PRODUCTION OF BENZYL ALCOHOL AND BENZALDEHYDE

Jacques Bonnart and Georges Poinel, Lyon, Rhone, France, assignors to Rhone-Poulenc S.A., Paris, France, a French body corporate

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ABSTRACT OF THE DISCLOSURE

Benzyl alcohol and benzaldehyde are produced by oxidizing liquid toluene at 170° C.—220° C. with gas containing less than 21% of oxygen until not more than 10% of the toluene has been oxidized, then preferably decomposing the hydroperoxides formed, and isolating the benzyl alcohol and benzaldehyde produced.

The invention relates to the oxidation of toluene to benzyl alcohol and benzaldehyde.

The most widely used industrial process for the preparation of benzyl alcohol and benzaldehyde consists in chlorinating toluene to a mixture of benzyl chloride and benzylidene chloride, which are then saponified. The benzyl alcohol and the benzaldehyde thus obtained contain chlorinated impurities, the elimination of which by distillation, or chemically, is always difficult, but is also essential when these products are intended for use in perfumery, as pharmaceutical products, or as intermediates in organic syntheses. Moreover, these chlorinated impurities are liable to cause corrosion, which necessitates the use of special materials.

It is possible to prepare benzaldehyde by catalytically oxidizing toluene in the vapour phase at temperatures from 300° to 500° C. The yields do not exceed 30—50% (see Ullmann's Enzyklopaedie, vol. 4, 238 (1953)). The process is dangerous to perform industrially because the mixture of toluene vapour and air used is explosive.

In addition, the oxidation of toluene in the liquid phase has been described. It is known that when hydrocarbons are oxidized, the first stage of the oxidation is the formation of hydroperoxides and that first alcohols and then aldehydes (or ketones) are formed from the hydroperoxides, both of which may subsequently be oxidized to the corresponding acids. In the liquid phase oxidation of toluene, all the oxidation stages have been observed. The problem is therefore to control the oxidation in such a manner as to obtain the maximum yield of benzyl alcohol and benzaldehyde, or of their precursor benzyl hydroperoxide, which can be readily converted into benzyl alcohol and benzaldehyde in a subsequent operation.

The previously described processes for oxidizing toluene in the liquid phase have given only negligible yields of benzyl alcohol and benzaldehyde. While the preparation of benzyl hydroperoxide from toluene has been described, it has only been possible to obtain this hydroperoxide in the presence of a considerable quantity of a peroxidic initiator, viz., cumene hydroperoxide (see United States patent specification No. 2,683,751). The separation of benzyl hydroperoxide, or of benzyl alcohol and benzaldehyde, from the product of this reaction is very difficult because of the presence of the cumene hydroperoxide or its reduction and degradation products. If the oxidation of toluene is carried out in the presence of catalysts such as heavy metals, substantially only benzene acid is obtained.

It has now been found that toluene may be oxidized in the liquid phase under certain specific conditions in good yields to a mixture of benzyl alcohol and benzaldehyde. The process of the invention comprises oxidizing liquid toluene at 170°—220° C. with gaseous oxygen in the presence of an inert gaseous diluent in amount such that the gaseous mixture contains not more than 21% of oxygen, the oxidation being discontinued when at most 10% of the toluene has been oxidized. In this process the diluted oxygen, preferably air of reduced oxygen content, is passed through the liquid toluene at a temperature between 170° and 220° C. under a pressure sufficient to maintain the toluene in the liquid state, in the absence of any metallic catalyst or peroxidic initiators, other than those formed from the toluene, and the oxidation is stopped at a degree of conversion of the toluene at most equal to 10%. A mixture of toluene, benzyl hydroperoxide, benzyl alcohol, benzaldehyde, benzoic acid and a few other by-products is thus obtained. This mixture is then ordinarily de-peroxided, for example by catalytic hydrogenation or by heating in an inert atmosphere to 180°—280° C., or to a lower temperature if the de-peroxidation is accelerated by the use of a de-peroxidation catalyst, such as a cobalt salt or a derivative of boric acid (e.g., the amhydride, an acid, or an ester). When the peroxide has been decomposed, the acid products are eliminated by washing with an aqueous alkali metal hydroxide solution, and the residual organic layer is then fractionally distilled.

When the crude oxidation product contains only a small proportion of hydroperoxide, the de-peroxidation treatment may optionally be omitted, since adequate de-peroxidation generally takes place in the separation of the constituents of the mixture.

It is preferred to oxidize the liquid toluene in the presence of a stabilizing agent for organic hydroperoxides so that the decomposition of the benzyl hydroperoxide, which is a primary product of the oxidation, is inhibited. The mixture obtained is then subsequently de-peroxided and separated as already described. As stabilizing agent, the products known for stabilizing hydrogen peroxide may be used, e.g., those appearing in the list given in R. E. Kirk and D. F. Othmer (Encyclopedia of Chemical Technology, Interscience Encyclopedia, New York, vol. 7, p. 730 (1951)). More especially, sodium pyrophosphate and sodium fluoride may be used. The proportion of stabilizing agent to be employed is conveniently between 0.01% and 0.5% by weight of the toluene employed.

The process of the invention gives a mixture of benzyl alcohol and benzaldehyde in yields from 50% when no stabilizer is employed, to 70% when a stabilizer is used.

The following examples illustrate the invention and show how it can be put into practice:

EXAMPLE 1

Into a stainless steel autoclave having a capacity of 3.6 litres and provided with a stirring system are introduced 2000 g. of toluene, and a pressure of 10 bars is established with a gas mixture consisting of 10% of oxygen and 90% of nitrogen. After heating to 165° C., when the pressure reaches 12 bars, a current of the same gas mixture is introduced into the reaction mass at a rate of 350 litres per hour, the heating being continued until the temperature reaches 185°—190° C. At the end of one hour, the heating and the passage of the gas mixture are stopped.

The percentage by weight of the oxidation products is determined on an aliquot fraction of the reaction product by evaporation of the toluene in vacuo, followed by determination of the benzyl hydroperoxide and of the acid products (expressed as benzoic acid) by alkaline titration. From the difference, the percentage of the oxidation products other than hydroperoxides and acids is obtained. The results are set out in Table I below.
The crude mixture is washed with 200 cc. of 5% aqueous sodium hydroxide solution, the aqueous layer is separated, the toluene is driven off in the organic fraction, and the residue is distilled. Benzyl alcohol, benzylande hyde and by-products are obtained in the yields shown in Table II below.

**EXAMPLE 2**

The procedure of Example 1 is followed, but 0.1% by weight of sodium pyrophosphate is added to the toluene. Analyses, carried out as in Example 1, give the results shown in Table I.

0.001% of cobalt in the form of cobalt 2-ethylhexanoate is added to the crude oxidation mixture, the autoclave is purged with nitrogen and the product is rapidly heated to 165 °C, while the inert atmosphere is maintained by bubbling nitrogen through the mixture. At the end of 10 minutes it is found by titration of an aliquot portion that no peroxide remains in the reaction mass. The latter is washed with 200 cc. of a 5% aqueous sodium hydroxide solution, the aqueous layer is decanted, and the organic layer is concentrated by distillation of the toluene in vacuo. The benzyl alcohol and the benzaldehyde are then separated from the other oxidation products, by fractional distillation under a vacuum of 7 mm. Hg, the aldehyde passing at 49°-50° C. and the alcohol at 82°-83° C. The yields obtained are set out in Table II.

**EXAMPLE 3**

The procedure of Example 1 is followed, but 0.1% by weight of sodium fluoride is added to the toluene. The composition of the mixture after oxidation, determined as indicated in Example 1, is given in Table I.

**TABLE I**

<table>
<thead>
<tr>
<th>Without stabilizer (Example 1)</th>
<th>With 0.1% of sodium pyrophosphate stabilizer (Example 2)</th>
<th>With 0.1% of sodium fluoride stabilizer (Example 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent by weight of oxidation products in the solution</td>
<td>4.8</td>
<td>8.0</td>
</tr>
<tr>
<td>Percent by weight of hydroperoxides in the oxidation products</td>
<td>4.1</td>
<td>41.8</td>
</tr>
<tr>
<td>Percent of acid products</td>
<td>16</td>
<td>14.9</td>
</tr>
<tr>
<td>Percent of other oxidation products (alcohol, various side-products)</td>
<td>79.9</td>
<td>42.4</td>
</tr>
</tbody>
</table>

**TABLE II**

<table>
<thead>
<tr>
<th>Product obtained</th>
<th>Without stabilizer (Example 1)</th>
<th>With sodium pyrophosphate stabilizer (Example 2)</th>
<th>With sodium fluoride stabilizer (Example 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl alcohol, percent</td>
<td>30.2</td>
<td>30.4</td>
<td>28.7</td>
</tr>
<tr>
<td>Benzaldehyde, percent</td>
<td>19.2</td>
<td>16.4</td>
<td>20.3</td>
</tr>
<tr>
<td>Non-recoverable by-products</td>
<td>34</td>
<td>14</td>
<td>34</td>
</tr>
</tbody>
</table>

Although the foregoing examples describe a batch-wise process, the process may also be carried out continuously.

We claim:

1. Process for the production of benzyl alcohol and benzaldehyde which comprises oxidizing liquid toluene at 170°-220° C. with a mixture of gaseous oxygen and an inert gaseous diluent such that the said mixture contains not more than 21% of oxygen, until at most 10% of the toluene has been oxidized, decomposing the hydroperoxides formed to benzyl alcohol and benzaldehyde by catalytic hydrogenation and separating the benzyl alcohol and benzaldehyde produced.

2. Process according to claim 1 in which, after the oxidation, the hydroperoxides in the oxidized toluene are decomposed by heating in an inert atmosphere in the presence of a catalyst.

3. Process according to claim 1 in which the gasous mixture is air of reduced oxygen content.

4. Process according to claim 1 in which the oxidation is discontinued when 4% to 7% of the toluene has been oxidized.

5. Process according to claim 1 in which the oxidation is carried out in the presence of a stabilizing agent for organic hydroperoxides.

6. Process according to claim 5 in which the stabilizing agent is sodium pyrophosphate used in amount of 0.01 to 0.5% by weight of the toluene.

7. Process according to claim 5 in which the stabilizing agent is sodium fluoride used in amount of 0.01 to 0.5% by weight of the toluene.

8. Process for the production of benzyl alcohol and benzaldehyde which comprises oxidizing liquid toluene at 170°-220° C. with a mixture of gaseous oxygen and an inert gaseous diluent such that the said mixture contains not more than 21% of oxygen, until at most 10% of the toluene has been oxidized, decomposing the hydroperoxides formed to benzyl alcohol and benzaldehyde by reacting with an inert atmosphere, and separating the benzyl alcohol and benzaldehyde produced.

9. Process according to claim 8 in which the gaseous mixture is air of reduced oxygen content.

10. Process according to claim 8 in which the oxidation is discontinued when 4% to 7% of the toluene has been oxidized.

11. Process according to claim 8 in which the oxidation is carried out in the presence of a stabilizing agent for organic hydroperoxides.

12. Process according to claim 11 in which the stabilizing agent is sodium pyrophosphate used in amount of 0.01 to 0.5% by weight of the toluene.

13. Process according to claim 11 in which the stabilizing agent is sodium fluoride used in amount of 0.01 to 0.5% by weight of the toluene.

14. Process for the production of benzyl alcohol and benzaldehyde which comprises oxidizing liquid toluene at 170°-220° C. with air of reduced oxygen content in the presence of 0.01 to 0.5% by weight of the toluene of sodium pyrophosphate until 4 to 7% by weight of the toluene has been oxidized, decomposing the benzyl hydroperoxide formed by heating in an inert atmosphere in the presence of a cobalt salt, and isolating benzyl alcohol and benzaldehyde from the product by fractional distillation.

15. Process for the production of benzyl alcohol and benzaldehyde which comprises oxidizing liquid toluene at 170°-220° C. with air of reduced oxygen content in the presence of 0.01 to 0.5% by weight of the toluene of sodium fluoride until 4 to 7% by weight of the toluene has been oxidized, decomposing the benzyl hydroperoxide formed by heating in an inert atmosphere in the presence of a cobalt salt, and isolating benzyl alcohol and benzaldehyde from the product by fractional distillation.

**References Cited**

<table>
<thead>
<tr>
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<tbody>
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**BERNARD HELFIN, Primary Examiner.**