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As described, the electrolytic reaction which occurs in the method of the invention is reduction, i.e., the addition of electrons to the hydrocarbon starting material. More specifically, it is the addition of two electrons. With some hydrocarbon starting materials such as butadiene and styrene the addition of two electrons there-to occurs at a single potential. In such a case the current-

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potential diagram referred to above has only a single inflection point and would be referred to by those skilled in the art as having a single wave. Other hydrocarbons such as naphthalene add two electrons in two steps. The first electron adds at a certain potential and the second electron adds at a different and larger potential. For example, the first electron might add at -1.2 volts and the second electron might add at -2.0 volts. In this case the current-potential diagram has two inflection points and would be referred to by those skilled in the art as having two waves. Although it would be technically correct to refer to such a hydrocarbon as having two half-wave potentials, since reduction occurs at each of two different potentials, for the present purpose the term half-wave potential as applied to such a compound means the second or larger half-wave potential, i.e., it means the potential of the second wave or the half-wave potential representing the addition of the second electron. In the above example the half-wave potential for the present purpose is -2.0 volts and not -1.2 volts.

The hydrocarbons which can be converted to carboxylic acids according to the invention are of three general types. One type is non-aromatic hydrocarbons containing conjugated unsaturation. Non-aromatic means that the hydrocarbon does not contain an aryl ring. The hydrocarbon can be cyclic or acyclic, examples of the former being 1,3-cyclohexadiene, 1-vinyl-1-cyclohexene, 5-methyl-1,3-cyclohexadiene, and 1-cyclohexyl-1,3-butadiene and examples of the latter being 1,3-butadiene, vinylacetylene, 1,3-hexadiene, 3-methyl-1,3-hexadiene, 1,3,5-octatriene, 4,5-dimethyl-1,3-octadiene, and the like. Preferably the hydrocarbon contains not more than 12, more preferably 4-8, carbon atoms. Also the hydrocarbon is preferably an acyclic hydrocarbon with 1,3-butadiene being preferred.

The second type of hydrocarbons suitable for the present purpose is substituted aromatics wherein the substituent contains conjugated unsaturation. A substituent means a non-aromatic hydrocarbon group attached to a nuclear carbon atom of an aryl nucleus. The unsaturation in the substituent can be conjugated with unsaturation in the aryl nucleus as in styrene, α -methylstyrene, vinylnaphthalene, and vinylbiphenyl or can be conjugated with other unsaturation in the substituent as in 1-phenyl-1,3-butadiene and 1-naphthyl-1,3-hexadiene. The aryl ring to which the substituent containing conjugated unsaturation is attached can if desired contain other hydrocarbon substituents as in 1-methyl-3-vinylbenzene, 1,3-diethyl-6-vinyl-naphthalene, 1,3-divinylbenzene, and the like. Preferably the substituent containing conjugated unsaturation contains 2-5 carbon atoms and is attached to a benzene or naphthalene nucleus. Preferably there is only one double bond in the substituent which therefore means that the double bond will be conjugated with unsaturation in an aryl nucleus. The aryl nucleus is preferably the benzene or naphthalene nucleus. The nucleus preferably contains no substituents other than the characteristic substituent containing conjugated unsaturation but if any other substituents are present they preferably contain not more than 2 carbon atoms and are preferably alkyl groups rather than alkylene groups, although the latter can be present if desired. Styrene is the preferred hydrocarbon of this second type.

The third type of hydrocarbons suitable for the present purpose is polycyclic hydrocarbons having certain characteristics. One characteristic is that the hydrocarbon contains an aryl ring. Another characteristic is that this aryl ring is condensed with another ring. The other ring can be saturated as in tetralin or can be another aryl ring as in naphthalene or can be a condensed aryl nucleus as in anthracene. Any of the rings in the polycyclic hydrocarbon can contain substituents, either saturated or unsaturated, but any such substituents are preferably alkyl groups containing 1-2 carbon atoms. The preferred hydrocarbons of this third type are naphthalene and anthracene.

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The cathodic reduction of the invention is carried out in the presence of an electrolyte, this being necessary since the hydrocarbon starting materials are not themselves conductive. In addition, it is desirable, but not essential that the electrolyte have a higher half-wave potential than the potential employed in the electrolysis, which in turn will be higher than the half-wave potential of the hydrocarbon starting material, in order to avoid reduction of the electrolyte simultaneously with the desired reduction of the hydrocarbon. This is not essential since reduction of the electrolyte does not prevent reduction of the hydrocarbon also but reduction of the electrolyte represents needless power consumption and often results in the formation of undesirable by-products. The hydrocarbon starting materials of the invention have rather high reduction potentials, i.e., the half-wave potential is a rather large negative voltage. The electrolyte preferably has 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 preferred electrolyte for use when anthracene or butadiene, which have half-wave potentials of -2 and -2.6 volts respectively, are being electrolyzed at a potential of -2.65 volts would be tetraethylammonium bromide which has a half-wave potential of greater than -2.7 volts. Triethanolethylammonium bromide has a half-wave potential of -2.4 volts (see the Schwabe reference mentioned *infra*) and could therefore be used as electrolyte in the reduction of anthracene without reduction of the electrolyte but could not be so used in the reduction of butadiene.

Selection of the electrolyte so as to avoid reduction of same in practicing the invention requires knowledge of the half-wave potential of various electrolytes. Similarly selection of the potential employed requires, as more fully discussed hereinafter, knowledge of the half-wave potential of the hydrocarbon starting material. The half-wave potential is a property readily determinable by known procedures. In addition, considerable information concerning half-wave potentials of various hydrocarbons and electrolytes is contained in K. Schwabe, *Polarographie und Chemische Konstitution Organischer Verbindungen* (1947). Since the tetraalkylammonium halides have half-wave potentials generally higher than the hydrocarbon starting materials of the invention they are the preferred electrolytes.

The cathodic reduction according to the invention is also carried out in the presence of a mutual solvent for both the hydrocarbon and the electrolyte, the use of the solvent being necessary since the electrolyte used is generally insoluble in the hydrocarbon starting material used. As in the case of the electrolyte it is desirable, but not essential, that the solvent have a decomposition potential more negative than the potential employed in the electrolysis in order to avoid reduction of the solvent simultaneously with reduction of the hydrocarbon. Decomposition potential is defined in the aforesaid Kirk and Othmer reference and constitutes the potential at which the current begins to turn sharply upward. In the case of a solvent, the decomposition potential is more meaningful 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. As with half-wave potential, the decomposition potential is negative for cathodic decomposition and positive for anodic decomposition. All decomposition potentials referred to herein are for cathodic decomposition.

Similarly to half-wave potential, decomposition potential is a property which is readily determinable by known procedure, and the criteria for selection of a preferred solvent are therefore available to a person skilled in the art. The preferred solvents for the present purpose are dioxane, aqueous dioxane, dimethylacetamide, acetonitrile, and dimethylformamide since these solvents have decomposition potentials higher, i.e., more negative, than -3

volts which is substantially higher than the potentials which will be employed in most cases. More preferably the solvent is dimethylformamide.

The electrolysis is also carried out in the presence of an alkali metal bicarbonate. As used herein an alkali metal is sodium, potassium, lithium, or cesium. For economic reasons sodium bicarbonate is preferred. The alkali metal bicarbonate is added to and, preferably, intimately mixed with the solution of hydrocarbon starting material and electrolyte in the solvent. The amount of alkali metal bicarbonate added can vary considerably but is preferably at least 1 mole per mole of hydrocarbon starting material. However, even if substantially more than 1 mole of bicarbonate per mole of hydrocarbon is added the product is still mainly monocarboxylic acid.

The electrolysis as described above produces a carboxylic acid anion which is then converted to carboxylic acid by reaction *in situ* with hydrogen ion. See, for example, Equations 3(a) and 3(b) *supra*. One suitable means of supplying this hydrogen ion is to add water or other hydrogen ion producing compound to the electrolyzed solution after completion of the electrolysis. In other words, after the solution has been electrolyzed, the potential can be shut off and the carboxylic acid anion can then be reacted with water to produce carboxylic acid. This use of water to supply the hydrogen ion for converting the carboxylic acid anion to carboxylic acid is not essential because the required hydrogen ion will almost invariably be abstracted from the solvent and/or electrolyte simultaneously with the formation of the carboxylic acid anion. In other words the solvent, e.g., dimethylformamide, acetonitrile, dimethylacetamide, etc. and/or electrolyte will liberate hydrogen ion under the conditions of electrolysis. So also will compounds such as methanol or ethanol and even though these latter materials are generally not suitable as solvents they can be added to the electrolysis medium in order to supply hydrogen ion.

The potential employed should be greater than the half-wave potential of the hydrocarbon. This requirement is, of course, inherent in the term cathodic reduction. Also as described hereinbefore, the potential employed is preferably less negative than both the decomposition potential of the solvent and the half-wave potential of the electrolyte. All other conditions being constant, higher potentials tend to favor the formation of dicarboxylic acid. Consequently, the potential employed is preferably only about 0.1 volt higher than the half-wave potential of the hydrocarbon although higher potentials can, if desired, be employed because regardless of the potential used the use of alkali metal bicarbonate as the source of



radicals results in a higher monocarboxylic acid:dicarboxylic acid ratio than when CO₂ is used.

During the electrolysis the hydrocarbon must be present at the surface of the cathode. This requirement is, of course, inherent in the term cathodic reduction. Preferably the electrodes are separated by a diaphragm which is permeable to the solvent and electrolyte but impermeable to the hydrocarbon starting material in order to prevent migration of the starting material to the anode and oxidation at that electrode. Conventional diaphragm materials such as porous Alundum can be used for this purpose.

The temperature at which the electrolysis is conducted is not critical but is preferably -30° to 40° C., more preferably about room temperature (25° C.), although higher temperatures of, say, 125° C. or somewhat lower temperatures of, say, -50° C. can be used if desired. If the starting material is a normally gaseous material such as butadiene the temperature should be such that in combination with the pressure employed the hydrocarbon is maintained in liquid phase.

The pressure at which the electrolysis is conducted is not critical and will normally be atmospheric. As mentioned above, when the starting material is normally gaseous the pressure should be such that in combination with the electrolysis temperature the hydrocarbon is maintained in liquid phase.

A variety of materials can be used as the electrodes. Examples of suitable materials are zinc, lead, tin, mercury, cadmium, etc. as the cathode and platinum, palladium, gold, etc. as the anode. The preferred cathode is mercury.

The carboxylic acid produced in the electrolysis can be separated from unreacted hydrocarbon, from electrolyte, and from solvent by any suitable procedure. Frequently a mixture of unreacted hydrocarbon, carboxylic acid, and a small amount of electrolyte can be separated from the solvent by fractional crystallization, from which mixture the electrolyte can be separated from unreacted hydrocarbon and carboxylic acid by washing with water. The carboxylic acid can then be separated from unreacted hydrocarbon by a subsequent fractional crystallization or by extraction with aqueous NaOH. Any other suitable procedure can also be employed, thus where the electrolyte is a tetrabutyl ammonium fluoride it can usually be separated by extraction with water after which carboxylic acid and unreacted hydrocarbon are separated from the solvent by fractional crystallization, vacuum distillation of the solvent, extraction, etc. Another suitable procedure for separating the carboxylic acid product is elution chromatography.

The following examples illustrate the invention more specifically.

Example 1

The electrolytic cell contains a pool of mercury on the bottom as the cathode and a platinum anode. A porous Alundum diaphragm separates the cell into an anode chamber and a cathode chamber. The anolyte is a 0.15 molar solution of tetrabutylammonium bromide in dimethylformamide, the halfwave potential of tetrabutylammonium bromide being greater than -3 volts. The catholyte is a similar solution saturated at 25° C. with naphthalene. The cell contains means for bubbling CO₂ into the catholyte as well as means for controlling the temperature of both the anolyte and catholyte. The surface of the catholyte (and the anolyte) is exposed to the atmosphere and when CO₂ is bubbled into the catholyte any CO₂ which does not dissolve therein escapes from the surface of the catholyte to the atmosphere.

The above described naphthalene solution is maintained at 25° C. while being electrolyzed at a potential of -2.7 volts for a period of 8 hours. Naphthalene has a half-wave potential of -2.5 volts. CO₂ is bubbled into the catholyte during the entire electrolysis, the total amount of CO₂ being 2 moles per mole of hydrocarbon starting material.

At the end of the electrolysis a small portion of the catholyte is analyzed by elution chromatography and is found to contain 1,4-dihydronaphthalene-1,4-dicarboxylic acid and 1,4-dihydro-1-naphthalene monocarboxylic acid as the sole carboxylic acid products. The total yield of carboxylic acids is 14% based on naphthalene and the carboxylic acid product contains about 50% dicarboxylic acid and about 50% monocarboxylic acid. All percentages herein are by weight. Thus the ratio of monocarboxylic acid to dicarboxylic acid is about 1:1.

The remainder of the catholyte is treated as follows to recover the carboxylic acids therefrom. A mixture of unreacted naphthalene, carboxylic acids, and a very small amount of electrolyte are separated from the catholyte by fractional crystallization. From this mixture the carboxylic acids are separated as their sodium salts by extraction with NaOH. The extract is then acidified with HCl and the resulting precipitate, which is a mixture of the monocarboxylic and dicarboxylic acids is separated by filtration. The dicarboxylic acid, i.e., the 1,4-dihydronaph-

thalene-1,4-dicarboxylic acid is separated from the precipitate by fractional crystallization from alcohol.

Example 2

The procedure is the same as in Example 1 except that 2 moles of powdered NaHCO_3 per mole of hydrocarbon starting material are added to and intimately mixed with the solution of naphthalene and electrolyte in the solvent prior to charging the solution to the cell, and no CO_2 is bubbled into the catholyte during the electrolysis. Chromatographic analysis of the catholyte shows that it contains 1,4-dihydronaphthalene-1,4-dicarboxylic acid and 1,4-dihydronaphthalene-1-monocarboxylic acid in a total yield of 15% based on the naphthalene starting material. The ratio of the monocarboxylic acid to the dicarboxylic acid is 9:1.

Example 3

The procedure is the same as in Example 1 except that (1) the catholyte contains styrene instead of naphthalene, the amount of styrene being 5% by weight of the electrolyte-solvent mixture in the catholyte, (2) the electrolysis is at 0°C . instead of 25°C ., and (3) the potential is -2.6 volts instead of -2.7 volts. The half-wave potential of styrene is -2.5 volts. Chromatographic analysis of the catholyte isolates 3-phenylpropionic acid and 1-phenyl-ethane-1,2-dicarboxylic acid as the only carboxylic acid products. The ratio of the monocarboxylic acid to the dicarboxylic acid is 0.75:1. The total yield of carboxylic acid is 21.7%.

Example 4

The procedure is the same as in Example 3 except that 2 moles of powdered NaHCO_3 per mole of hydrocarbon starting material are added to and intimately mixed with the solution of hydrocarbon and electrolyte in the solvent prior to charging the solution to the cell and no CO_2 is bubbled into the catholyte during the electrolysis. Chromatographic analysis of the catholyte isolates 3-phenylpropionic acid as the sole carboxylic acid product in a yield of 25.6%.

Example 5

The procedure is the same as in Example 1 except that the catholyte contains 1,3-butadiene instead of naphthalene, the amount of 1,3-butadiene being 5% by weight of the electrolyte-solvent mixture in the catholyte, the temperature of the electrolysis is -20°C ., and the potential is -3.0 volts instead of -2.7 volts. Chromatographic analysis of the catholyte at the end of the electrolysis isolates hexenedioic acid and pentenoic acid as the sole carboxylic acid products in a total yield of

16% based on butadiene. The ratio of hexenedioic acid to pentenoic acid is 1.6:1.

Example 6

The procedure is the same as in Example 5 except that 2 moles of powdered NaHCO_3 per mole of hydrocarbon starting material are added to and intimately mixed with the solution of hydrocarbon and electrolyte in the solvent prior to charging the solution to the cell and no CO_2 is bubbled into the catholyte during the electrolysis. Chromatographic analysis of the catholyte isolates the same carboxylic acid products as in Example 5 in a total yield of 18% with a hexenedioic acid: pentenoic acid ratio of 0.5:1.

The invention claimed is:

1. In a process in which a hydrocarbon selected from the group consisting of hydrocarbons containing conjugated unsaturation and polycyclic hydrocarbons containing an aryl ring condensed with another ring is cathodically reduced in the presence of an electrolyte, a mutual solvent for said hydrocarbon and said electrolyte, and in the presence of a source of



radicals to form a dicarboxylic acid anion which is subsequently reacted in situ with hydrogen ion to form a dicarboxylic acid, the improvement which comprises carrying out said cathodic reduction in the presence of an alkali metal bicarbonate as said source, whereby monocarboxylic acid is formed.

2. Process according to claim 1 wherein said hydrocarbon is styrene.

3. Process according to claim 1 wherein said hydrocarbon is 1,3-butadiene.

4. Process according to claim 1 wherein said hydrocarbon is naphthalene.

5. Process according to claim 1 wherein said solvent is dimethylformamide.

6. Process according to claim 5 wherein said alkali metal bicarbonate is NaHCO_3 .

7. Process according to claim 1 wherein said alkali metal bicarbonate is NaHCO_3 .

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