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CATALYTIC PURIFICATION OF UNSATURATED HYDROCARBONS

Harry A. Cheney, Berkeley, Calif., assignor to
Shell Development Company, San Francisco,
Calif., a corporation of Delaware

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The present invention relates to an improved process for producing acetylenic hydrocarbons free from any substantial amounts of other unsaturated hydrocarbons. The invention relates more particularly to the vapor phase selective halogenation of normally gaseous olefinic hydrocarbons in admixture with normally gaseous acetylenic hydrocarbons. A particular aspect of the invention relates to the vapor phase catalytic selective chlorination of ethylene in admixture with acetylene.

Suitability of acetylenic hydrocarbons, such as, for example, acetylene, methyl acetylene, etc., as starting or intermediate material in many processes for the production of chemical derivatives therefrom is often dependent upon their state of purity. Processes enabling the large scale production of the acetylenic hydrocarbons, such as those comprising the pyrogenic treatment of normally gaseous or normally liquid petroleum hydrocarbons, generally yield products containing the desired acetylenic hydrocarbons in admixture with other unsaturated hydrocarbons not readily separable therefrom by practical scale separating means available heretofore. In the production of acetylene by the thermal treatment of petroleum hydrocarbons complex mixtures are obtained containing acetylene in admixture with substantial amounts of other normally gaseous hydrocarbons such as, for example, methane, ethylene, ethane, propylene, propane, butylenes, butanes, etc. Removal of higher boiling hydrocarbons, such as propane, propylene and still higher boiling materials, is relatively simple. However, for many uses the residual acetylene-containing gas is unsuitable because the ethylene which it still contains interferes with the subsequent processes. Heretofore such mixtures could only be utilized in relatively uneconomical ways. Processes have been disclosed heretofore enabling the separation, with relatively high efficiency, of an acetylene-containing fraction from such complex mixtures which is relatively free of any substantial amounts of saturated hydrocarbons and of unsaturated hydrocarbons having more than two carbon atoms to the molecule such as propylene and higher boiling olefins and the diolefins. Such crude acetylene is, however, often contaminated with substantial amounts of ethylene rendering the material unsuitable where starting or intermediate material of high purity is required. Heretofore, the production of commercially pure acetylene from such complex mixtures was gen-

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erally obtainable only by relatively uneconomical methods.

It is an object of the present invention to provide an improved process for the more efficient production of acetylenic hydrocarbons free of any substantial amounts of olefinic hydrocarbons having the same number of carbon atoms to the molecule as the acetylenic hydrocarbons.

Another object of the invention is the provision of an improved process for the more efficient production of acetylene free of any substantial amounts of ethylene from crude acetylene-containing gaseous mixtures comprising the acetylene in admixture with ethylene.

A more particular object of the invention is the provision of an improved process for the more efficient production of acetylene of high purity from hydrocarbon mixtures obtained by the pyrogenic treatment of petroleum hydrocarbons and containing the acetylene in admixture with substantial amounts of ethylene.

Still another object of the invention is the provision of an improved process for the efficient vapor phase selective halogenation of ethylene in the presence of substantial amounts of acetylene. Other objects and advantages of the invention will become apparent from the following detailed description thereof.

In accordance with the invention acetylenic hydrocarbons which are free from any substantial amounts of other unsaturated hydrocarbons are obtained from mixtures comprising the acetylenic hydrocarbons in admixture with other unsaturated hydrocarbons having the same number of carbon atoms to the molecule as said acetylenic hydrocarbons by contacting the acetylenic hydrocarbon-containing mixture in the vapor phase, in the presence of a halogen, with an alkali metal halide and/or an alkaline earth metal halide, thereby selectively halogenating substantially all of the olefins in the mixture in the absence of any substantial reaction of the acetylenic hydrocarbons.

The process of the invention is broadly applicable to the selective halogenation of olefins in the presence of acetylenic hydrocarbons which are not readily separable therefrom by practical scale separating means available heretofore. It is, however, applied with particular advantage to the production of acetylenic hydrocarbons of high purity from mixtures consisting essentially of a lower acetylenic hydrocarbon, such as, for example, acetylene, methyl acetylene, ethyl acetylene, and the like, in admixture with an olefinic hydrocarbon having the same number of carbon

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atoms to the molecule as the acetylenic hydrocarbon. The process of the invention is of particular value because of its ability to produce acetylene which is substantially free of ethylene from gaseous mixtures containing unsaturated hydrocarbons consisting essentially of acetylene and ethylene with unusually high efficiency.

A particular advantage of the invention resides in its ability to effect the efficient selective halogenation of the olefinic content of acetylene-olefin mixtures consisting predominantly of acetylenic hydrocarbons. Thus acetylene having a purity of 99.5% is readily obtained from acetylene-ethylene mixtures the ethylene contents of which range from about 1.5 to about 11 mole per cent. The invention is, however, in no wise limited to the treatment of mixtures of acetylenic and olefinic hydrocarbons containing acetylene in any specific amount and the olefinic content of the hydrocarbon charge to the process may range from a fraction of a per cent to fifty mole per cent, and higher, of the mixture. Materials substantially inert under the conditions of execution of the process, such as, for example, normally gaseous paraffinic hydrocarbons, hydrogen, nitrogen and the like, may be comprised in the charge to the reaction zone.

The halogens employed in the selective halogenation of the process are the halogens whose atomic numbers lie in the range of from 17 to 33 inclusive, that is, chlorine and bromine. Of the suitable halogens, chlorine, because of its generally greater availability, is usually preferred. Halogen is introduced into the system at a rate which will assure its passage into the reaction zone in an amount substantially equal to the stoichiometrical amount required to effect the addition halogenation of the olefin-content of the hydrocarbon charge. Although the halogen may be introduced into the reaction zone in amounts exceeding such stoichiometrical amount, its introduction in substantial excess is preferably avoided. It is further to be understood that the amount of halogen added will be governed by the degree of purity of the acetylenic hydrocarbons desired. When it is not intended to effect the removal of substantially all of the olefins from the acetylenic hydrocarbons, the halogen is added in amounts below the stoichiometrical equivalent of the olefinic content of the charge.

The selective halogenation in accordance with the process of the invention is effected in the presence of a catalyst the effective component of which consists of one or more alkali and/or alkaline earth metal halides. The suitable halides employed are the halides of the members of the left-hand sub-group of groups I and II of the periodic table. Suitable halides of the alkali and/or alkaline metal halides which are employed, comprise the chlorides, bromides, fluorides, iodides and mixed halide salts. Examples of such suitable catalysts are: NaCl, KCl, LiCl, RbCl, CsCl, CaCl₂, BaCl₂, SrCl₂, NaBr, KBr, LiBr, CaBr₂, SrBr₂, BaBr₂, KI, NaI, NaF, BaF₂, CaI₂, CaF₂, CsI, CsBr, KF, etc. Of these salts the chlorides, bromides and fluorides are preferred. Of these materials those of granular form, as distinct from those of crystalline form, are generally preferred.

The salts may be employed as such by themselves, or may be used in admixture with or supported upon, suitable solid carriers which are not attacked by the halogen and which are substantially inert under the reaction conditions,

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Such solid support or diluent materials comprise, for example, silica, Celite, magnesia, carbon, Carborundum, silicon carbide, crushed brick, gravel, diatomaceous earths, asbestos, etc. Of these carrier and/or diluent materials those of porous structure are particularly preferred. The invention is in no wise limited to the utilization of catalysts and carriers comprised in the above-defined broad class obtained from any specific source or produced by any specific method of preparation. The halide salts are preferably employed in the anhydrous state.

In the process of the invention the hydrocarbon charge is contacted with the catalyst at a temperature in the range of from about -50 to about 300° C., and preferably from about 50 to 200° C. Pressures employed may vary widely within the scope of the invention. Subatmospheric, atmospheric and superatmospheric pressures enabling the maintenance of at least a substantial part of the hydrocarbon charge in vapor phase are employed. Pressures in the range of, for example, from about atmospheric to about 150 p. s. i. g. have been found satisfactory in the treatment of acetylene-ethylene containing mixtures. Time of contact will vary of course with variations in composition of the charge, the type of catalyst, operating conditions and degree of purity of the acetylenic hydrocarbons desired.

Under the above-defined conditions substantially all of the olefin content of the charge will be selectively halogenated and converted to organic reaction products consisting essentially of the halo-olefin addition product. Thus, in the treatment of a mixture consisting essentially of acetylene and ethylene with chlorine under the above-defined conditions, the ethylene in the charge is selectively converted to reaction products consisting essentially of ethylene dichloride in the absence of any substantial reaction of the acetylene. When bromine is employed as the halogen the ethylene is selectively halogenated to reaction products consisting essentially of ethylene dibromide.

The process of the invention is executed in any suitable type of conventional apparatus enabling the contact of the hydrocarbon and halogen charge with the catalyst in the vapor phase under the above-described operating conditions. The reactors employed may comprise one or more zones of enlarged cross-sectional area, such as a chamber, and/or of restricted cross-sectional area, such as an elongated coil. Suitable means are provided for introduction of reactants and catalysts and for the maintenance of the operating conditions of temperature and pressure therein. The hydrocarbon charge and the halogen may be mixed prior to introduction into the reaction zone at one or a plurality of points along the length thereof. A part of the hydrocarbon charge and/or the halogen may be introduced separately into the reaction zone.

Effluence from the reaction zone is passed to conventional product-separating means wherein the acetylenic hydrocarbon is separated from the organic reaction products comprising olefin halides and any remaining unconverted halogen. The separating means may comprise, for example, one or more such steps as adsorption, distillation, solvent extraction, scrubbing, and the like.

The following examples are illustrative of the production of an acetylenic hydrocarbon in a high state of purity from a mixture consisting essentially of an acetylenic hydrocarbon and an olefin:

Example I

A 10 ft. long tubular reactor having an inside diameter of one inch is packed with 4-6 mesh granular calcium chloride. A gaseous mixture consisting essentially of 89 mole per cent acetylene and 11 mole per cent ethylene is passed through the reactor at a rate of 10 gram-moles per hour. Chlorine is mixed with the hydrocarbon charge prior to its passage into the reactor at the rate of 1.16 gram moles per hour. The pressure in the reactor is maintained at 6.5 atm. and the temperature at 100° C. Suitable precautions are taken to prevent acetylene explosions. Reaction of the chlorine proceeds to substantial completion. Effluence from the reactor is passed through charcoal absorbers wherein chlorinated hydrocarbons are removed. The gas leaving the charcoal absorbers is analyzed and found to contain about 99.4 per cent acetylene and only about 0.6 per cent ethylene. About 99 mole per cent of the acetylene charged is recovered.

At intervals the charcoal absorbers are regenerated by passage of steam through them. The effluent steam is condensed and organic chlorides separated from the water by stratification. Analysis of the separated organic chlorides shows that they contain about 92 per cent ethylene dichloride, about 8 per cent trans-dichloroethylene with minor traces of cis-dichloroethylene and high boiling compounds.

Example II

A catalyst is prepared by soaking 0.5 inch pellets of diatomaceous earth in sodium chloride solution, draining excess liquid therefrom and drying the impregnated diatomaceous earth. The pellets are found to contain 5 per cent sodium chloride by weight. A 10 foot long reactor having an inside diameter of 12 inches is packed with the dried sodium chloride-impregnated pellets.

A gaseous mixture consisting essentially of 98.5 per cent acetylene and 1.5 per cent ethylene is fed to the reactor at a feed rate of 100 gram-moles per hour. Chlorine is mixed with the hydrocarbon stream at a rate of 3.3 gram-moles per hour. The pressure in the reactor is maintained at one atmosphere and the temperature at 150° C. Effluence from the reaction zone is scrubbed with kerosene to absorb chlorinated hydrocarbons. The scrubbed gas is analyzed and found to contain over 99.9 per cent acetylene and less than 0.1 per cent ethylene.

The claimed invention is:

1. The process for separating a normally gaseous acetylenic hydrocarbon in a high state of purity from a hydrocarbon mixture consisting essentially of a normally gaseous acetylenic hydrocarbon and an olefin having the same number of carbon atoms to the molecule as said acetylenic hydrocarbon, which comprises contacting said mixture in admixture with a halogen having an atomic number in the range of from 17 to 35 inclusive in the vapor phase with a solid halide of a member of the left-hand sub-group of groups I and II of the periodic table at a temperature of from about -50 to about 300° C., said halogen being present in an amount substantially equal to the stoichiometrical amount required to effect the addition halogenation of the olefin content of said mixture, thereby selectively halogenating said olefin leaving substantially all of said acetylenic hydrocarbon unchanged, and recovering the acetylenic hydrocarbon originally present in said mixture from the resulting halogenated olefin.

2. The process for removing olefins from a

gaseous mixture containing unsaturated hydrocarbons consisting essentially of a normally gaseous acetylenic hydrocarbon and an olefin having the same number of carbon atoms to the molecule as said acetylenic hydrocarbon, which comprises contacting said mixture in admixture with a halogen having an atomic number in the range of from 17 to 35 inclusive in the vapor phase with a solid halide of a member of the left-hand sub-group of groups I and II of the periodic table at a temperature of from about -50 to about 300° C., said halogen being present in an amount substantially equal to the stoichiometrical amount required to effect the addition halogenation of the olefin content of said mixture, thereby selectively halogenating said olefin leaving substantially all of said acetylenic hydrocarbon unchanged, and recovering the acetylenic hydrocarbon originally present in said mixture from the resulting halogenated olefin.

3. The process for separating a normally gaseous acetylenic hydrocarbon in a high state of purity from a hydrocarbon mixture consisting essentially of a normally gaseous acetylenic hydrocarbon and an olefin having the same number of carbon atoms to the molecule as said acetylenic hydrocarbon, which comprises contacting said mixture in admixture with chlorine in the vapor phase with solid calcium chloride at a temperature of from about 50 to 200° C., said chlorine being present in said admixture in an amount substantially equal to the stoichiometrical amount required to effect the addition chlorination of the olefin content of said mixture, thereby selectively chlorinating said olefin leaving substantially all of the acetylenic hydrocarbon unchanged, and recovering the acetylenic hydrocarbon originally present in said mixture from the resulting chlorinated olefin.

4. The process for separating normally gaseous acetylenic hydrocarbon in a high state of purity from a hydrocarbon mixture consisting essentially of a normally gaseous acetylenic hydrocarbon and an olefin having the same number of carbon atoms to the molecule as said acetylenic hydrocarbon, which comprises contacting said mixture in admixture with chlorine in the vapor phase with solid sodium chloride at a temperature of from about 50 to about 200° C., said chlorine being present in said admixture in an amount substantially equal to the stoichiometrical amount required to effect the addition chlorination of the olefin content of said mixture, thereby selectively chlorinating said olefin leaving substantially all of the acetylenic hydrocarbon unchanged, and recovering the acetylenic hydrocarbon originally present in said mixture from the resulting chlorinated olefin.

5. The process for separating acetylene in a high state of purity from a hydrocarbon mixture consisting essentially of acetylene and ethylene which comprises contacting said mixture in admixture with a halogen having an atomic number in the range of from 17 to 35 inclusive in the vapor phase with a solid halide of a member of the left-hand sub-group of groups I and II of the periodic table at a temperature of from about -50 to about 300° C., said halogen being present in said admixture in an amount substantially equal to the stoichiometrical amount required to effect the addition halogenation of the ethylene content of said mixture, thereby selectively halogenating said ethylene leaving substantially all of the acetylene unchanged, and recovering the

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acetylene originally present in said mixture from the resulting halogenated ethylene.

6. The process for removing ethylene from a gaseous mixture containing unsaturated hydrocarbons consisting essentially of acetylene and ethylene which comprises contacting said mixture in admixture with a halogen having an atomic number in the range of from 17 to 35 inclusive in the vapor phase with a solid halide of a member of the left-hand sub-group of groups I and II of the periodic table at a temperature of from about -50 to about $300^{\circ}\text{C}.$, said halogen being present in said admixture in an amount substantially equal to the stoichiometrical amount required to effect the addition halogenation of the ethylene content of said mixture, thereby selectively halogenating said ethylene leaving substantially all of the acetylene unchanged, and recovering the acetylene originally present in said mixture from the resulting halogenated ethylene.

7. The process for separating acetylene in a high state of purity from a hydrocarbon mixture consisting essentially of acetylene and ethylene which comprises contacting said mixture in admixture with chlorine in the vapor phase with a solid chloride of a member of the left-hand sub-group of groups I and II of the periodic table at a temperature of from about -50 to about $300^{\circ}\text{C}.$, said chlorine being present in said admixture in an amount substantially equal to the stoichiometrical amount required to effect the addition chlorination of the ethylene content of said mixture, thereby selectively chlorinating ethylene leaving substantially all of the acetylene unchanged, and recovering the acetylene originally present in said mixture from the resulting chlorinated ethylene.

8. The process for removing ethylene from a gaseous mixture containing unsaturated hydrocarbons consisting essentially of acetylene and ethylene which comprises contacting said mixture in admixture with chlorine in the vapor phase with a solid chloride of a member of the left-hand sub-group of groups I and II of the periodic table at a temperature of from about -50 to about $300^{\circ}\text{C}.$, said chlorine being present in said mixture in an amount substantially equal to the stoichiometrical amount required to effect the addition chlorination of the ethylene content of said mixture, thereby selectively chlorinating ethylene leaving substantially all of the acetylene unchanged, and recovering the acetylene originally present in said mixture from the resulting chlorinated ethylene.

9. The process for separating acetylene in a high state of purity from a hydrocarbon mixture consisting essentially of acetylene and ethylene which comprises contacting said mixture in admixture with chlorine in the vapor phase with solid sodium chloride at a temperature of from about 50 to about $200^{\circ}\text{C}.$, said chlorine being present in said admixture in an amount substantially equal to the stoichiometrical amount re-

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quired to effect the addition chlorination of the ethylene content of said mixture, thereby selectively chlorinating ethylene leaving substantially all of the acetylene unchanged, and recovering the acetylene originally present in said mixture from the resulting chlorinated ethylene.

10. The process for separating acetylene in a high state of purity from a hydrocarbon mixture consisting essentially of acetylene and ethylene which comprises contacting said mixture in admixture with chlorine in the vapor phase with solid calcium chloride at a temperature of from about 50 to about $200^{\circ}\text{C}.$, said chlorine being present in said admixture in an amount substantially equal to the stoichiometrical amount required to effect the addition chlorination of the ethylene content of said mixture, thereby selectively chlorinating ethylene leaving substantially all of the acetylene unchanged, and recovering the acetylene originally present in said mixture from the resulting chlorinated ethylene.

11. The process for treating a normally gaseous acetylenic hydrocarbon containing an olefinic hydrocarbon having the same number of carbon atoms to the molecule as said acetylenic hydrocarbon, which comprises contacting said mixture in admixture with a halogen having an atomic number in the range of from 17 to 35 inclusive in the vapor phase with a solid halide of a member of the left-hand sub-group of groups I and II of the periodic table at a temperature of from about $-50^{\circ}\text{C}.$ to about $300^{\circ}\text{C}.$, said halogen being present in said admixture in an amount substantially equal to the stoichiometrical amount required to effect the addition halogenation of the olefin content of said mixture, thereby selectively halogenating said olefin leaving substantially all of the acetylenic hydrocarbon unchanged.

12. The process for treating a normally gaseous acetylenic hydrocarbon containing an olefinic hydrocarbon having the same number of carbon atoms to the molecule as said acetylenic hydrocarbon, which comprises contacting said mixture in admixture with chlorine in the vapor phase with solid sodium chloride at a temperature of from about $-50^{\circ}\text{C}.$ to about $300^{\circ}\text{C}.$, said chlorine being present in said admixture in an amount substantially equal to the stoichiometrical amount required to effect the addition chlorination of said olefinic hydrocarbon, thereby selectively chlorinating said olefinic hydrocarbon leaving substantially all of said acetylenic hydrocarbon unchanged.

HARRY A. CHENEY.

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