United States Patent Office 3,308,188 Patented Mar. 7, 1967

3,308,188

OXIDATIVE DEHYDROGENATION PROCESS

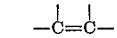
Laimonis Bajars, Princeton, N.J., assignor to Petro-Tex Chemical Corporation, Houston, Tex., a corporation of Delaware

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14 Claims. (Cl. 260—680)

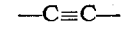
This application is a continuation-in-part of my earlier filed pending application Serial Number 250,019 filed January 8, 1963, entitled, "Process of Dehydrogenation," now abandoned, which in turn was a continuation-in-part of my now abandoned applications Serial Number 52,766 filed August 30, 1960, 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 possess 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

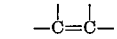


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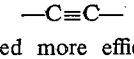


grouping.

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

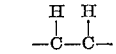


or



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 of Groups I*a* and II*a* (i.e. the alkali and alkaline earth metals) together with a second component which is a member selected from the group consisting of metals and compounds thereof of Periodic Table [1] Group VIII*b*.

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

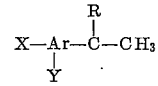


grouping, that is, adjacent carbon atoms each containing at least one hydrogen atom and having a boiling point

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

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, 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 contigous 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.

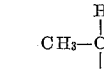
As shown by the examples below and the disclosures herein, the novel process of this invention is applicable to a great variety of organic compounds containing 2 to 20 carbon atoms and at least one pair of adjacent carbon atoms bonded together and each carbon atom possessing at least one hydrogen atom 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



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 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 mole of HBr.

The amount of bromine usually will be in an amount greater than about 0.0001 mol 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 mole of bromine per mol 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 mols 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 of 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 moles 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 moles 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 or 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 on 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 absolute 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 atomspheric 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 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 atomspheric 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 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 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 that 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 as about ½ to 200 square meters per gram,[2] 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 preparations 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 bindingagents 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

[2] 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).

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 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 I*a* and II*a* 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 I*a* and II*a* 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 I*a* and II*a* 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 I*a* metal compound or Group II*a* 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 Group I*a* or II*a* 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 I*a* or Group II*a* 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 I*a* and/or II*a* will be from at least about 0.001 atoms 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 I*a* and II*a* per atom of the elements from the second specified group, such as from about 0.01 or 0.02 to 0.5 atoms of Group I*a* and II*a* per atom of the elements from the second specified group.

A variety of metals or metal compounds of Periodic Table Group VIII*b* may be used as the second component in conjunction with the Group I*a* and II*a* 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 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 palladium oxide, ferric oxide, ferrous oxide, iron phosphate, iron phosphide, nickel oxide, iron carbonate, iron sulfate, cobalt nitrate, cobaltous oxide, cobaltic oxide, ferric phosphate, ferrous chloride, and the like. Preferably the catalyst will be solid under the conditions of reaction. Excellent catalysts are those comprising atoms of iron, cobalt, nickel and palladium, such as the oxides, phosphates, iodides, bromides, chlorides or fluorides of these elements. Many of the salts, oxides and hydroxides of the metals of the listed groups 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 catalyst is present in a catalytic amount in contact with the reaction gases. Useful catalyst combinations include iron oxide and lithium chloride, iron oxide and calcium chloride, ferrous chloride and potassium chloride, ferrous chloride and rubidium chloride, ferrous chloride and lithium hydroxide, iron oxide and lithium hydroxide, ferrous sulfate and potassium sulfate, ferric oxide plus lithium oxide and barium oxide, ferric oxide, lithium chloride and barium hydroxide, cobalt chloride and calcium chloride and the like. In Group VIII*b* the preferred elements are those in the fourth period, i.e., iron, cobalt and nickel. Iron is particularly preferred and superior results have been obtained with iron.

In Examples 1 to 6 tubular Vycor [3] reactor, containing the described solid contact masses, equipped with an external electric furnace is used. The reaction conditions and the active materials used are set forth in the specific examples. The organic compound and oxygen are added at the top of the reactor, the bromine material is added to this stream as it enters the reactor and steam is added separately opposite this stream. The results are reported as mol percent conversion, selectivity and yield of desired unsaturated product per pass.

Example 1

The Vycor reactor was loaded with 6 mm. Vycor Raschig rings which are coated with iron oxide containing 2.5 percent lithium hydroxide. n-Butane was de-

[3] 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.

hydrogenated in this example. n-Butane, steam and oxygen in a molar ratio of 15 mols of steam and 1.0 mol of oxygen per mol of n-butane are fed to the reactor at a n-butane flow rate of 0.11 liter per minute STP, equivalent to a flow rate of ½ liquid v./v./hr. Aqueous hydrogen bromide is added in a molar ratio of 0.056 mol per mol of n-butane. n-Butane is converted to butadiene-1,3 at 600° C. at a conversion of 66 percent and selectivity of 63 percent for a yield of 42 percent per pass.

Example 2

Another contact mass is prepared by evaporating an aqueous dispersion containing Fe_2O_3 and CaO onto 4 to 8 mesh Alundum granules. The coated particles contain about 90 percent Fe_2O_3 and 10 percent CaO. The Vycor reactor is loaded with this contact mass and butene-2, steam, oxygen, and hydrogen bromide as an aqueous 48 percent solution are fed into the reactor at a flow rate of butene-2 of 1 liquid v./v./hr. over an eight inch deep catalyst bed. The molar ratio of reactants is one mol of butene-2, 12.5 mols of steam, 0.7 mol of oxygen, and 0.01 mol of Br_2. At 615° C. a yield of 85 percent butadiene-1,3 per pass is obtained at a conversion of 90 percent and selectivity of 95 percent. With 0.02 mol of Br_2 per mol of butene-2 at 580° C., a yield of butadiene-1,3 of 89 percent at a conversion of 92 percent and selectivity of 97 percent is obtained.

Example 3

Iron oxide is deposited by evaporation on 6 mm. Vycor Raschig rings from a water slurry thereof which contains 2.5 percent lithium hydroxide, based on the iron oxide, and the coated rings are air dried. Butene-2, oxygen, steam, and hydrogen bromide as an aqueous 48 percent solution are 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, 0.35 mol of oxygen, 15 mols of steam and 0.028 mol of Br_2 at 550° C. The yield of butadiene-1,3 per pass for the iron oxide-lithium hydroxide contact mass is 76 percent at a conversion of 92 percent and selectivity of 83 percent.

When Example 3 is repeated with the exception that the Vycor Raschig rings had coated thereon lithium hydroxide or iron oxide only, the yield of butadiene-1,3 was less than that obtained from the mixed catalyst. An unexpected synergistic effect is involved since use of an active surface containing only iron oxide or lithium hydroxide resulted in yields of much less than that obtained when the two were used together.

Example 4

A mixture of 90 percent Fe_2O_3 and 10 percent barium oxide is deposited on 4 to 8 mesh Alundum chips from an aqueous dispersion. The coated pellets are air dried and placed in a reactor. Butene-2 is dehydrogenated over this contact mass at a flow rate of one v./v./hr. of butene-2 at 1100° F. and with a ratio of reactants of one mol of butene, 0.03 mol of Br_2 supplied as a 30 percent aqueous solution of ammonium bromide, 0.8 mol of oxygen supplied as air, and 12 mols of steam. A yield of 86 percent butadiene-1,3 per pass is obtained over this contact mass at a conversion of 91 percent and selectivity of 95 percent.

When the examples above are repeated with other contact masses such as mixtures of iron sulfate and calcium oxide; ferric oxide and lithium oxide; good yields of butadiene-1,3 are obtained from butene.

Example 5

Isopentane is dehydrogenated over a solid contact mass comprising 80 percent ferrous chloride, 10 percent lithium chloride, and 10 percent calcium chloride, at a flow rate of isopentane of one-half liquid v./v./hr. in a molar ratio of one mol of isopentane, 15 mols of steam, 1.5 mols of oxygen and 0.11 mol of bromine (as 48 percent hydrobromic acid) at a temperature of 525° C. The selectivity to pentenes is 16 percent and to isoprene 49 percent for a total selectivity of 65 mol percent.

Example 6

A solid contact mass is prepared by depositing from solution a mixture of 91 percent cobalt chloride and 9 percent calcium chloride onto 4 to 8 mesh AMC pellets. Butene is dehydrogenated over this solid contact mass with reactants in a ratio of one mol of butene-2, 12.5 mols of steam, 0.7 mol of oxygen added as air, and 0.01 mol of bromine as 48 percent hydrobromic acid, at a reaction temperature of about 600° C. Butadiene-1,3 is obtained in a yield of 77 percent at a conversion of 82 percent and selectivity of 94 percent.

Example 7

Another demonstration of the value of the contact masses of this invention is shown by a contact mass prepared in the same way as described above with 84.5 percent cobalt chloride and 15.5 percent calcium chloride, under the same reaction conditions (12.5 steam and 0.7 oxygen per mol of butene) at 577° C. and with 0.005 mol of bromine. A yield of 54 percent butadiene-1,3 per pass was obtained from butene at a conversion of 62 percent and selectivity of 88 percent.

Example 8

Isopentane is dehydrogenated to isoprene and amylenes by passing it through a catalyst bed of 90 weight percent Fe_3O_4 and 10 weight percent LiOH. The temperature is 525° C., the flow rate is 0.5 LHSV and the ratios of reactants are 0.11 mols bromine, 15 mols steam and 1.5 mols of oxygen per mol of isopentane. The selectivity is 76 percent.

Example 9

Example 8 is repeated substituting a catalyst of 80% $FeCl_2$ and 20% KCl and by using a temperature of 500° C. The selectivity is 76 percent.

Example 10

Ethyl benzene is dehydrogenated to styrene in a one inch internal diameter Vycor reactor according to the general procedure used above. The flow rate of ethylbenzene is 0.5 LHSV, the mol ratio of oxygen to ethylbenzene is 1.0 and 10 mols of steam are used per mol of ethyl benzene. Hydrogen bromide solution was added at a rate equivalent to 0.07 mol of Br_2 per mol of ethylbenzene. The catalyst is 90 percent by weight Fe_2O_3 and 10 percent CaO on a carrier. At 600° C. styrene is produced in a yield of 40 mol percent.

Example 11

Isobutane is dehydrogenated to isobutylene employing a catalyst which is by weight 97 percent Fe_3O_4 and 3 percent LiOH. 15 mols of steam, 1.0 mol of oxygen and .085 mol of bromine (fed as HBr) are employed per mol of isobutane. At a flow rate of 1 LHSV and a reactor temperature of 600° C. isobutylene is produced at a selectivity of 63 percent.

Example 12

Example 11 is repeated substituting propane for isobutane to produce propylene.

Example 13

Isopentane is dehydrogenated to isoprene and amylenes using a catalyst of 80 percent by weight $NiCl_2$ and 20 percent KCl. 15 mols of steam are used, 1.5 mols of oxygen and 0.11 mol of bromine (fed as HBr) per mol of isopentane. At a flow of 0.5 LHSV and a reactor temperature of 500° C. the selectivity is 68 percent.

Example 14

Propionitrile is dehydrogenated to acrylonitrile in a one inch internal diameter reactor according to the gen-

eral procedure above. Based on the propionitrile the molar ratio of oxygen is 1.0 and of iodine (fed as HI) is 0.04. Helium is also present in the mixture in a ratio of 15 mols per mol of propionitrile. The catalyst is a 90 weight percent Fe_3O_4 and 10 weight percent CaO. The flow rate of propionitrile is 0.5 LHSV. At 675° C. the conversion is 77 percent, the selectivity is 76 percent and the yield is 58 mol percent.

Examples 15 to 21

A series of runs are made to demonstrate the invention for the dehydrogenation of n-butane. A Vycor reactor is used. The molar ratio of reactants is 1.25 mol of oxygen, 20 mols of helium and 0.08 mol of Br_2 per mol of butane. The flow rate is .2 LHSV.

Example	Catalyst	Reaction Temp., ° C.	Butene plus Butadiene		
			Conv.	Selec.	Yield
15	Fe_3O_4	530	55	72	40
16	Fe_3O_4+0.2% Na_2SO_4	515	62	85	53
17	Fe_3O_4+5.0% Na_2SO_4	525	73	80	58
18	Fe_3O_4+1% Na_3PO_4	525	77	81	63
19	Fe_3O_4+0.5% NaOH	520	75	81	61
20	Fe_3O_4+0.3% LiOH	520	76	81	62
21	Fe_3O_4+0.3% KOH	520	67	81	54

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 organic compounds selected from the group consisting of hydrocarbons and nitriles 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. said organic compound having a



group with oxygen in a molar ratio of greater than one-fourth mol of oxygen per mol of said organic compound, bromine in an amount of less than 0.5 mol of bromine per mol of said organic 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 organic 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) metals or compounds thereof of Periodic Table Group VIII*b*.

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

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

4. The method of claim **1** wherein the said organic 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 the 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 in 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.

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 metal compound of a Group VIII*b* metal and mixtures thereof.

11. The method of claim **1** wherein the metal of said (2) comprises iron.

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

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

14. The method of claim **10** wherein the said (2) comprises iron oxide.

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DELBERT E. GANTZ, *Primary Examiner.*

G. E. SCHMITKONS, *Assistant Examiner.*