United States Patent Office

3,032,489

Patented May 1, 1962

3,032,489

ELECTROLYTIC PRODUCTION OF ACYCLIC CARBOXYLIC ACIDS FROM HYDROCARBONS

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No Drawing. Filed June 15, 1959, Ser. No. 820,113
7 Claims. (Cl. 204—73)

This invention provides a manner of obtaining carboxylic acids from acyclic hydrocarbons having conjugated unsaturation. Dicarboxylic acids having carboxyl groups attached to the outer carbon atoms of the four-carbon-atom conjugated system are obtained in one embodiment. The process of the invention involves cathodic reduction of the conjugated hydrocarbon to produce a free radical which subsequently reacts with carbon dioxide to produce a carboxyl anion. The latter subsequently reacts with hydrogen ion to produce carboxylic acid. The process provides a novel and economical manner of producing carboxylic acids, such as hexenedioic acids, from hydrocarbons, such as butadiene.

The cathodic reduction is carried out in the presence of an electrolyte having half-wave potential which is more negative than the half-wave potential of the hydrocarbon which is reduced. The half-wave potential is a property which is determinable polarographically according to the procedure described for example in Kirk and Othmer, Encyclopedia of Chemical Technology, volume 10, pages 886 to 890. It is the potential of the inflection point of a current-potential diagram obtained under the described conditions. It is a measure of the potential at which electrolytic reaction, usually reduction, takes place in the material in question. The potentials referred to herein are all expressed as voltages relative to an auxiliary calomel reference electrode.

Acyclic conjugated hydrocarbons have relatively rather high reduction potentials, i.e. the half-wave potential is a rather large negative voltage. The electrolyte should have a higher reduction potential: its half-wave potential should be a larger negative voltage, i.e. more negative, than that of the hydrocarbon. For example, a satisfactory electrolyte for use with butadiene, which has half-wave potential of —2.63 volts, is tetraethyl ammonium bromide, which has half-wave potential of —2.7 volts.

The half-wave potentials of hydrocarbons and electrolytes are properties readily determinable by known procedures, and considerable information concerning half-wave potentials of various hydrocarbons and electrolytes is contained in K. Schwabe, "Polarographie and Chemische Konstitution Organischer Verbindungen" (1957). Electrolytes having the indicated half-wave potential relationship are generally suitable for use according to the invention, and the criteria for selection are available to a person skilled in the art.

The cathodic reduction according to the invention is carried out in the presence of a solvent in which the hydrocarbon and the electrolyte are both soluble. The decomposition potential of the solvent is more negative than the half-wave potential of the electrolyte. Decomposition potential is defined in the Kirk and Othmer reference given previously, and constitutes the potential at which the current begins to turn sharply upward. This potential is more meaningful in the case of the solvent, than is the half-wave potential, since the solvent frequently does not exhibit the typical S-shaped curve that admits of the determination of a half-wave potential.

Similarly to half-wave potential, decomposition potential is a property which is readily determinable by known procedure, and the criteria for selection of solvent are therefore available to a person skilled in the art. Suitable solvents include dioxane, acrylonitrile, and dimethyl

formamide, but others having suitable decomposition potential relationship and solubility characteristics can be employed.

The products obtained according to the invention may be either monocarboxylic acids or dicarboxylic acids. Generally, higher voltages favor the formation of dicarboxylic acids. Typical reactions are the following, using butadiene as an example of charge stock:

(1) $CH_2=CHCH=CH_2+2e\rightarrow {}^-CH_2CH=CHCH_2{}^-$

(2) $-CH_2CH=CHCH_2{}^-+CO_2\rightarrow -CH_2CH=CHCH_2COO^-$

(3) $-CH_2CH=CHCH_2COO^-+CO_2\rightarrow -OOCCH_2CH=CHCH_2COO^-$

(4) $-CH_2CH=CHCH_2COO^-+2H^+\rightarrow CH_3CH=CHCH_2COOH$

(5) $-OOCCH_2CH=CHCH_2COO^-+2H^+\rightarrow HOOCCH_2CH=CHCH_2COOH$

Reactions 3 and 5, which produce a hexenedioic acid, can be made, by the use of relatively high potential, to prevail over Reaction 4, which produces a pentenoic acid.

The potential employed is greater than the half-wave potential of the hydrocarbon charge, and is preferably not greater than the half-wave potential of the electrolyte. Where dicarboxylic acid is desired, the potential is preferably about the same magnitude as the half-wave potential of the electrolyte. The current which flows in the cell is a function primarily of the concentration of the conjugated hydrocarbon, though also to some extent of the potential and the resistance of the electrolysis medium.

A diaphragm is preferably employed between the electrodes in order to minimize migration of reaction product to the anode and oxidation of the product at that electrode. Any suitable known type of diaphragm can be employed. Where elevated pressure is employed, a strong diaphragm such as porous Alundum diaphragm may be needed to withstand the pressure.

The electrolysis medium preferably contains a small amount of water, either as a source of hydrogen ions or as a solubilizing agent for the electrolyte, or both. In some instances, where hydrogen ion is available from other sources, e.g. the solvent, and where the electrolyte is sufficiently soluble in the anhydrous solvent, water is unnecessary. Preferably, however, the medium contains 0.5 to 25 weight percent of water based on solvent, the exact amount depending on the requirements for the functions desired in a given system.

The temperature of the electrolysis can be room temperature or elevated temperature. Elevated temperatures favor the reaction in that they decrease the resistance of the electrolysis system and therefore promote the flow of current. On the other hand, elevated temperatures decrease the amount of gaseous hydrocarbon and CO_2 which is dissolved in the solvent, and therefore tend to decrease the amount of reaction product that can be formed at a given reaction rate. It is therefore desirable to use moderately elevated temperatures to obtain the most favorable combinations of reaction rate and amount of reactants in solution. Preferred temperatures are those in the range from 150° F. to 250° F., though higher or lower temperatures can be employed.

Elevated pressure promotes the formation of reaction product in that it increases the amount of gaseous reactants in solution. The practical upper limit of pressure depends on economic considerations with respect to the strength of equipment required. Usually, it is desirable to employ a pressure in the range from 50 to 250 p.s.i.g., though higher or lower pressures can be employed.

The hexene carboxylic acids and substitution products thereof which are produced in the electrolytic process can be converted by known hydrogenation techniques to the corresponding hexane carboxylic acids. This may be

accomplished for example by the procedures disclosed in H. Gilman, "Organic Chemistry," volume 1, 2d ed., page 779, "Catalytic Hydrogenation and Hydrogenolysis." Other suitable procedures can be employed.

The carboxylic acid produced in the electrolysis can be separated from unreacted hydrocarbon, from electrolyte and from solvent by any suitable procedure. Frequently, the hydrocarbon can be stripped from the solution by moderate heating, and the carboxylic acid can subsequently be precipitated from the solution by cooling, salting out or other known procedure. Any other suitable know procedure can be employed for the separation, such as distillation of solvent, extraction with additional solvents, etc.

The following example illustrates the invention:

A 0.15 molar solution of tetraethyl ammonium bromide in dimethyl formamide, containing one percent of water based on the amide, is placed in an electrolytic cell having mercury cathode and carbon anode. The solution is saturated with butadiene at 200° F. and 150 p.s.i.g., and the resulting solution is electrolyzed at a voltage of 2.7 volts, as referred to an auxiliary calomel reference electrode, while bubbling carbon dioxide into the solution. Butadiene is introduced to replace that which is converted hexenedioic acid. The electrolysis is continued for 5 hours.

The product is a solution of hexenedioic acid,

$$HOOCCH_2CH{=}CHCH_2COOH$$

unreacted butadiene, and tetraethyl ammonium bromide in dimethyl formamide. The butadiene is stripped out by heating and recycled to the cell. The dibasic acid is separated from the quaternary salt and the amide by fractional precipitation. Ultimate yields in the neighborhood of 50% or higher are obtainable by recycling.

Generally similar results are obtained, with other hydrocarbons such as pentadiene-1,3, isoprene, 2,3-dimethyl butadiene-1,3, the products being the methyl hexenedioic acids, $HOOCCH(CH_3)CH{=}CHCH_2COOH$ and $HOOCCH_2C(CH_3){=}CHCH_2COOH$, and the dimethyl hexenedioic acid,

$$HOOCCH_2C(CH_3){=}C(CH_3)CH_2COOH$$

respectively. Monocarboxylic acids are produced when lower potentials, e.g. 2.65 volts in the case of butadiene, are employed. Mono and dicarboxylic acids are also obtainable in generally similar fashion, from conjugated hydrocarbons having triple bonds, e.g. vinyl acetylene and diacetylene.

Generally similar results are obtained with other electrolytes having suitable half-wave potential, e.g. tetramethyl ammonium hydroxide, etc.

Generally similar results are obtained with other solvents having suitable decomposition potential and solvent characteristics, e.g. acetonitrile, a solution of 20% water in dioxane, etc.

Suitable electrodes for use according to the invention include, as cathode, zinc, lead, tin, cadmium or other material having comparably high hydrogen overvoltage, and as anode, platinum, iron, gold, nickel or other suitable material. The suitability of various other electrodes will be apparent to a person skilled in the art.

The invention claimed is:

1. Process for preparing carboxylic acids which comprises cathodically reducing an acyclic hydrocarbon containing conjugated unsaturation in the presence of an electrolyte having half-wave potential more negative than that of the hydrocarbon and a mutual solvent for the hydrocarbon and the electrolyte, the solvent having decomposition potential more negative than the half-wave potential of the electrolyte, thereby to produce a hydrocarbon free radical, and reacting the latter in situ with carbon dioxide and hydrogen ion to form a carboxylic acid said carbon dioxide being introduced into said hydrocarbon during said reducing.

2. Process according to claim 1 wherein the hydrocarbon is butadiene.

3. Process according to claim 1 wherein the electrolyte is a tetra-alkyl ammonium halide.

4. Process according to claim 1 wherein the solvent is dimethyl formamide.

5. Process according to claim 1 wherein the solvent is acetonitrile.

6. Process according to claim 1 wherein the solvent is dioxane.

7. Process according to claim 1 wherein water is present.

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