is added, preferably through the oxygen- or air-inlet, thus avoiding that adipic acid is deposited on the filter plate. In order to separate adipic acid formed from the

reaction mixture, part thereof is withdrawn from the reaction vessel continuously or from time to time. The adipic acid crystallized out by allowing the solution to cool is filtered off or centrifuged, the cold mother-liquor being returned into the reaction vessel.

The crude adipic acid contains a small amount of acetic acid and of cyclohexanone. It may suitably be worked up in the following manner: The crude adipic acid is washed with part of the cyclohexanone which is to be introduced into the reaction vessel. Thus, the acetic acid contained in the crude adipic acid is removed and rendered useful in the oxidation thereby avoiding substantial losses thereof. The adipic acid now contains but a small amount of cyclohexanone which may be recovered by heating the adipic acid below its melting point and condensing the vapors emerging therefrom.

The adipic acid containing cyclohexanone may also be introduced slowly into nitric acid of sufficient strength to effect oxidation of cyclohexanone, e. g. 50 to 60 per cent nitric acid, heated to 60-70° C. The adipic acid is dissolved and the cyclohexanone oxidized forming adipic acid also dissolving in the nitric acid. By cooling the nitric acid, the adipic acid is obtained in the form of crystals. After washing with water, it is so pure that it may be employed directly for many technical purposes, e. g. for the preparation of hexamethylene diamine.

As already mentioned, the cyclohexanone admixed with the crude adipic acid may also be recovered wholly or partly by distillation. The adipic acid thus obtained may be recrystallized from water or nitric acid. On the other hand, the crude adipic acid freed from acetic acid but still containing cyclohexanone may be at once recrystallized from water, the cyclohexanone being separated from the aqueous solution and being returned into the reaction vessel.

It will be understood that the above given explanation of the reaction temperature, the catalysts and the method of carrying out the oxidation and the purification of the adipic acids is merely given for purpose of illustration and that the specific methods described are not an essential part of my invention but that numerous modifications of these methods may be made without departure from the spirit of my invention.

The invention will be described in greater detail in the following example which illustrates a typical embodiment of my invention. The in-

vention, however, is not restricted to this example.

*Example*

30 liters of oxygen per hour are introduced at 80° C into a mixture consisting of 100 grams of acetic acid, 300 grams of cyclohexanone, 0.3 gram of manganese acetate and 0.15 gram of barium acetate. Under these conditions, about 50 grams of cyclohexanone are oxidized per hour. This amount is continuously supplied by adding 50 grams of fresh cyclohexanone per hour. From time to time part of the reaction mixture is removed and allowed to cool. The adipic acid which deposits in the form of crystals is filtered off by suction and washed with cyclohexanone. The mother liquor and the cyclohexanone used for washing the adipic acid are returned into the reaction vessel.

The adipic acid is slowly introduced into twice its amount of 50 per cent nitric acid at 60° C, while cooling. The solution obtained is kept at 60° C for further 30 minutes and then allowed to cool. The adipic acid crystallized out is filtered off by suction and washed with 30 per cent of its amount of water. For 100 grams of cyclohexanone there are thus obtained 137 grams of adipic acid.

If carrying out the oxidation under otherwise identical conditions while starting from a mixture consisting of 70 per cent of acetic acid and 30 per cent of cyclohexanone, only 101 grams of

adipic acid are obtained for 100 grams of cyclohexanone.

The reaction may also be carried out with air as the oxidizing agent. In order to avoid losses of acetic acid, the spent gas should then be cooled vigorously or even washed with cyclohexanone. For example, the spent gases may be led through a tower through which cyclohexanone of low temperature is allowed to trickle.

The following table also shows the advantages residing in the use of a reaction mixture containing less than 40 per cent and more than 10 per cent of acetic acid. The amount of carbon dioxide formed corresponds to the rate at which adipic acid is converted into its lower homologues:

Composition of the reaction mixture	Percentage of CO <sub>2</sub> in the total increase of weight of the reaction mixture
<i>Percent</i>	
300 grams of acetic acid .....	10
100 grams of cyclohexanone .....	
200 grams of acetic acid .....	6
200 grams of cyclohexanone .....	
100 grams of acetic acid .....	2.2
300 grams of cyclohexanone .....	
40 grams of acetic acid .....	6.5
300 grams of cyclohexanone .....	

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