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3,492,207

ELECTROCHEMICAL REDUCTION
OF BENZENE

Kang Yang and James D. Reedy, Ponca City, Okla., and
Robert L. Hartshorn, Lima, Ohio, assignors to Con-
tinental Oil Company, Ponca City, Okla., a corporation
of Delaware

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3 Claims

ABSTRACT OF THE DISCLOSURE

A process for electrochemically reducing benzene to 1,4 cyclohexadiene in the presence of hexamethylphosphoramide, a lithium halide, and an alcohol.

This invention relates to a method of electrochemically reducing benzene to selectively produce 1,4 cyclohexadiene.

Benzene can be reduced chemically to a mixture of products, such as 1,3 and 1,4 cyclohexadienes, cyclohexene, and cyclohexane, in anhydrous low molecular weight amines with metallic lithium or sodium. These alkali metal reductions are of considerable synthetic use, however, the cost of lithium or sodium metal and the amines makes this process too expensive for large scale use. The products formed by this chemical reduction have similar properties and separation into pure components is nearly impossible. Aromatic compounds have been reduced electrolytically. Benzene has been reduced in methylamine while using lithium chloride as a current carrier.

Electrolytic solvents which have been used for electrochemical reductions include liquid ammonia, methyl amine, ethyl amine and ethylenediamine. The first three solvents mentioned above boil at below room temperature and require that low temperature or high pressure apparatus be used. The last solvent, namely ethylenediamine, does not permit the selective reduction of benzene to 1,4 cyclohexadiene.

It has now been unexpectedly discovered that benzene can be reduced to selectively produce 1,4 cyclohexadiene when said reduction is carried out electrolytically in the presence of hexamethylphosphoramide and an alcohol with a current carrier of a lithium halide. For highest yields it has been discovered that said reaction should be carried out at atmospheric pressure and at temperatures of room temperature up to about 100° C.

The lithium halides which are useful in this reaction are LiCl, LiBr and LiI with LiCl being the preferred material. The amount of benzene and alcohol present can vary over a large range; however, the preferred quantity is from about 0.1 to about 10 moles of benzene per mole of alcohol. The alcohols which are useful in this process are propyl alcohol, ethyl alcohol, methyl alcohol and all other alcohols which are soluble in hexamethylphosphoramide under the conditions of the electrochemical reaction.

An outstanding feature of this reaction is its selectivity of products. Benzene was converted to 1,4-cyclohexadiene with selectivity of greater than 98 percent, and in most cases about 100 percent.

Numerous materials can be used as cathodes. The desirable properties of the cathode are: (1) high hydro-

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gen overvoltages, (2) resistance to attack by hexamethylphosphoramide, (3) good conductor, (4) readily available, and (5) low cost. Aluminum, zinc, and platinum have been used with aluminum being preferred because of its availability and low cost.

Numerous materials were tested as anodes. Included were platinum, gold, titanium, cast iron, stainless steel, nickel, zirconium, molybdenum, tungsten, antimony, tin, and carbon. Good current efficiencies can be obtained with a platinum anode with 1 percent alcohol present.

Separation of the products formed can be accomplished by fractional distillation.

For a fuller understanding of the present invention, reference will be had to the following example.

EXAMPLE

Cell -----H-type cell with coarse, sintered glass divider.

Electrodes -----Aluminum cathode and carbon anode.

Cathodic solution .025 mole of hexamethylphosphoramide, 0.12 mole of benzene, 0.33 mole of propyl alcohol, and 0.024 mole of LiCl.

Electrolysis -----100 milliamperes for 19,260 seconds.

Products ----- 6.65×10^{-3} moles of 1,4 cyclohexadiene (analyzed by GLPC).

Percent current efficiency -----66.5%.

Having thus described the invention by providing a specific example thereof, it is to be understood that no undue limitations or restrictions are to be drawn by reason thereof and that many variations and modifications are within the scope of the invention.

What is claimed is:

1. A process for electrochemically reducing benzene to 1,4 cyclohexadiene which comprises:

(a) dissolving benzene, a lithium halide and an alcohol in hexamethylphosphoramide in a vessel containing an anode and a cathode;

(b) passing a direct current of electricity through said solution for a period of time sufficient to produce a mixture of essentially 1,4 cyclohexadiene and benzene; and

(c) recovering said 1,4 cyclohexadiene from said mixture.

2. The process of claim 1 wherein said lithium halide is lithium chloride.

3. The process of claim 1 wherein the recovery step of (c) is by fractional distillation.

References Cited

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JOHN H. MACK, Primary Examiner

H. M. FLOURNOY, Assistant Examiner

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