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PROCESS FOR THE PRODUCTION OF ADIPIC ACID

Wilhelm Nikolaus Mathes and Ludwig Seelmann, Ludwigshafen/Rhein, Germany; vested in the Alien Property Custodian

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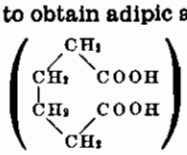
It is known to produce adipic acid from cyclohexane by boiling it with nitric acid. Furthermore adipic acid has been produced by the oxidation of cyclohexanol by means of nitric acid. Finally processes have been described which obtain adipic acid mixed with other products viz. in small quantities by submitting cyclohexen to strong oxidation conditions.

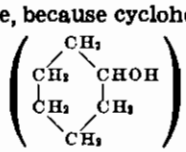
According to the present invention is has now been found that cyclohexen may be easily oxidized to adipic acid under ordinary conditions of oxidation, i. e. using nitric acid of preferably about 40–75% by weight. If simultaneously air is introduced into the reaction mixture it is possible to work with the theoretical amount of nitric acid or with a small excess. Of course it is also possible to use an excess up to about e. g. five times of the theoretical amount. Furthermore it is advisable to use catalysts favourable to oxidation, for instance oxides of manganese, iron, chrome or vanadium. Thereby the yields are improved.

The time of reaction depends on the temperature. The better the temperature of reaction will be kept constant by cooling the faster the cyclohexen may be added. Preferably the time of reaction takes about 1–2 hours and the reaction temperature may vary between 20° C and the boiling temperature of the nitric acid used. It is possible to apply pressure but thereby no important advantage is obtained.

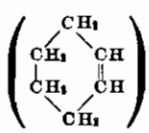
The process mentioned above in the first place (oxidation of cyclohexene) has never been used on a large scale. Compared with the known oxidation of cyclohexanol by means of nitric acid it is surprising that the new process works at least as satisfactorily to obtain adipic acid



as the known one, because cyclohexanol



already contains oxygen and it should be thought that it is more easily to oxidize cyclohexanol than cyclohexen



which does not contain oxygen. Furthermore cyclohexanol is soluble in watery nitric acid but not cyclohexen. Also this circumstance seems to show that the known oxidation should be more easily carried out than the oxidation according to the invention.

When finally comparing the known process of treating cyclohexen under strong conditions of oxidation it is surprising that cyclohexen may be transformed to adipic acid under normal conditions of oxidation whilst in the case of strong conditions of oxidation only small amounts of adipic acid are obtained.

Example 1

A mixture of 90 g HNO_3 (80%) and 30 g H_2O are boiled under reflux and 20 g cyclohexen are added during 30 minutes. After further 30 minutes distillation by means of steam is carried out in order to remove small amounts of a contamination; finally 17,5 g raw adipic acid is obtained by evaporation.

Example 2

A round-bottomed flask provided with means for agitating, reflux-cooler and dropping funnel is filled with 425 g nitric acid of 50% and 0,3 g pentoxide of vanadium; 45 g cyclohexen are added under agitation during one hour, keeping the temperature of the acid to 55° C. In order to start the reaction it is advisable to heat at the beginning for a short time up to 70° C. If all of the cyclohexen has been filled in the temperature is raised to 100° C and maintained for an hour. Atfer evaporation a paste of crystals is obtained consisting of 49,3 g raw adipic acid and small amounts of other acids.

Example 3

The device described in example 2 is furthermore provided with an inlet pipe for air. The conditions of reaction are the same and only the amount of nitric acid is reduced to 212,5 g; furthermore air is led in a moderate manner through the reaction mixture. Yield: 47,8 g raw adipic acid.

Example 4

In the device according to example 2 335 g of nitric acid of 65% and 0,3 g of pentoxide of venadium are filled in. Thereto at first some drops of cyclohexen are added at 45° C and then during two hours at 30–35° C the rest of 47 g cyclohexen. The reaction mixture is kept to 40° C and then treated as described above. Yield: 56,5 g raw adipic acid.

Example 5

Instead of the pentoxide of vanadium according to example 2 0,5 g hydrate of the oxide of manganese are used. 47,4 g raw adipic acid are obtained.

WILHELM NIKOLAUS MATHES,
LUDWIG SEELMANN.