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3,677,916

**ELECTROLYTIC REDUCTION OF 1,2,3,4-TETRACHLOROBENZENE TO OBTAIN 1,2,4-TRICHLOROBENZENE**

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No Drawing. Filed Mar. 11, 1971, Ser. No. 123,464

Int. Cl. C07b 29/06; C07c 17/00, 25/10

U.S. Cl. 204—59 R **6 Claims**

**ABSTRACT OF THE DISCLOSURE**

1,2,3,4 - tetrachlorobenzene is electrolytically reduced to obtain 1,2,4-trichlorobenzene.

**BACKGROUND OF THE INVENTION**

It is known that halogens can be removed from aromatic compounds by electrolytic reduction, see for example, Allen et al. in J. Electrochem. Soc., 103, 682 (1956).

The removal of a specific halogen from an aromatic compound cannot be predicted. Moreover, the effect of substituents or the lack of substituents on the aromatic ring can cause alteration in the behavior of a compound during electrolytic reduction.

The specific electrolytic reduction of 1,2,3,4 - tetrachlorobenzene is important because the only reduction product of substantial utility is the 1,2,4 - trichlorobenzene. This isomer is rechlorinated to obtain a predominant yield of the desired 1,2,4,5-tetrachlorobenzene.

**SUMMARY OF THE INVENTION**

It has now been discovered according to the present invention that 1,2,3,4 - tetrachlorobenzene is selectively dehalogenated by electrolytic reduction to obtain 1,2,4-trichlorobenzene. The electrolysis is conducted by preparing a solution of 1,2,3,4-tetrachlorobenzene containing as an electrolyte a dissolved ammonium or substituted ammonium salt and electrolyzing the solution in a cell having a cathode of lead or mercury at a cathode potential of about -1.3 to about -3 volts while maintaining the pH at about 7 or greater. This selective reduction gives high yields of the desired trichlorobenzene without the formation of substantial quantities of deleterious by-products.

In the practice of the electrolytic reduction of the invention, it is important: (1) that the electrolytic cell have a cathode of lead or mercury; (2) that the cathode potential is maintained between about -1.3 and about -3 volts; (3) that the pH of the cell fluid be maintained at about 7 or greater; and (4) that an electrolyte be a dissociable ammonium or substituted ammonium salt. Aside from these conditions, the electrolytic reduction of the invention is carried out by techniques that are generally known. These techniques are described below and exemplified in the Specific Embodiments.

Electrolytic cells used in the invention have cathodes of mercury or lead, and anodes of essentially any inert, electrically conductive material, with graphite and platinum being especially preferred. The design of the electrolysis cell used in the present invention is generally not critical. Numerous batch and continuous electrolytic cells known in the art may be readily employed in the present invention.

In the operation of the electrolysis cell, the cathode potential is maintained between about -1.3 and about -3 volts versus the standard calomel electrode, with cathode potentials of -1.5 to -2.5 volts being especially preferred. The applied voltage provided by the power

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source may vary widely depending upon the IR drop of the reaction mixture. The IR drop is preferably minimized to prevent overheating of the reaction cell.

The pH of the electrolysis cell fluid in the invention is about 7 or greater but not so high that the components of the cell are attacked. Preferably the pH is maintained between 9 and 10. Control of the pH is most conveniently maintained with ammonia gas or use of a buffer solution, e.g., ammonium acetate, with the use of ammonia gas being preferred.

The electrolyte used in the present invention may vary as different solvent systems and cathode materials are employed. The electrolyte must, however, be a dissociable ammonium or substituted ammonium salt, the anion of which is not oxidized under the electrolysis conditions. Suitable substituted ammonium cations include alkyl, aryl, alkaryl or aralkyl ammonium, whereas suitable anions include halide, acetate and phosphate. Specific examples of preferred electrolytes include ammonium chloride, ammonium fluoride, tetramethylammonium chloride, ammonium phosphate, ammonium acetate, tetraethylammonium chloride, phenylammonium chloride and tolylammonium fluoride. Especially preferred is the use of ammonium chloride, ammonium acetate, tetraalkylammonium chlorides or trialkyl benzylammonium chloride as the electrolyte. The concentration of the electrolyte may vary widely as different reactant concentrations, electrolytes, solvent systems, current densities and cathode potentials are employed.

The solvent employed in the electrolysis solution may vary widely. The solvent system should dissolve all or most of the 1,2,3,4-tetrachlorobenzene, it should be an ionizing solvent for the electrolyte and it should be essentially inert under the electrolysis conditions. Solvents preferred in the present invention include the lower alcohols, alkylene ethers, lower alkylene glycol mono- or dialkyl ethers and lower amides. Representative examples of these preferred solvents include: alcohols such as methanol, ethanol, isopropanol and isobutyl alcohol; alkylene ethers such as dioxane and tetrahydrofuran; lower alkylene glycol monoalkyl ethers and dialkyl ethers such as 2-methoxypropanol, ethoxyethanol, dimethoxyethane and 1,2-dimethoxypropane; and lower amides such as dimethylformamide and acetamide. These solvents of the present invention may be used either alone or preferably with up to about 30% by weight of water to assure proper solubility of the electrolyte.

The current density may preferably range from about 0.01-8 amp./in.<sup>2</sup> of electrode with 0.1 to 1.0 amp./in.<sup>2</sup> being especially preferred. At higher current densities, the selectivity of the reaction decreases; therefore, the current density should be adjusted to give the desired minimization of by-products.

The temperature of the electrolysis reaction may vary widely. The temperatures may be varied to maintain the reaction mixture in the liquid phase with temperatures from about 20° to about 100° C. or more being preferred.

The cell is usually and most conveniently operated at less than 100% conversion to minimize the over-reduction of the product under the reaction conditions. As a general rule, 70 to 95% of the reduction theoretically required gives the most favorable yields of the desired product with minimum by-product. After the electrolysis, the product may be isolated by any conventional method.

**SPECIFIC EMBODIMENT**

An electrolysis cell was constructed from a 600 ml. beaker having an anode of graphite, a cathode consisting of a stirred pool of mercury in the bottom of the beaker and a constant voltage power source. The electrolysis cell was equipped with an ammonia sparger, and 12.9 g. of

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1,2,3,4-tetrachlorobenzene was electrolyzed in a fluid of 150 cc. of ethanol-2B, 2.0 g.  $\text{NH}_4\text{Cl}$  and 15 g. tetramethylammonium chloride. The fluid was heated to 75° C. to dissolve the tetrachlorobenzene and saturated with ammonia gas. The electrolysis was begun at an applied voltage of 9.0 volts, a cathode potential of -1.7 volts and a current density of 0.90 amp./in.<sup>2</sup>. The cell was operated under these conditions at 63° to 53° C. with continuous ammonia sparging to maintain saturation. The analysis of samples of the chlorobenzene product taken at various times is given in Table I. The overall current efficiency was 71%.

TABLE I

Reduction of 1,2,3,4-tetrachlorobenzene in the presence of ammonia

| Sample time, minutes: | Chlorobenzene, VPC percent |           | Di    |
|-----------------------|----------------------------|-----------|-------|
|                       | 1,2,3,4-tetra              | 1,2,4-tri |       |
| 30                    | 85.8                       | 14.2      |       |
| 90                    | 61.9                       | 38.1      | Trace |
| 160                   | 43.8                       | 55.3      | 0.9   |
| 210                   | 24.1                       | 73.5      | 2.5   |

In the same manner as described above, an electrolysis cell is constructed having a cathode of lead and an anode of graphite. A fluid is prepared containing 1,2,3,4-tetrachlorobenzene and an electrolyte/buffer of ammonium acetate dissolved in methanol, 1,2-dimethoxyethane and water. The electrolysis cell is run to selectively reduce 1,2,3,4-tetrachlorobenzene to 1,2,4-trichlorobenzene.

We claim:

1. A process for electrolytically reducing 1,2,3,4-tetrachlorobenzene to obtain 1,2,4-trichlorobenzene comprising preparing a solution of 1,2,3,4-tetrachlorobenzene containing as an electrolyte a dissolved nonoxidizing ammonium or substituted ammonium salt, the solvent being an organic compound which is essentially inert under the

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electrolysis conditions and is an ionizing solvent for the electrolyte and containing up to 30% by weight of water, and electrolyzing the solution of tetrachlorobenzene in an electrolysis cell having an inert anode and a lead or mercury cathode at a cathode potential of about -1.3 to about -3.0 volts while maintaining the pH of the solution at at least about 7 but below the point the components of the cell are attacked at a current density of about 0.01 to 8 amp./in.<sup>2</sup>.

2. The process of claim 1 wherein the electrolyte is ammonium chloride, ammonium acetate, tetraalkylammonium chloride, trialkylbenzylammonium chloride or mixtures thereof.

3. The process of claim 1 wherein the cathode is mercury.

4. The process of claim 1 wherein the cathode potential is about -1.5 to about -2.5 volts.

5. The process of claim 1 wherein the pH is maintained between about 9 and about 10.

6. The process of claim 1 wherein the pH is maintained with ammonia gas.

## References Cited

## UNITED STATES PATENTS

|           |         |            |              |
|-----------|---------|------------|--------------|
| 1,627,881 | 5/1927  | Bellone    | 204-73 R XV  |
| 3,064,059 | 11/1962 | Lervisi    | 260-650 R    |
| 3,595,931 | 7/1971  | Hay et al. | 160-650 R XV |

## FOREIGN PATENTS

|         |        |         |          |
|---------|--------|---------|----------|
| 848,807 | 9/1952 | Germany | 204-73 R |
| 805,142 | 1/1969 | Canada  | 204-73 R |

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U.S. Cl. X.R.

204-73; 260-650 R