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OXIDATIVE DEHYDROGENATION PROCESS

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This application is a continuation-in-part of my earlier filed pending application Serial Number 250,020 filed January 8, 1963, entitled, "Dehydrogenation Process," now abandoned, which in turn was a continuation-in-part of my now abandoned applications Serial Number 52,776 filed August 30, 1960, entitled, "Improved Dehydrogenation Process," Serial Number 72,327 filed November 29, 1960, entitled, "Dehydrogenation Process," Serial Number 145,992 filed October 18, 1961, entitled, "Dehydrogenation of Hydrocarbons," Serial Number 145,993 filed October 18, 1961, entitled, "Dehydrogenation Process," Serial Number 156,953 filed December 4, 1961, entitled, "Dehydrogenation Process," Serial Number 156,956 filed December 4, 1961, entitled, "Dehydrogenation," Serial Number 196,870 filed May 23, 1962, entitled, "Dehydrogenation Process," Serial Number 207,105 filed July 2, 1962, entitled, "Improved Dehydrogenation Process," and Serial Number 825,656 filed July 8, 1959, entitled, "Dehydrogenation Process."

This invention relates to a process for dehydrogenating organic compounds and relates more particularly to the dehydrogenation of organic compounds in the vapor phase at elevated temperatures in the presence of oxygen, iodine and an improved inorganic contact mass.

It has been found recently that a great variety of dehydrogenatable organic compounds may be dehydrogenated by reacting a mixture of an organic compound containing at least one pair of adjacent carbon atoms, each of which possess at least one hydrogen atom, iodine, or an iodine-liberating material, and oxygen under specified conditions at an elevated temperature, and at a reduced partial pressure of the organic compound, in the presence of certain metals or compounds thereof to obtain the corresponding unsaturated organic compound containing at least one



or —C≡C— grouping.

I have found, quite unexpectedly, that this process may be improved so that increased selectivities and yields of unsaturated organic compound derivatives containing the



or —C≡C— grouping are obtained more efficiently even with less iodine and under less stringent process conditions, e.g. at lower temperatures, when such reaction is conducted in the presence of a contact mass comprising as a first component at least one element of a metal of Groups I*a* and II*a*, (i.e. the alkali and alkaline earth metals) together with a second component which is manganese or a manganese compound.

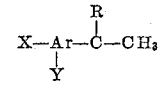
The process of this invention can be applied to a great variety of organic compounds to obtain the corresponding unsaturated derivative thereof. Such compounds normally will contain from 2 to 20 carbon atoms, at least one



grouping, that is, adjacent carbon atoms each containing at least one hydrogen atom and having a boiling point below about 350° C. Such compounds may contain in

addition to carbon and hydrogen, oxygen, halogens, nitrogen and sulphur. Among the classes of organic compounds which are dehydrogenated by means of the novel process of this invention are alkanes, alkenes, alkyl halides, ethers, esters, aldehydes, ketones, organic acids, alkyl aromatic compounds, alkyl heterocyclic compounds, cyanoalkanes, cycloalkanes and the like. Illustrative dehydrogenation include ethylbenzene to styrene, isopropyl-benzene to α-methyl styrene, ethylcyclohexane to styrene, cyclohexane to benzene, ethane to ethylene and acetylene, ethylene to acetylene, propane to propylene, isobutane to isobutylene, n-butane to butene and butadiene-1,3, butene-1 to butadiene-1,3 and vinyl acetylene, cis or trans butent-2 to butadiene-1,3, butane or butene to vinyl acetylene, butadiene-1,3 to vinyl acetylene, methyl butene to isoprene, isobutane to isobutylene, propionaldehyde to acrolein, ethyl chloride to vinyl chloride, propionitrile to acrylonitrile, methyl isobutyrate to methyl methacrylate, and the like. Other representative materials which are readily dehydrogenated in the novel process of this invention include ethyl toluene, the alkyl chlorobenzenes, ethyl naphthalene, isobutyronitrile, propyl chloride, isobutyl chloride, ethyl fluoride, ethyl dichloride, butyl chloride, the chlorofluoroethanes, methylethyl ketone, diethyl ketone, methyl propionate, and the like. This invention is useful in the preparation of vinylidene compounds containing at least one $CH_2=C<$ group, that is, a compound possessing at least one group containing a terminal methylene group attached by a double bond to a carbon atom, and 2 to 12 carbon atoms and is particularly useful in the dehydrogenation of hydrocarbons containing 2 to 5 carbon atoms or aliphatic nitriles of 3 to 4 carbon atoms. Preferred compounds to be dehydrogenated are hydrocarbons of 4 to 8 carbon atoms having at least four contiguous non-quaternary carbon atoms. Aliphatic acyclic hydrocarbons of from 4 to 5 or 6 carbon atoms are preferred. The invention is further particularly adapted to provide butadiene-1,3 from butane and butene and isoprene from isopentane and isopentene in high yields and excellent conversion and selectivity.

As shown by the examples below and the disclosures herein, the novel process of this invention is applicable to a great variety of organic compounds containing 2 to 20 carbon atoms and at least one pair of adjacent carbon atoms bonded together and each carbon atom possessing at least one hydrogen atom including the following: hydrocarbons including both alkanes and alkenes, especially those containing 2 to 6 or 8 carbons; carbocyclic compounds containing 6 to 12 carbon atoms, including both alicyclic compounds and aromatic compounds of the formula



wherein Ar is phenyl or naphthyl, R is hydrogen or methyl and X and Y are hydrogen or alkyl radicals containing 1 to 4 carbon atoms, or halogen; alkyl ketones containing 4 to 6 carbon atoms; aliphatic aldehydes containing 3 to 6 carbon atoms; cyanoalkanes containing 2 to 6 carbon atoms; halo-alkanes and halo-alkenes containing 2 to 6 carbon atoms, particularly chloro- and fluoro-alkanes and the like. Vinylidene compounds containing the



group, that is, containing a terminal methylene group attached by a double bond to a carbon atom, are

readily obtained from organic compounds containing 2 to 12 carbon atoms and at least one



group wherein adjacent carbon atoms are singly bonded and possess at least one hydrogen each. For example, vinylidene halides; vinyl esters; acrylic acid and alkyl- and halo-acrylic acids and esters; vinyl aromatic compounds; vinyl ketones; vinyl heterocyclic comounds; diolefins containing 4 to 6 carbon atoms, olefins containing 2 to 8 carbon atoms, and the like are obtained as products. The vinylidene compounds normally contain from 2 to 12 carbon atoms and are well known as a commercially useful class of materials for making valuable polymers and copolymers therefrom.

Useful feeds as starting materials may be mixed hydrocarbon streams such as refinery streams. For example, the feed material may be the olefin-containing hydrocarbon mixture obtained as the product from the dehydrogenation of hydrocarbons. Another source of feed for the present process is from refinery by-products. Although various mixtures of hydrocarbons are useful, the preferred hydrocarbon feed contains at least 50 weight percent butene-1, butene-2, n-butane and/or butadiene-1,3 and mixtures thereof, and more preferably contains at least 70 percent n-butane, butene-1, butene-2 and/or butadiene-1,3 and mixtures thereof. Any remainder usually will be aliphatic hydrocarbons. The process of this invention is particularly effective in dehydrogenating acyclic aliphatic hydrocarbons to provide a hydrocarbon product wherein the major unsaturated product has the same number of carbon atoms as the feed hydrocarbon.

Iodine may be employed as free iodine or as any iodine-containing material which liberates the specified amount of free iodine under the conditions of reaction as defined hereinafter. For example, iodine, hydrogen iodide, the alkyl iodides, such as methyl iodide and ethyl iodide, wherein the alkyl groups preferably contain 1 to 6 carbon atoms; ammonium iodide and the like. Additional iodine compounds are iodohydrins such as ethylene iodohydrin; iodo substituted aliphatic acids such as iodoacetic acid; organic amine iodide salts such as methyl amine hydroiodide; and other iodine compounds such as SI_4, SI_6, SOI_2, IO_2, I_2O_5, CHI_3, Cl_4, and the like. Generally, the iodine compound will have a boiling or decomposition point of less than 400° C., and usually no greater than 100° C. Preferred are ammonium iodide, molecular or elemental iodine and/or hydrogen iodide. It is an advantage of this invention that hydrogen iodide or ammonium iodide may be employed as the iodine source, with one advantage being that the hydrogen iodide or ammonium iodide in the effluent from the reactor may be fed directly back to contact the hydrocarbons in the dehydrogenation reactor without any necessity of converting the hydrogen iodide to iodine. It is understood that when a quantity of iodine is referred to herein, both in the specification and the claims, that this refers to the calculated quantity of iodine in all forms present in the vapor state under the conditions of reaction regardless of the initial source or the form in which the iodine is present. For example, a reference to 0.05 mol of iodine would refer to the quantity of iodine present whether the iodine was fed as 0.05 mol of I_2 or 0.10 mol of HI.

The amount of iodine usually will be in an amount greater than about 0.0001 mol of iodine, such as at least 0.001 mol, or the equivalent amount of iodine-liberating material per mol of organic compound to be dehydrogenated, more usually at least about 0.01 mol equivalent of iodine per mol of organic compound will be employed. It is one of the unexpected advantages of this invention that only very small amounts of iodine are required, such as up to 0.2 and normally less than about 0.2 mol total equivalent of iodine and more desirably less than 0.1 mol of iodine per mol of organic compound to be dehydrogenated. Amounts of iodine between 0.001 or 0.005 and 0.08 or 0.09 mol of iodine per mol of the organic compound to be dehydrogenated are preferred, with the range of about 0.001 to 0.05 being particularly preferred. Preferably the iodine will be present in an amount no greater than 5 or 10 mol percent of the total feed to the dehydrogenation zone.

The amount of oxygen employed will be at least one-fourth mol of oxygen per mol of organic compound to be dehydrogenated. Generally greater than 0.25 mol of oxygen per mol of the organic compound will be used. Excellent yields of the desired unsaturated derivatives have been obtained with amounts of oxygen from about 0.4 to about 1.5 mols of oxygen per mol of organic compound, and within the range of or about 0.25 or 0.4 to 2 mols of oxygen per mol of organic compound economic, production and process considerations will dictate more exactly the normal ratio of oxygen to be used. A preferred range for oxygen is from 0.5 to 1.2 mols of oxygen per mol of compound to be dehydrogenated. Oxygen is supplied to the reaction system as pure oxygen, or as oxygen diluted with inert gases such as helium, carbon dioxide or as air and the like. In relation to iodine, the amount of oxygen employed is greater than one mol, as 1.25 of oxygen per atom of iodine present in the reaction mixture, usually greater than about 1.5 mols of oxygen per atom of iodine. Usually the ratio of the mols of oxygen to the mols of iodine will be at least 3 such as from 5 or 8 to 500 and preferably will be between 15 and 300 mols of oxygen per mol of iodine.

While the total pressure on systems employing the process of this invention normally will be at or in excess of atmospheric pressure, vacuum may be used. Higher pressures, such as about 100 or 200 p.s.i.g. may be used. The partial pressure of the organic compound under reaction conditions usually will be equivalent to below 10 inches mercury absolute when the total pressure is atmospheric. Better results and higher yields of desired product are normally obtained when the partial pressure of the organic compound is equivalent to less than about one-third or one-fifth of the total pressure. Also because the initial partial pressure of the hydrocarbon to be dehydrogenated is generally equivalent to less than about 10 inches of mercury at a total pressure of one atmosphere, the combined partial pressure of the hydrocarbon to be dehydrogenated plus the dehydrogenated hydrocarbon will also be equivalent to less than about 10 inches of mercury. For example, under these conditions, if butene is being dehydrogenated to butadiene, at no time will be combined partial pressure of the butene and butadiene be greater than equivalent to about 10 inches of mercury at a total pressure of one atmosphere. Preferably the hydrocarbon to be dehydrogenated should be maintained at a partial pressure equivalent to less than one-third the total pressure, such as no greater than six inches or no greater than four inches of mercury, at a total pressure of one atmosphere. The desired pressure is obtained and maintained by techniques including vacuum operations, or by using helium, organic compounds, nitrogen, steam and the like, or by a combination of these methods. Steam is particularly advantageous and it is surprising that the desired reactions to produce high yields of product are effected in the presence of large amounts of steam. Steam is particularly advantageous to obtain the required low partial pressure of the organic compound in the process. When steam is employed, the ratio of steam to organic compound is normally above about two mols of steam per-mol of organic compound such as within the range of about 2 or 5 to 20 or 30 mols, although larger amounts of steam as high as 40 mols have been employed. The degree of dilution of the reactants with steam and the like is related to maintaining the partial pressure of the organic compound in the system at below about one-third atmosphere and preferably below 10 inches mercury ab-

solute when the total pressure on the system is one atmosphere. For example, in a mixture of one mol of butene, three mols of steam and one mol of oxygen under a total pressure of one atmosphere the butene would have an absolute pressure of one-fifth of the total pressure, or roughly six inches of mercury absolute pressure. Equivalent to this six inches of mercury butene absolute pressure at atmospheric pressure would be butene mixed with oxygen and iodine under a vacuum such that the partial pressure of the butene is six inches of mercury absolute. A combination of a diluent such as steam together with a vacuum may be utilized to achieve the desired partial pressure of the hydrocarbon. For the purpose of this invention, also equivalent to the six inches of mercury butene absolute pressure at atmospheric pressure would be the same mixture of one mol of butene, three mols of steam and one mol of oxygen under a total pressure greater than atmospheric, for example, a total pressure of 15 or 20 inches mercury above atmospheric. Thus, when the total pressure on the reaction zone is greater than one atmosphere, the absolute values for the pressure of butene will be increased in direct proportion to the increase in total pressure above one atmosphere. Another feature of this invention is that the combined partial pressure of the hydrocarbon to be dehydrogenated plus the iodine-liberating material will preferably also be equivalent to less than 10 inches of mercury, and preferably less than 6 or 4 inches of mercury, at a total pressure of one atmosphere. The lower limit of organic compound partial pressure will be dictated by commercial considerations and normally will be greater than about 0.1 inch of mercury absolute.

The temperature of the reaction is from above 400° C. to about 800° C. or 1000° C. Preferably the temperatures will be from at least 450° C. to 900° C., and generally will be at least about 500° C. The optimum temperature may be determined as by thermocouple at the maximum temperature of the reaction. Usually the temperature of reaction will be controlled between about 450° C. and about 750° C. or 800° C.

The flow rates of the gaseous reactants may be varied quite widely and good results have been obtained with organic compound gaseous flow rates ranging from about 0.25 to about 3 liquid volumes of organic compound per volume of reactor packing per hour, the residence or contact time of the reactions in the reaction zone under any given set of reaction conditions depending upon the factors involved in the reaction. Generally, the flow rates will be within the range of about 0.10 to 25 or higher liquid volumes of the hydrocarbon to be dehydrogenated, calculated at standard conditions of 0° C. and 760 mm. of mercury per volume of reactor space containing catalyst per hour (referred to as either LHSV or liquid v./v./hr.). Usually the LHSV will be between 0.15 and 15. The volume of reactor containing catalyst is that volume of reactor space including the volume displaced by the catalyst. For example, if a reactor has a particular volume of cubic feet of void space, when that void space is filled with catalyst particles the original void space is the volume of reactor containing catalyst for the purpose of calculating the flow rates. The residence or contact time of the reactants in the reaction zone under any given set of reaction conditions depends upon all the factors involved in the reaction. Contact times ranging from about 0.01 to about two seconds at about 450° C. to 750° C. have been used. A wider range of residence times may be employed, as 0.001 second to about 10 or 15 seconds. Residence time is the calculated dwell time of the reaction mixture in the reaction zone assuming the mols of product mixture are equivalent to the mols of feed mixture.

For conducting the reaction, a variety of reactor types may be employed. Fixed bed reactors may be used and fluid and moving bed systems are advantageously applied to the process of this invention. In any of the reactors suitable means for heat removal may be provided. Tubular reactors of large diameter which are loaded or packed with the solid contact mass are satisfactory.

Good results have been obtained when the exposed surface of the solid contact mass is greater than about 25 square feet, preferably greater than about 50 square feet per cubic foot of reactor as 75 or 100 or higher. Of course, the amount of catalyst surface may be much greater when irregular surface catalysts are used. When the catalyst is in the form of particles, either supported or unsupported, the amount of catalyst surface may be expressed in terms of the surface area per unit weight of any particular volume of catalyst particles. The ratio of catalytic surface to weight will be dependent upon various factors including the particle size, particle distribution, apparent bulk density of the carrier, and so forth. Typical values for the surface to weight ratio are such about ½ to 200 square meters per gram,[1] although higher and lower values may be used.

Excellent results have been obtained by packing the reactor with catalyst particles as the method of introducing the catalytic surface. The size of the catalyst particles may vary widely but generally the maximum particles size will at least pass through a Tyler Standard Screen which has an opening of 2 inches, and generally the largest particles of catalyst will pass through a Tyler Screen with one inch openings. Thus, the particle size when particles are used preferably will be from about 10 microns to a particle size which will pass through a Tyler Screen with openings of 2 inches. If a carrier is used the catalyst may be deposited on the carrier by methods known in the art such as by preparing an aqueous solution or dispersion of the catalyst, mixing the carrier with the solution or dispersion until the active ingredients are coated on the carrier. The coated particles may then be dried, for example, in an oven at about 110° C. Various other methods of catalyst preparation known to those skilled in the art may be used. Very useful carriers are the Alundums, silicon carbide, the Carborundums, pumice, kieselguhr, asbestos, and the like. When carriers are used, the amount of catalyst composition on the carrier will generally be in the range of about 2 to 80 weight percent of the total weight of the active catalytic material plus carrier. Another method for introducing the required surface is to utilize as a reactor a small diameter tube wherein the tube wall is catalytic or is coated with catalytic material. If the tube wall is the only source of catalyst generally the tube will be of an internal diameter of no greater than one inch such as less than ¾ inch in diameter or preferably will be no greater than about ½ inch in diameter. The technique of utilizing fluid beds lends itself well to the process of this invention.

In the above descriptions of catalyst compositions, the composition described is that of the surface which is exposed in the dehydrogenation zone to the reactants. That is, if a catalyst carrier is used, the composition described as the catalyst refers to the composition of the surface and not to the total composition of the surface coating plus carrier. The catalytic compositions are intimate combinations or mixtures of the ingredients. These ingredients may or may not be present as alloys. Catalyst binding agents or fillers may be used, but these will not ordinarily exceed about 50 percent or 65 percent by weight of the catalytic surface. The defined catalytic components will be the main active constituents in the catalyst and the catalyst may consist essentially of the defined catalytic components. The weight percent of the defined catalytic atoms will generally be at least 20 percent, and are preferably at least 35 percent of the composition of the catalyst surface exposed to the reaction gases and will generally be at least 51 or about 80 atomic weight percent

[1] As measured by the Innes nitrogen absorption method on a representative unit volume of catalyst particles. The Innes method is reported in Innes, W. B., Anal. Chem., 23, 759 (1951).

of any cations in the surface, such as at least 80 atomic percent of any metal cations in the surface.

The defined catalyst combinations may be employed in any form, e.g., as pellets, tablets, as coatings on carriers or supports, and the like, in both fixed and fluidized beds. Other methods of catalyst preparation known to those skilled in the art may also be used.

According to this invention, the catalyst is autoregenerative and thus the process is continuous. Little or no energy input is required for the process and it may be operated essentially adiabatically. Moreover, small amounts of tars and polymers are formed as compared to prior art processes. It is also an advantage of this invention that triple bond containing compounds are more easily obtained than with catalysts containing only one of the defined components.

In the examples given below the conversions, selectivities and yields are expressed as mol percent based on the mols of the compound to be dehydrogenated fed to the reactor. The temperature of reaction listed is approximately the maximum temperature in the reactor. The catalysts are present as fixed beds.

The Group *Ia* and *IIa* compounds used include, for example, oxides, hydroxides and salts such as the phosphates, sulfates, halides and the like. Useful compound include, for example, lithium chloride, lithium oxide, lithium bromide, lithium fluoride, lithium phosphate, sodium hydroxide, sodium oxide, sodium chloride, sodium sulfate, beryllium oxide, sodium bromide, sodium iodide, sodium phosphate, sodium fluoride, potassium chloride, potassium bromide, potassium sulfate, potassium iodide, potassium nitrate, potassium citrate, potassium hydroxide, potassium oxide, potassium phosphate, rubidium chloride, rubidium bromide, rubidium iodide, rubidium oxide, magnesium acetate, magnesium bromide, magnesium oxide, magnesium iodide, calcium oxide, calcium acetate, calcium oxalate, calcium chloride, calcium bromide, calcium iodide, calcium phosphate, calcium fluoride, strontium oxide, strontium hydroxide, strontium chloride, strontium bromide, barium oxide, barium chloride, barium hydroxide, barium sulfate, barium bromide, barium iodide, beryllium chloride, and the like, and mixtures thereof. Preferred Group *Ia* and *IIa* metal elements are lithium, sodium, magnesium, potassium, calcium, strontium and barium, such as the oxides, phosphates, iodides, bromides, chlorides or fluorides of these metals. The oxides and halides and mixtures thereof are particularly preferred. Many of the Group *Ia* and *IIa* compounds may change during the preparation of the catalyst, during heating in a reactor prior to use in the process of this invention, or are converted to another form under the described reaction conditions, but such materials still function as an effective compound in the defined process. For example, the halides may be converted to the oxides or vice versa under the conditions of reaction. The amount of Group *Ia* metal compound or Group *IIa* metal compound with the additional metal or inorganic compound thereof may be varied quite widely and while small amounts, as low one-tenth percent based on the total catalyst, have been used, much larger amounts may be employed in concentrations up to where the Group *Ia* or *IIa* metal compound is present, such as up to 50 weight percent. Normally up to, or less than, 50 percent, and more usually about one to about twenty-five percent of the Group *Ia* or Group *IIa* compound, such as about one to ten percent, with the remainder being the defined second inorganic metal compound, is satisfactory. On an atomic basis, the combined amount of the metal atoms of Group *Ia* and/or *IIa* will be from at least about 0.001 atom per atom of the defined second catalyst component and mixtures thereof. Excellent results are obtained at ratios of about 0.01 to 1.0 or 1.5 atoms of Group *Ia* and *IIa* per atom of the elements from the second specified group, such as from or about 0.01 to 0.02 to 0.5 atom of Group *Ia* and *IIa* per atom of the elements from the second specified group.

Manganese or a variety of manganese compounds may be used as the second component in conjunction with the Group *Ia* and *IIa* metal compounds. Metals of the described second component group in elemental form may be employed and are included within the scope of this invention. The metals generally are changed to inorganic compounds thereof, at least on the surface, under the reaction conditions set forth herein. Particularly effective are inorganic compounds such as the oxides and salts including the prosphates and the halides, such as the iodides, bromides, chlorides and fluorides. Inorganic compounds which are useful as the second component in the compounded contact mass for the process of this invention include manganese oxide, manganese phosphate, manganese, managanous chloride, and the like. Preferably the catalyst will be solid under the conditions of reaction. Many of the salts, oxides and hydroxides of manganese may change during the preparation of the catalyst, during heating in the reactor in the process of this invention, but such materials still function as an effective compound in the defined process. For example, manganese nitrates or carbonates or acetates may be converted to the corresponding oxide or iodide under the reaction conditions defined herein. Salts which are stable or partially stable at the defined reaction temperatures are likewise effective under the conditions of the described reaction, as well as such compounds which are converted to another form in the reactor. At any rate, the catalysts are effective if the defined catalysts are present in a catalytic amount in contact with the reaction gases. Useful catalyst combinations include manganese dioxide and lithium chloride, manganese phosphate and lithium chloride or lithium hydroxide, manganese oxide together with lithium bromide and potassium hydroxide, manganese chloride and potassium chloride, manganese chloride and lithium chloride, and the like.

In Examples 1 to 5, a tubular one inch diameter Vycor [2] reactor, filled with the described solid contact masses, equipped with an external electric furnace was used. The reaction conditions and the active materials used are set forth in the specific examples. The organic compound and oxygen were added at the top of the reactor; the hydrogen iodide solution was added to this stream as it entered the reactor and steam was added separately opposite this stream. The results are reported as mol percent conversion, selectivity and yield of desired unsaturated product per pass.

Example 1

A contact mass was prepared by depositing a water slurry containing manganese oxide and 2.6 percent lithium chloride, calculated on the manganese oxide, on 3/16 inch AMC [3] granules by evaporation. The coated pellets were dried and placed in the one-inch diameter reactor to a depth of eight inches. Butene was dehydrogenated over this contact mass at a temperature of 1115° F. The molar ratio of reactants passed over this contact mass was one mol of butene at a flow rate of one LHSV, liquid hourly space velocity, 0.025 mol of I_2 supplied as a 25 percent solution of ammonium iodide in water, 0.65 mol of oxygen supplied as air, and 13 mols of steam. A yield of 85.7 percent butadiene-1,3 per pass was obtained at a conversion of 87.2 percent and selectivity of 98.3 percent.

Example 2

A similar contact mass to that of Example 1 containing manganese oxide and 30 percent lithium chloride was pre-

[2] Vycor is the trade name of Corning Glass Works, Corning, N.Y., and is composed of approximately 96 percent silica with the remainder being essentially B_2O_3.

[3] Supplied by The Carborundum Company, type AMC pellets are poly-surface pellets of fused aluminum oxide characterized as having medium porosity (40–50 percent), coarse grain and 300–350 micron pore size.

pared in the same way and evaluated under the same reaction conditions. Butadiene-1,3 was obtained in a yield of 85.1 percent at a conversion of 86.4 percent and selectivity of 98.5 percent. At 1196° F., the yield of butadiene-1,3 was 97.9 percent per pass; at 1240° F., the yield of butadiene per pass was 91 percent.

Example 3

For comparison purposes with Examples 1 and 2, a contact mass prepared from manganese oxide alone on AMC granules was evaluated and at 1202° F., butene was dehydrogenated to butadiene-1,3 in a yield of 75 percent at a conversion of 82 and selectivity of 91.5 percent.

When Example 1 above is repeated at 650° C. with a 95 percent manganese oxide-5 percent lithium chloride contact mass, deposited on 4 to 6 mesh fused alumina pellets with 0.05 mol of I_2 as aqueous hydrogen iodide (hydroiodic acid), 10 mols of steam and 0.85 mol of oxygen per mol of organic compound being dehydrogenated, isobutylene is obtained from isobutane, acrylonitrile from propionitrile, acrolein from propionaldehyde, isoprene from 2-methyl butene-2, styrene from ethylbenzene, vinyl chloride from ethyl chloride, ethylene from ethane, styrene from ethylcyclohexane, methyl isopropenyl ketone from methyl isopropyl ketone in good yields.

When the examples above are repeated with other contact masses such as mixtures of 95% manganese chloride and 5% calcium chloride, manganese oxide and sodium chloride, 97.5% manganese phosphate and 2.5% rubidium chloride or 2.5% K_2CO_3, good yields of butadiene-1,3 are obtained from butene-1.

Example 4

A mixture of 99 percent manganese oxide and 1 percent lithium nitrate was deposited on 4 to 8 mesh Alundum[4] pellets from water by evaporation. The dried coated pellets were placed in a reactor and heated to convert the lithium nitrate to lithium oxide. Butene-2 was dehydrogenated over this contact mass at a liquid hourly space velocity (LHSV) of butene of one, and a molar ratio of reactants of 1 mol of butene-2, 0.025 mol of I_2 added as a 25 percent aqueous solution of ammonium iodide, 0.65 mol of oxygen added as air and 13 mols of steam. At 1188° F., the butene-2 was dehydrogenated to butadiene-1,3 at a yield of 87.2 percent, conversion of 93.1 percent and selectivity of 93.7 percent.

Example 5

Using another contact mass consisting solely of manganese oxide deposited on AMC granules and under the same reaction conditions used in Example 4 and molar ration of reactants at 1202° F., a yield of 75 percent butadiene-1,3 was obtained at a conversion of 82 percent and selectivity of 91.5 percent.

The process of this invention is particularly applicable to the dehydrogenation of hydrocarbons, including dehydroisomerization and dehydrocyclization, to form a variety of acyclic compounds, cycloaliphatic compounds, aromatic compounds, and mixtures thereof. For example, 2-ethylhexene-1 may be converted to a mixture of aromatic compounds such as toluene, ethyl benzene, p-xylene, o-xylene and styrene.

I claim:

1. The method for dehydrogenating hydrocarbon compounds having 2 to 20 carbon atoms to produce a dehydrogenated product having the same number of carbon atoms and the same structure with the exception of the removed hydrogen atoms which comprises heating in the vapor phase at a temperature of above 400° C. a hydrocarbon compound having a



group with oxygen in a molar ratio of greater than one-fourth mol of oxygen per mol of said hydrocarbon compound, iodine in an amount of less than about 0.2 mol of iodine per mol of said hydrocarbon compound, the ratio of the mols of said oxygen to the mols of said iodine being at least 2.5, the partial pressure of said hydrocarbon compound being equivalent to less than one-half the total pressure in the presence of a catalyst comprising as its main active constituent (1) a compound selected from the group consisting of oxides, salts and hydroxides of alkali and alkaline earth metals and mixtures thereof, and (2) manganese or a manganese compound.

2. The method of claim 1 wherein the said compound is a hydrocarbon having from 2 to 12 carbon atoms.

3. The method of claim 1 wherein the said compound is an acyclic aliphatic hydrocarbon of 4 to 6 carbon atoms.

4. The method of claim 1 wherein the said compound is a hydrocarbon selected from the group consisting of n-butene, n-butane, isopentene, isopentane and mixtures thereof.

5. The method of claim 4 wherein the said temperature is at least 450° C.

6. The method of claim 4 wherein steam is employed in the said vapor phase in an amount of from 2 to 30 mols of steam per mol of said hydrocarbon.

7. The method of claim 4 wherein the oxygen is present in an amount of greater than 3.0 mols of oxygen per mol of said hydrocarbon and the said iodine is present in an amount of from .001 to 0.09 mol of iodine per mol of said hydrocarbon.

8. The method of claim 4 wherein the alkali and alkaline earth metal compounds are present in an amount of from about .01 to 0.5 atom of the alkali or alkaline earth metal elements per atom of the metal elements of the said (2).

9. The method of claim 4 wherein the iodine is present in an amount of no greater than 10 mol percent of the total gaseous mixture in the dehydrogenation zone.

10. A method for dehydrogenating hydrocarbons containing 4 to 5 carbon atoms which comprises reacting in the vapor phase at a temperature between 400° C. and about 750° C. an aliphatic hydrocarbon containing 4 to 5 carbon atoms with oxygen in a molar ratio of about 0.4 mol to about 2 mols of oxygen per mol of hydrocarbon, and above 0.001 mol to less than 0.2 mol per mol of aliphatic hydrocarbon of iodine, at a partial pressure of said hydrocarbon of less than about one-third the total pressure in the presence of a mixture of (1) a compound selected from the group consisting of alkali metal oxides, alkaline metal hydroxides, alkaline earth metal oxides and alkaline earth metal hydroxides, and (2) manganese or an inorganic manganese compound.

11. The method of claim 1 wherein the said (1) is selected from the group consisting of lithium, sodium, magnesium, potassium, calcium, strontium, barium, and mixtures thereof.

12. The method of claim 1 wherein the said (1) and (2) are present as oxides, halides or mixtures thereof.

13. The method of claim 11 wherein the said (1) is a lithium compound.

14. The method of claim 11 wherein the said (1) is a calcium compound.

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G. E. SCHMITKONS, *Assistant Examiner.*

[4] Trademark for alumina carriers.