

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF CONDENSATION PRODUCTS

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The invention relates to a process of producing low molecular condensation products, using formaldehyde as a reacting component. It is an object of the invention to produce particularly those organic compounds which contain 3 carbon atoms in the molecule, such as hydacryl-
aldehyde, acrolein, acrylic acid, propylene glycol, glycerine, allyl alcohol, propionic aldehyde, propanol etc.

According to the invention, formaldehyde is reacted with aliphatic aldehydes such as acetaldehyde in the presence of condensing agents and in a medium which does not contain any or only small quantities of water. Instead of aliphatic aldehydes, alcohols or esters may be reacted with formaldehyde in the same way, also derivatives of these compounds may be used, such as paraldehyde, ethyl alcohol, methyl alcohol, or mixtures of same, ethers, dimethyl ether, diethyl ether, acetals, dimethylformal, diethylformal, dimethylacetal. Also inorganic or organic esters of aliphatic alcohols are well suited such as methyl formate, ethyl formate, methyl acetate, halogen compounds as chloroethyl, ethyl bromide, beta-chloroethyl alcohol. The compounds may be used in the form of their mixtures with each other.

The condensing agent which is used according to the invention is preferably an alkaline substance, such as potassium hydroxide, calcium hydroxide, borax, sodium amide, sodium phosphate, sodium acetate, sodium ethylate, metallic sodium, when alcohols are present, magnesium oxide, calcium oxide.

We prefer to apply such quantities and such an alkalinity of the condensing agent as to cause the least possible quantities of undesirable by products such as resinous substances, e. g. trisodium phosphate is well used for condensing formaldehyde with acetaldehyde according to the invention. When reacting mixtures which contain acetals instead of acetaldehyde, it is preferable to do that in the presence of substances which are more alkaline, such as potassium hydroxide. In such cases it may be useful to apply acidic condensation agents such as aluminum chloride, phosphoric acid, sulfuric acid, beryllium chloride, or the anhydrides of these acids.

As mentioned above, when carrying through the condensation in the liquid phase, it is essential that the reaction mixture contain no water or only small quantities, that is less than 10%, of water. Care is to be taken that the formaldehyde which is to be reacted is as free from water as possible. Thus we prefer to digest usual paraformaldehyde with methyl or ethyl alcohol and

after filtering from the undissolved particles to join it with the other compounds of the reaction. Instead of methyl or ethyl alcohol, there are also other solvents which may be used as reaction media, such as higher boiling alcohols, esters, ketones, phenol ethers etc. By using such higher boiling solvents or diluent agents the formation of undesired polymerisation products of acrolein may be efficiently avoided. We prefer to use as solvents especially butanol, glycerine, butylacetate, glycerine triacetate, glycol diacetate etc. The paraformaldehyde may be used in its known slightly soluble form. In order to dry the solution of paraformaldehyde in the solvents such as alcohol, the solutions to be used may be previously mixed with esters or hydrocarbons and subsequently subjected to a distillation whereby the water is removed in the form of an azeotropic mixture. Of course, the water may be eliminated also by chemical agents as for example, by means of metallic sodium. We also use successfully solutions which are obtained by introducing gaseous formaldehyde into water-free solvents or diluent agents as above mentioned. It is also possible to introduce the gaseous formaldehyde immediately into the reaction mixture.

When carrying through the invention, we use a mixture which contains, e. g. equimolecular quantities of the reaction compounds and only small quantities of water. When adding to this mixture, while stirring, several percents of trisodium phosphate, the temperature of the mixture rises instantaneously to 50-60° C. In order to regulate the course of the reaction, we prefer to add the acetaldehyde, and eventually also the catalyst, portion by portion. The mixture is well stirred for several hours and heated when necessary. Thereafter the mixture is subjected to a fractionating distillation. When starting from acetaldehyde and formaldehyde large quantities of acrolein are obtained, whereas by-products such as crotonaldehyde are formed in small quantities only. It is possible to vary the proportions of the reaction components such as of formaldehyde and acetaldehyde. However, it is useful to avoid a large excess of formaldehyde so that the formation of higher molecular products like pentaerythrite may not be favoured. In most cases it is not necessary to isolate the reaction products such as acrolein when they are to be transformed into other valuable substances; e. g. the reaction product, which is formed in the medium containing formaldehyde and acetaldehyde, is advantageously treated by oxidizing agents, whereby acrylic acid is pro-

duced. The reaction mixture obtained after the reaction has been completed may also be treated in such a way as to form glycerine from acrolein, that is, by a directly hydrating process or by adding halogen, hydrolizing and finally reducing the glycerine aldehyde obtained by the previous steps.

In most cases it is only necessary to heat weakly the reaction mixture, as the temperatures of the reaction are in most cases relatively low, that is, below the boiling point of the liquid reaction mixture. If the temperatures necessary for the reaction are high, we prefer to carry through the reaction in the presence of one of the above mentioned high boiling solvents, such as phenol ether.

Higher pressure, especially much higher than atmospheric pressure, may be applied. We prefer to use the elevated pressure when acetals instead of the trialdehydes are to be reacted. Besides that, it is useful to apply higher temperatures or higher pressures or both if formaldehyde or its acetals are reacted with methyl or ethyl alcohol or their esters in the liquid phase, e. g. we heat a solution of formaldehyde or paraformaldehyde or formals in methyl or ethyl alcohol, which solution contains no water or only small quantities of water, in the presence of condensing agents such as calcium hydroxide, barium hydroxide or sodium methylate, at a pressure of several atmospheres. Higher boiling solvents or diluents may be present. Advantageously we add to the reaction mixture also dehydrogenating catalysts such as copper, nickel, iron, etc.

The reaction is generally not stopped until the quantity of the unsaturated compounds, which absorb bromine, is found to have reached an optimum point. In order to avoid the formation of undesirable by products, we often prefer to stop the reaction before this point, which measure may be favourably influenced by rapidly cooling and neutralizing the catalyst.

As we have further found, it is possible to react formaldehyde with alcohols, aldehydes, ketones, esters or ethers in the vapor state, whereby low molecular condensation products are formed, e. g. formaldehyde and acetaldehyde react in yielding hydracrylaldehyde, which is easily transformed into acrolein. The same result is obtained when passing formaldehyde with paraldehyde or with aldehyde or acetals of the acetaldehyde or the isomers of the acetaldehyde such as ethylene oxide at elevated temperatures over catalysts. Instead of acetaldehyde, also the homologues, as propionaldehyde, butyraldehyde, etc., may be used. The ketones react in the same way as the aldehydes, first forming the corresponding methylol compounds. Instead of formaldehyde the acetals such as dimethylformal may enter the reaction, according to the invention. When carrying through the reaction in the vapor phase, water may be present, so that ordinary aqueous commercial formaldehyde may be used as a starting material. In certain cases, especially in order to avoid the Cannizzaro reaction we prefer to use a reaction medium containing no water or only small quantities of water. In this way paraformaldehyde or slightly soluble paraformaldehyde may be dissolved in acetaldehyde or paraldehyde or even in methyl alcohol or ethyl alcohol, and these mixtures may be vaporized and then reacted at higher temperatures, according to the invention. It is not necessary that the reaction mixture be completely homogenous, e. g. paraformaldehyde may be immediately vapor-

ized in mixture with the other reaction components and then treated in the manner described above. The reaction which takes place in the vapor state is not dependent upon the presence of a catalyst, but by means of catalysts higher yields are obtained. Generally also catalysts are to be used which have a condensing or a dehydrating effect, such as alkaline substances like magnesium oxide, alumina, zinc oxide, calcium oxide, beryllium oxide, sodium carbonate, and alkaline phosphates, or also acidic condensing agents like silica gel, aluminum phosphate, boron phosphate, and phosphoric acid on carriers like activated carbon, or even gaseous catalysts, such as phosphorus oxychloride, titanium dioxide, tungstic acid, molybdic acid, etc. Also mixtures or other compounds of these catalysts may be used. We prefer to combine with these catalysts also those substances which have a dehydrating action, such as copper, nickel, iron or their oxides, etc. Also inert gases or gaseous diluents such as carbon dioxide, nitrogen, etc., may be present during the reaction. Thus the acrolein formed by the reaction is prevented from being destroyed. We obtain the same effect when passing the reaction mixture over catalysts with relatively high velocity, which is very useful if very strong conditions such as highly active catalysts, high temperatures, or elevated pressure are applied.

Advantageously the reaction takes place under decreased pressure, that is, in vacuo, because in this way the formation of by products is prevented. When carrying through the process in vacuo, even the hydroxyl containing methylol compounds which are the primary products of the reaction may be isolated.

We have found that polymerisation processes are inhibited if the reaction mixtures are cooled, immediately after they have left the reaction chamber. It is also desirable to add inert diluent agents to the reaction mixture before or after the reaction. These diluent agents may be higher molecular hydrocarbons and, in several cases, water too. The temperature of the reaction may vary within wide limits. At any event, the temperature must be sufficiently high so as to prevent the components from condensing on the catalyst, but not so high as to cause undesirable decomposition. We prefer to use temperatures between 150-400°.

The present invention is shown by the following example:

Example

An aqueous solution of about 30% formaldehyde is vaporized, together with about the equimolecular quantity of acetaldehyde. The vaporous mixture is passed over alumina at temperatures between about 260° and about 300° C. In the reaction mixture acrolein is obtained in a yield of about 50% of the theoretical yield. By the measures mentioned above, the yield of acrolein may be increased.

According to the conditions of the reaction, the reaction product contains hydracrylaldehyde, dimethylol-acetaldehyde, glycerine, glycol, propylene glycol, acetol, butanol, or unsaturated compounds, such as acrolein, vinyl acetol and the like. The products may be isolated from the reaction mixture by fractional distillation or by extraction. It is also possible to treat the reaction mixture without isolating the different products, in order to transform these products into other valuable substances, e. g. a reaction product which contains principally acrolein may be subjected to

an oxidizing process whereby crotonic acid or crotonic esters are obtained. The reaction mixture may also be treated to form glycerine directly.

Although the invention has been described in connection with a preferred embodiment, it will be observed that variations may be resorted to

and are within the purview of the appended claims.

The present application is a division of our co-pending application Ser. No. 197,374, filed 8 March 22, 1938.

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