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OXIDATIVE DEHYDROGENATION PROCESS

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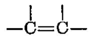
12 Claims. (Cl. 260—680)

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 Hyrocarbons," 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.

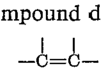
It has been found recently that a great variety of dehydrogenatable organic compounds may be dehydrogenated by reacting a mixture of an organic compound containing at least one pair of adjacent carbon atoms, each of which possess at least one hydrogen atom, iodine or an iodine-liberating material, and 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



$$-\overset{|}{C}=\overset{|}{C}-$$

or $-C\equiv C-$ grouping.

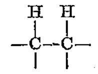
I have found, quite unexpectedly, that this process may be improved so that increased selectivities and yields of unsaturated organic compound derivatives containing the



$$-\overset{|}{C}=\overset{|}{C}-$$

or $-C\equiv C-$ 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 a metal or compound thereof of Periodic Table Group III*b*.[1]

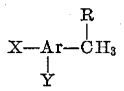
The process of this invention can be applied to a great variety of organic compounds to obtain the corresponding unsaturated derivative thereof. Such compounds normally will contain from 2 to 20 carbon atoms, at least one



$$-\underset{|}{\overset{\overset{H}{|}}{C}}-\underset{|}{\overset{\overset{H}{|}}{C}}-$$

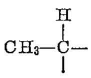
grouping, that is, adjacent carbon atoms each containing at least one hydrogen atom and having a boiling point below about 350° C. Such compounds may contain in addition to carbon and hydrogen, oxygen, halogens, nitrogen and sulphur. Among the classes of organic compounds which are dehydrogenated by 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, isopropylbenezene 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 contiguous nonquaternary 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



$$X-\underset{\underset{Y}{|}}{Ar}-\overset{\overset{R}{|}}{C}H_3$$

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



$$CH_3-\underset{|}{\overset{\overset{H}{|}}{C}}-$$

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

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.

Usefud 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 hereinfter. 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, CI_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 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 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 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 commerical considerations and normally will be greater than abut 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 actalyst 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 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 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 of any cations in the surface, such as at least 80 atomic percent of any metal cations in the surface.

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[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).

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 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 the 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 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 I*a* and II*a* per atom of the elements from the second specified group, such as from or about 0.01 or 0.02 to 0.5 atom of Group I*a* and II*a* per atom of the elements from the second specified group.

A great variety of metals or metal compounds of III*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 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., 45–56% La_2O_3, 1–2% CeO_2, 9–10% Pr_6O_{11}, 33–33% 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 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 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 combined with didymium oxide or rare earth oxides.

In Examples 1 and 2 a tubular Vycor[3] reactor, filled with 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 specified examples. The organic compound and oxygen are added at the top of the reactor, the hydrogen iodide is added to this stream as it enters the reactor and the steam is added separately opposite this stream. The results are reported as mol percent conversion, selectivity and yield of desired unsaturated product per pass. All other percentages are by weight percent, unless expressed otherwise.

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[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.

Examples 1 and 2

Cerium oxide was deposited on 6 mm. Vycor Raschig rings from a water slurry and another similar slurry containing 2.5 percent lithium hydroxide based on the oxide was added thereto and deposited on Raschig rings and both materials were air dried. The contact masses were placed in Vycor reactors equipped with an external electric furnace, and butene-2, oxygen, steam and hydrogen iodide were fed into the reactor at a flow rate of ½ 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 0.025 mol of molecular iodine. The reaction temperatures are set forth in the table below. The results obtained reported in terms of butadiene-1,3 and conversion, selectivity and yield are shown in the table as C/S/Y.

Example No.	Coating	Temperatures	
		500° C. C/S/Y	550° C. C/S/Y
1	Ceric Oxide		72/90/65
2	Ceric Oxide plus 2.5% LiOH	76/94/71	83/94/78

These data demonstrate that the use of a small amount of lithium hydroxide improves the yield of butadiene over an active surface such as ceric oxide with iodine at a given temperature, and more important, that lower temperatures may be used with the alkali metal compounded active surface to obtain the same yield as obtained at higher temperatures when the noncompounded contact mass is employed. Good results are also obtained when the ceric oxide contains 5 percent calcium oxide. When this example is repeated with elemental iodine, ethyl iodide and ammonium iodide, similar results are obtained.

When Example 1 above is repeated at 650° C. with the ceric oxide-lithium hydroxide contact mass, with 0.05 mol 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 Examples 1 and 2 above are repeated with other contact masses such as mixtures of cerium chloride, lithium oxide and calcium oxide, good yields of butadiene-1,3 are obtained from butene.

Example 3

A contact mass was 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 were 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 was dehydrogenated over this contact mass at a temperature of 700° C. 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), 0.03 mol of I_2 supplied as a 47 percent solution of hydrogen iodide in water, 0.7 mol of oxygen, and 12.5 mols of steam. A yield of 94 percent butadiene-1,3 per pass was obtained at a conversion of 100 percent and selectivity of 94 percent. A similar contact mass containing thorium oxide alone prepared in the same way and evaluated under the same reaction conditions gave a yield of 55 percent butadiene-1,3 at lower conversion and selectivity. 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 4

Another solid contact mass was prepared from uranium nitrate and lithium chloride. The contact mass was prepared by adding lithium chloride to an aqueous uranium nitrate solution in an amount so that the catalyst contained 15 percent lithium chloride based on uranium oxide. ¼ inch Vycor Raschig rings were coated with this solution by evaporation to deposit the solid contact mass. Eight inches of the contact mass was used in the one-inch internal diameter Vycor tubular reactor and the mass was heated in air to convert the uranium nitrate to uranium oxide. Butene was 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, 0.03 mol of iodine supplied as aqueous hydrogen iodide of 47 percent concentration. The butene was converted to butadiene-1,3 at a yield of greater than 60 percent. When the run was repeated with a catalyst consisting of uranium oxide alone, less butadiene-1,3 per pass was obtained. When this example was 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 5

n-Butane was dehydrogenated to a mixture of butadiene-1,3 and butene (ratio of butadiene to butene in the effluent is approximately 50 to 1) at a selectivity of 64 percent. The catalyst comprised a mixture of rare earth compounds together with CaO. The catalyst was rare earth hydrate (Lindsay Code 201) which contained (by weight calculated as the oxides) approximately 76 percent CeO_2, 4 percent of a mixture of other rare earth oxides, thoria of less than .25 percent, and 2 percent CaO. Also present was sulfur, phosphorus and silica in amounts of 1 percent each, calculated as SO_3, P_2O_5 and SiO_2. Iodine (as an aqueous solution of HI) was 0.144 mol, oxygen was 1.5 mol and steam was 15 mols respectively per mol of butane. The l.v./v./hr. was ½ for a flow rate of butane of 0.11 ltr./min. STP and the reactor temperature was 600° C.

Example 6

Butene-2 was dehydrogenated using a catalyst of the same composition as in Example 5. Iodine was fed as an aqueous solution equivalent to .009 mol I_2, the reactor temperature was 625° C. and the l.v./v./hr. was 1.0. The ratios were: 7.5 mols of steam and 1.25 mols of oxygen per mol of butene-2. The selectivity was 86 percent and the yield 82 percent.

Examples 7 to 9

2-ethylhexene-1 is dehydrogenated to a mixture of aromatics (dehydrocyclization). First, a comparative run was made employing CaO alone, and then CeO_2 was added to show the improvement resulting from the addition of CeO_2.

Example 7

2-ethylhexene-1 is fed to a one-inch diameter Vycor reactor together with 1.0 mol of oxygen, 0.14 mol I_2 (fed as aqueous hydrogen iodide) and 10 mols of steam per mol of 2-ethylhexene-1. The catalyst was CaO deposited from a water slurry on 6 mm. x 6 mm. Vycor Raschig rings. The LHSV was 0.5 (based on the 100 ml. catalyst bed) and the reactor temperature was 500° C. The selectivity to aromatics was 30 percent based on the 2-ethylhexene-1 fed. The product distribution was 29 percent toluene, 13 percent ethyl benzene, 35 percent p-xylene, 18 percent o-xylene and 6 percent styrene.

Example 8

Example 7 is repeated with the exception that the catalyst contains CeO_2 and 90 percent by weight CaO based on the weight of CeO_2. The selectivity to aromatics was 44 percent with the product distribution of 23 percent toluene, 10 percent ethyl benzene, 39 percent p-xylene, 16 percent o-xylene and 6 percent styrene.

Example 9

Example 7 is repeated with the exception that the catalyst is CeO_2 mixed with 10 percent CaO by weight of the CeO_2. The selectivity to aromatics is 56 percent with the product distribution being 20 percent toluene, 16 percent ethyl benzene, 40 percent p-xylene, 17 percent o-xylene and 8 percent styrene.

Example 10

n-Butane was dehydrogenated with a $CeCl_3$-$CaCl_2$ mixture. The ratios were 0.05 I_2 (fed as HI), 20 helium and 1.25 oxygen per mole of butane. The LHSV was 0.2 and the reaction temperature was 525° C. The selectivity is 79 percent.

Example 11

Example 10 was repeated with the exception that LiCl was substituted for the $CaCl_2$ and the reactor temperature was 550° C. The selectivity was 76 percent.

Example 12

Propionitrile was dehydrogenated to acrylonitrile in a Vycor reactor. The catalyst was a mixture of CeO_2 containing approximately 2 weight percent CaO and 1 percent MgO based on the total. A mixture of 5 mols of air and 0.04 mol of I_2 (fed as HI) per mol of propionitrile was fed to the reactor. At a maximum temperature in the reactor of 675° C. the conversion was 82 percent, the selectivity was 72 percent and the yield of acrylonitrile was 59 mol percent.

Examples 13 and 14

To further show the effect of the combination catalyst containing a metal element from Group I*a* and II*a* together with an element of the defined second component comparative examples were made.

The runs were made in a Vycor reactor which was one inch internal diameter; the overall length of the reactor was about 36 inches with the middle 24 inches of the reactor being encompassed by a heating furnace; the bottom 6 inches of the reactor was empty; at the top of this 6 inches was a retaining plate, and on top of this plate were placed 16 inches of the catalyst particles. The catalyst particles were prepared by coating the designated catalytic compounds on ¼ x ¼ inch Vycor Raschig rings by pouring a thin aqueous slurry of the catalytic compound through the 16 inches of rings contained in the reactor. This procedure was repeated several times until the rings were thoroughly coated with the catalyst. The coated rings were then dried in the reactor under a stream of nitrogen at a reactor temperature of appoximately 500° C. On top of the dried catalyst particles were placed 6 inches of uncoated ¼ x ¼ inch Vycor Raschig rings to form a preheat zone. The flow rates were calculated on the volume of the 16 inch long by one inch diameter portion of the reactor which was at or near the reaction temperature and was filled with catalyst particles. At a 700° C. maximum bed temperature, butene-2 of a purity of at least 99 mol percent was dehydrogenated to butadiene-1,3. The flow rate of butene-2 was maintained at one liquid volume of butene-2 (calculated at 0° C. and 760 mm. mercury) per volume of the 16 inch section of the reactor packed with catalyst which was at or near the reaction temperature per hour (liquid v./v./hr.). The flow rate of butene-2 was 0.22 liters per minute (calculated at 0° C. and 760 mm. mercury). Oxygen and steam were also fed to the reactor at a mol ratio of oxygen to butene-2 of 0.85, and a mol ratio of steam to butene-2 of 16. Hydrogen iodide was added as a 19 weight percent aqueous solution at a rate which is equivalent to 0.017 mol of iodine (calculated as I_2) per mol of butene-2. The steam, butene-2, oxygen and aqueous solution of hydrogen iodide were added at the top of the reactor. The conversion of butene-2 is reported as mol percent, the percent selectivity to butadiene-1,3 and the resulting yields of butadiene-1,3 are reported as mol percent of butadiene-1,3 based on the amount of butene-2 fed to the reactor.

Example 13

The catalyst was La_2O_3. The conversion was 94 percent, the selectivity was 86 percent and the yield was 81 percent.

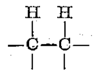
Example 14

Example 13 was repeated with the exception that the catalytic coating on the Vycor rings consisted of by weight 95 percent La_2O_3 and 5 percent CaO. The conversion was 96 percent, the selectivity was 97 percent and the yield was 93 percent.

The process of this invention is particularly applicable to the dehydrogenation of hydrocarbons, including dehydroisomerization and hebydrocyclization, 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



$$-\overset{H}{\underset{|}{\overset{|}{C}}}-\overset{H}{\underset{|}{\overset{|}{C}}}-$$

group with oxygen in a molar ratio of greater than one-fourth mol of oxygen per mol of said organic compound, iodine in an amount of less than about 0.2 mol of iodine per mol of said organic 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 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) an inorganic compound of a metal selected from the Periodic Table Group III*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 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) an inorganic compound selected from the group consisting of metals of Periodic Table Group III*b* 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.

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