PROCESS FOR REDUCING CYCLO-OCTATETRAENE

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This invention relates to a method of reducing cyclooctatetraene by electrolytic reduction of cyclooctatetraene. I have now found that cyclooctatetraene can be readily prepared in good yield by electrolytic reduction of cyclooctatetraene. This reduction has been found to take place in neutral and alkaline solutions. However, the present evidence indicates that the reduction does not proceed readily in acidic solutions. The final structure of the cyclooctatetraene obtained by electrolytic reduction of cyclooctatetraene has not been definitely established. Some evidence exists that the product of the electrolysis may be a mixture of cyclooctatetraene-1,3,5 and cyclooctatetraene-1,3,6. However, since the material has drying properties, it appears probable that if the product is considered to be a single substance cyclooctatetraene-1,3,6 is formed.

The cyclooctatetraene obtained by the process of this invention absorbs 3 moles of hydrogen to form the well known compound cyclooctane. It polymerizes readily with boron trifluoride and other polymerization catalysts and readily absorbs oxygen to form CaH2O5, the structure of which is unknown at present. It has the comparatively rare property of absorbing oxygen to form a horny resin and as a result is of interest as a substitute for drying oils, such as linseed oil. It is also of interest as a monomer for polymerization reactions and as an intermediate in the synthesis of organic chemicals.

The process of the present invention may most readily be described by consideration of the following specific example thereof:

Example

A solution of one hundred grams of tetramethyl-ammonium bromide in one litre of fifty per cent aqueous ethyl alcohol was placed in a two-litre resin pot. The bottom of the still pot was covered with mercury to serve as a cathode to which electrical connection was made. A porous electrolysis cup containing 20% sodium hydroxide as anolyte was suspended in the catholyte media. The anode was a steel rod. To the catholyte was added 100 grams of cyclooctatetraene and the resin pot was covered and fitted with a condenser, to prevent volatilization of cyclooctatetraene and cyclooctatriene, and a stirrer to produce agitation of the two phase system. The electrolysis was now carried out with a current of 6-8 amperes. After 8 hours the electrolysis was discontinued and the catholyte extracted repeatedly with petroleum ether, P. B. 35-60°. The ether extracts were dried over Na2SO4 and fractionally distilled. Cyclooctatriene, P. B. 46-47°/24 mm., was obtained in 88% yield.

It will be understood that the foregoing example is illustrative of the invention and that the process embodied in this invention is not limited thereto. As mentioned above, the catholyte media should be neutral to alkaline rather than acidic. It appears that there may be employed as the catholyte any conductive water-organic solvent solution in which cyclooctatetraene is at least partially soluble and which is inert to cyclooctatetraene and cyclooctatriene. Examples of suitable catholyte (mixtures) include low molecular weight organic quaternary compound (tetramethyl ammonium hydroxide, tetramethyl ammonium chloride, tetraethylammonium chloride, trimethylbenzyl chloride, or mixtures thereof) in the water-organic solvent mixtures. As examples of organic solvents, one may include ethanol, isopropanol, ethylene glycol, dioxane, tetrahydrofuran, ethylene glycol, monomethyl ether and the like. It will also be understood that while mercury was employed as a cathode in the above specific example, other metallic cathodes such as platinum, nickel, copper, iron, etc., may be used if desired.

In the above specific example the reduction was carried out at a temperature of about 25° C., and while definite temperature limitations have not been established, it appears that the temperature is not highly critical and temperatures within the range of 0 to 80° C. are operative. Current densities within the range of 10 to 20 amperes per dm.² have been found to be effective. The voltage of the cell is in the range of 10 to 20 volts, depending on the particular catholyte, anolyte and diaphragm.

1 claim:

1. The method of producing cyclooctatriene which comprises subjecting cyclooctatetraene to electrolytic reduction in a catholyte which consists of an aqueous lower alkanol containing a lower tetraalkyl ammonium halide at a temperature of 0–80° C., a current density within the range of 10–20 amperes per dm.² and a voltage of 10–20 volts.

2. The method of producing cyclooctatriene which comprises subjecting cyclooctatetraene to electrolytic reduction in a catholyte which consists of an aqueous lower alkanol containing a lower tetraalkyl ammonium halide.

References Cited in the file of this patent

UNITED STATES PATENTS
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OTHER REFERENCES