

1

3,308,186

OXIDATIVE DEHYDROGENATION PROCESS
Laimonis Bajars, Princeton, N.J., assignor to Petro-Tex
Chemical Corporation, Houston, Tex., a corporation
of Delaware
No Drawing. Filed Oct. 22, 1965, Ser. No. 502,488
12 Claims. (Cl. 260—680)

This application is a continuation-in-part of my earlier filed pending application Serial Number 250,019 filed January 8, 1963, entitled, "Process of Dehydrogenation," 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 145,992 filed October 18, 1961, entitled, "Dehydrogenation of Hydrocarbons," Serial Number 145,993 filed October 18, 1961, entitled, "Dehydrogenation Process," Serial Number 156,955 filed December 4, 1961, entitled, "Process of Dehydrogenation," Serial Number 156,957 filed December 4, 1961, entitled, "Dehydrogenation Method," and Serial Number 207,105 filed July 2, 1962, entitled, "Improved 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, bromine 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 possesses at least one hydrogen atom, bromine or a bromine-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



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



grouping are obtained more efficiently even with less bromine 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 or Groups Ia and IIa (i.e. the alkali and alkaline earth metals together with a second component which is a metal or compound thereof of Periodic Table Group IIIb.¹

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



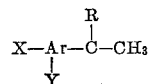
grouping, that is, adjacent carbon atoms each containing at least one hydrogen atom and having a boiling point

¹ Periodic Table, e.g., is found in Smith's Introductory College Chemistry, 3rd edition (Appleton-Century-Crofts, Inc., 1950).

2

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, isopropylbenzene 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 butene-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, methyl ethyl 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 $CH_2=C<$ 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



3

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 compounds; 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.

Bromine may be employed as free bromine or as any bromine-containing material which liberates the specified amount of free bromine under the conditions of reaction as defined hereinafter. For example, bromine, hydrogen bromide, the alkyl bromides, such as methyl bromide and ethyl bromide, wherein the alkyl groups preferably contain 1 to 6 carbon atoms; ammonium bromide and the like. Additional bromine compounds are bromohydrins such as ethylene bromohydrin; bromo substituted aliphatic acids such as bromoacetic acid; organic amine bromide salts such as methyl amine hydrobromide; and other bromide compounds such as SBr_4 , CHBr_3 , CBr_4 , and the like. Generally, the bromine compound will have a boiling or decomposition point of less than 400°C . and usually no greater than 100°C . Preferred are ammonium bromide, molecular or elemental bromine and/or hydrogen bromide. It is an advantage of this invention that hydrogen bromide or ammonium bromide may be employed as the bromine source, with one advantage being that the hydrogen bromide or ammonium bromide 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 bromide to bromine. It is understood that when a quantity of bromine is referred to herein, both in the specification and the claims, that this refers to the calculated quantity of bromine in all forms present in the vapor space under the conditions of reaction regardless of the initial source or the form in which the bromine is present. For example, a reference to 0.05 mol of bromine would refer to the quantity of bromine present whether the bromine was fed as 0.05 mol of Br_2 or 0.10 mol of HBr .

The amount of bromine usually will be in an amount greater than about 0.0001 mole of bromine, such as at least 0.001 mol, or the equivalent amount of bromine-liberating material per mol of organic compound to be dehydrogenated, more usually at least about 0.01 mol equivalent of bromine per mol of organic compound will be employed. Large amounts of bromine may be used, as high as one-half to one mol or more per mol of organic compound to be dehydrogenated, but it is one of the unexpected advantages of this invention that only very small amounts of halogen are required, normally less than about 0.2 mol total equivalent of bromine and more desirably less than 0.1 mol of bromine per mol of organic compound to be dehydrogenated. Amounts of bromine between 0.001 or 0.005 and 0.08 or 0.09 mol of bromine per mol

4

of the organic compound to be dehydrogenated are preferred, with the range of about 0.01 to 0.05 being particularly preferred. Preferably the bromine 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 normally be at least about 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 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. Large amounts of oxygen may be used with short contact time and high dilutions as with steam, for example, 30 to 50 mols per mol of organic compound. 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 bromine, excellent results are obtained when the amount of oxygen employed is greater than one mol, as 1.25, of oxygen per atom of bromine present in the reaction mixture, usually greater than about 1.5 mols of oxygen per atom of bromine. Usually the ratio of the mols of oxygen to the mols of bromine will be at least 3 such as from 5 to 8 to 500 and preferably will be between 15 and 300 mols of oxygen per mol of bromine.

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 the 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

51

6

the system at below about one-third atmosphere and preferably below 10 inches mercury absolute when the total pressure on the system is one atmosphere. For example, in a mixture of one mole 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 bromine under a vacuum such that the partial pressure of the butene is six inches of mercury absolute. A combination of 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 of 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 bromine-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 40° 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 and 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 of 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 com-

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).

position of the catalyst surface exposed to the reaction gases and will generally be at least 51 or about 80 atomic weight percent 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 compounds 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 as 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 the larger constituent in the composition, such as up to 50 weight percent or more, as 95 percent. Normally up to 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 Group 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 sec-

ond 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.

A great variety of metals or metal compounds of IIIb 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 forms 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 phosphates 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 scandium bromide, lanthanum oxide, yttrium oxide, cerium bromide, ceric oxide, ceric chloride, cerium phosphate, thorium dioxide, or uranium dioxide, and mixtures thereof. Particularly useful are mixed or pure rare earth chlorides, oxides and hydrates such as Lindsay ceric oxides Code 210B (e.g., 90% CeO_2 , 4% other rare earths, 1% P_2O_5 , 1.0% SiO_2 , and other minor ingredients); Lindsay ceric oxide Code 217 (e.g., 99.9% cerium oxide); didymium chlorides, hydrates, nitrates or oxides (e.g., 45–46% La_2O_3 , 1–2% CeO_2 , 9–10% Pr_6O_{11} , 32–33% Nd_2O_3 , 5–6% Sm_2O_3 , 3–4% Gd_2O_3 , 0.4% Y_2O_3 , and 1–2% other rare earth oxides). Preferably the catalyst will be solid under the conditions of reaction. Excellent catalysts are those comprising atoms of cerium, thorium and uranium, such as the oxides, phosphates, iodides, bromides, chlorides or fluorides of these elements. As the second component the rare earth compounds, such as the oxides or halides, are preferred. Many of the salts, oxides and hydroxides of the metals 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, many of the metal nitrates, nitrites, carbonates, hydroxides, acetates, and the like, may be converted to the corresponding oxide or bromide 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 cerium oxide and calcium chloride, cerium oxide and calcium oxide, cerium oxide and magnesium oxide, calcium chloride with magnesium oxide and cerium oxide, cerium oxide and potassium chloride, cerium oxide and strontium hydroxide, cerium oxide and sodium chloride, cerium oxide with magnesium oxide and calcium oxide, cerium oxide and barium hydroxide, ceric oxide and sodium hydroxide, cerium oxide and barium oxide, cerium oxide and lithium chloride, and potassium bromide combine with didymium oxide or rare earth oxides.

Example 1

Cerium oxide was deposited by evaporation on 6 mm. Vycor¹ Raschig rings from a water slurry thereof which contained 2.5 percent lithium hydroxide, based on the cerium oxide, and the coated rings were air dried. Butene-2, oxygen, steam and hydrogen bromide as an aqueous 48 percent solution, were fed into the Vycor reactor containing the coated rings at a flow rate of one-half liquid v./v./hr. of butene-2 in a molar ratio of one mol of butene-2, 0.85 mol of oxygen, 15 mols of steam, and 0.028 mol of Br_2 at 550° C. The yield of butadiene-1,3 per

¹ Vycor is the trade name of Corning Glass Works, Corning, N.Y., and is composed of approximately 96% silica with the remainder being essentially BaO .

Example 5

pass for the cerium oxide-lithium hydroxide contact mass is 80 percent, the selectivity is 89 percent, and the yield is 71 percent.

When Example 1 is repeated at 650° C. with a ceric oxide-lithium oxide contact mass with 0.05 mol of Br₂ as aqueous hydrogen bromide (hydrobromic 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, and methyl isopropenyl ketone from methyl isopropyl ketone in good yields.

Example 2

A contact mass is prepared by depositing from a water slurry thorium nitrate and 17 percent calcium oxide, calculated on the equivalent amount of thorium oxide, on ¼ inch Vycor Raschig rings, by evaporation. The coated pellets are dried and placed in the one-inch internal diameter Vycor reactor to a depth of eight inches and heated in air to convert the thorium nitrate to the oxide. Butene is dehydrogenated over this contact mass at a temperature of 700° C. The molar ratio of reactants passed over this contact mass is one mol of butene at a flow rate of one LHSV (liquid hourly space velocity), 0.06 mol of Br₂ supplied as a 48 percent solution of hydrogen bromide in water, 0.7 mol of oxygen, and 12.5 mols of steam. A conversion, selectivity and yield of butadiene-1,3 is obtained at high levels. Excellent yields of butadiene-1,3 are obtained under equivalent reaction conditions over contact masses containing 90 percent thorium oxide and 10 percent calcium chloride; and 90 percent thorium oxide and 10 percent lithium oxide.

Example 3

Another solid contact mass is prepared from uranium nitrate and lithium chloride. The contact mass is prepared by adding lithium chloride to an aqueous uranium nitrate solution in an amount so that the catalyst contains 15 percent lithium chloride based on uranium oxide. ¼ inch Vycor Raschig rings are coated with this solution by evaporation to deposit the solid contact mass. Eight inches of the contact mass is used in the one-inch internal diameter Vycor tubular reactor and the mass is heated in air to convert the uranium nitrate to uranium oxide. Butene is dehydrogenated under reaction conditions of a flow rate of one LHSV of butene at a temperature of 700° C. and at a molar ratio of reactants of one mol of butene, 12.5 mols of steam, 0.7 mol of oxygen and equivalent to 0.06 mol of Br₂ (supplied as aqueous hydrogen bromide of 47 percent concentration). The butene is converted to butadiene-1,3 at a conversion of 80 percent and a selectivity of 74 percent for a yield of 59 percent. When the run is repeated with a catalyst consisting of uranium oxide alone, less butadiene-1,3 per pass is obtained. When this example is repeated with catalysts containing (1) 85 percent uranium oxide and 15 percent calcium oxide and (2) 90 percent uranium oxide and 10 percent lithium oxide, good yields of butadiene-1,3 are obtained from butene.

Example 4

In a one-inch internal diameter Vycor reactor butene-2 is dehydrogenated to butadiene-1,3 using a combination La₂O₃ and CaO catalyst. The catalyst contains by weight 95 percent La₂O₃ and 5 percent CaO coated on ¼ inch Vycor Raschig rings. Steam is added at a ratio of 10 mols of steam per mol of butene-2 and oxygen is added at a ratio of 0.85 mol of oxygen per mol of butene-2. Hydrogen bromide is added at a ratio equivalent to 0.028 mol of Br₂ per mol of butene. The flow rate is one LHSV. At a reactor temperature of 700° C. the yield of butadiene is 60 mol percent of the butene fed.

5

10

15

20

25

30

35

40

45

50

55

60

65

70

75

Butene-2 is dehydrogenated at 625° C. using 7.5 mols of steam, 1.25 mol of oxygen and .006 mol of bromine (fed as HBr) respectively per mol of butene. The flow rate is 1.0 liquid hourly space velocity. The catalyst is a cerium hydrate (Lindsay 201) containing by weight (calculated as the oxides) approximately 76% cerium oxide, 4% other rare earth oxides, .25% thorium oxide, minor amounts of other elements, and 2% by weight calcium oxide. The conversion is 76 mol percent, the selectivity is 80 percent and the yield per pass is 60 percent butadiene.

Example 6

Isopentane is dehydrogenated to isoprene and amylenes by employing a catalyst using the cerium hydrate catalyst of Example 5 mixed with 5 percent by weight lithium hydroxide. The temperature of reaction is 560° C. and the flow rate is 0.5 LHSV. The ratio of bromine, steam, and oxygen per mol of isopentane is .11/15/1.5, respectively. The selectivity is 73 mol percent per pass.

Example 7

Isobutane is dehydrogenated to isobutylene employing 15 mols steam, 1.0 mol oxygen and .085 mol bromine per mol of isobutane. The catalyst is of the same composition as used in Example 5. Isobutylene is obtained at a selectivity of 61 mol percent at a temperature of 550° C.

Example 8

Example 7 is repeated at 600° C. substituting propane for the isobutane. Propylene is obtained at a selectivity of 69 percent per pass.

Example 9

n-Butane is dehydrogenated to a mixture of butene and butadiene. The flow rate is 0.2 LHSV. The catalyst is CeCl₃ modified with approximately 57 CaCl₂. The molar ratios of reactants are 20 helium, 1.25 oxygen and .09 bromine (fed as HBr) per mol of n-butane. At a reactor temperature of 525° C. the selectivity is 50 mol percent.

Example 10

Example 9 is repeated substituting lithium chloride for the calcium chloride modifier of Example 9. The selectivity under the same reaction conditions is 53 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, bromine in an amount of less than 0.5 mol of bromine per mol of said hydrocarbon compound, the ratio of the mols of said oxygen to the mols of said bromine 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 com-

11

prising 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) an inorganic compound of a metal selected from the Periodic Table Group IIIb.

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 bromine and the said bromine is present in an amount of from .001 to .09 mol of bromine 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 bromine is present in an amount of no greater than 10 mol percent of the total gaseous mixture in the dehydrogenation zone.

12

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 bromine, 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) an inorganic compound selected from the group consisting of metals of Periodic Table Group IIIb and mixtures thereof.

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 and the said (2) is selected from the group consisting of rare earth compounds.

12. The method of claim 11 wherein the said (1) and (2) are present as oxides or halides.

References Cited by the Examiner

UNITED STATES PATENTS

3,130,241	4/1964	Baijle et al.	260—680
3,207,806	9/1965	Bajars	260—680

DELBERT E. GANTZ, *Primary Examiner*.

G. E. SCHMITKONS, *Assistant Examiner*.