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IN THE PRESENCE OF IODINE
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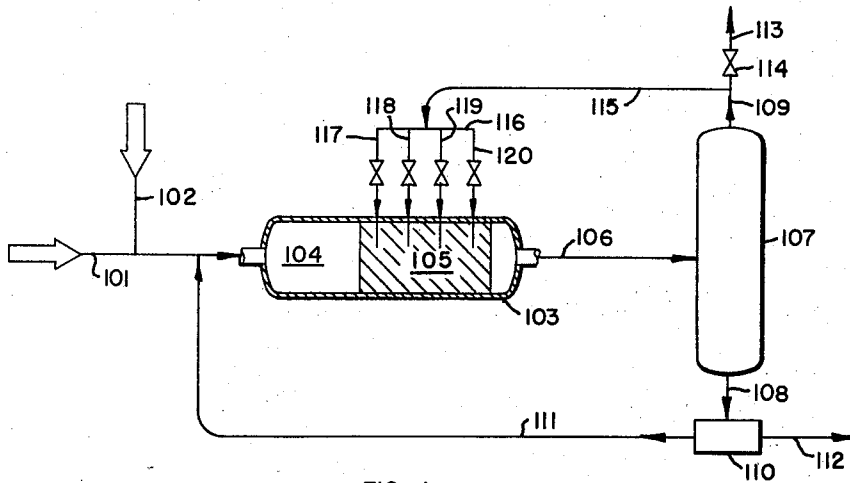


FIG. 1

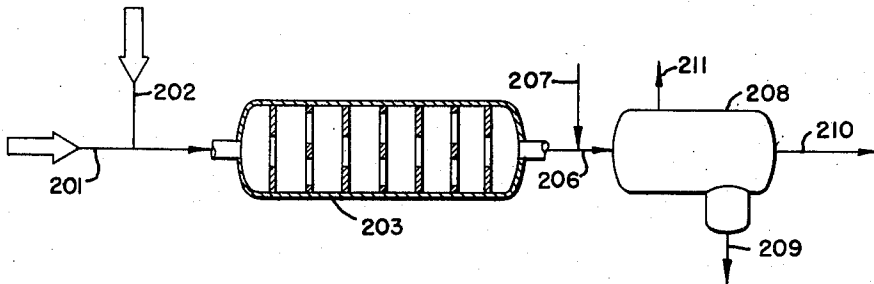


FIG. 2

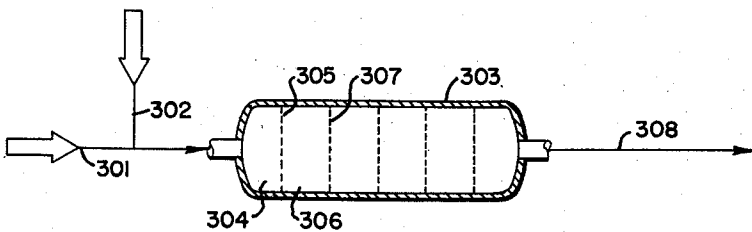


FIG. 3

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1

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CATALYTIC PROCESS FOR CONVERSION OF HYDROCARBONS IN THE PRESENCE OF IODINE

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17 Claims. (Cl. 260-666)

This invention relates to an improved process for the conversion of hydrocarbons, including the breaking of carbon-to-hydrogen bonds. It relates more particularly to an improvement in the conversion of hydrocarbons by reaction at an elevated temperature in the presence of iodine.

It is a principal object of this invention to provide an improved process for the conversion of hydrocarbons containing at least two carbon atoms and containing non-aromatic carbon-to-hydrogen bonds to different hydrocarbons having a different carbon-to-carbon linkage and a higher carbon to hydrogen ratio. Specific objects of the invention are to dehydrogenate aliphatic saturated hydrocarbons to aliphatic olefins and diolefins and alicyclic saturated hydrocarbons to cyclic olefins and aromatics, and to dehydrocyclize aliphatic hydrocarbons to aromatics. These objects will be more fully understood and others will become apparent from the description of the invention.

Briefly, the present invention is directed to a process for converting hydrocarbons containing at least two carbon atoms and containing non-aromatic carbon-to-hydrogen bonds to different hydrocarbons having a different carbon-to-carbon linkage and a higher carbon-to-hydrogen ratio by contact with iodine at an elevated temperature, and particularly to the improvement in said process which comprises contacting a mixture comprising said first named hydrocarbon and hydrogen iodide with a catalyst capable of converting hydrogen iodide to elemental iodine and hydrogen at an elevated temperature in vapor phase to produce a mixture comprising said first named hydrocarbon and iodine, and forming in said mixture, at reaction conditions, said different hydrocarbon and hydrogen iodide.

The invention will be described by reference to the accompanying drawing, wherein Figs. 1 to 3 thereof are schematic representations of several modes of carrying out the process of the invention.

It has been found, as disclosed in copending U.S. application Serial No. 489,301 of J. H. Raley, filed February 18, 1955, that new or different carbon-to-carbon linkages can be formed in an efficient manner by subjecting a mixture of a hydrocarbon containing at least two carbon atoms and containing non-aromatic carbon-to-hydrogen bonds and a reactive proportion of free iodine to an elevated temperature sufficient to effect a C-to-H bond cleavage in the molecule in the presence of free iodine. The new linkages may include, inter alia, one or more unsaturated linkages and/or a cyclic structure and/or a higher molecular weight structure and/or a new structure having a different number of carbon atoms bonded directly to a given carbon atom.

The breaking of a C-to-H bond in the presence of a reactive proportion of free iodine occurs under suitable conditions with the reaction of an iodine atom with the hydrogen atom to form a molecule of hydrogen iodide. To convert one aliphatic to a corresponding olefinic bond

2

it is necessary to remove two hydrogen atoms; two atoms of iodine are, therefore, required. Similarly, to convert cyclohexane to benzene six hydrogen atoms must be removed and six atoms of iodine are required per molecule, and to convert normal hexane to benzene eight hydrogen atoms must be removed and eight iodine atoms are required per molecule.

It has now been found that the amount of iodine which is required to be charged with the compound to be converted can be substantially reduced by subjecting the reaction mixture containing the original and the converted compound and resulting hydrogen iodide in vapor phase to contact with a catalyst capable of converting hydrogen iodide to elemental iodine and hydrogen, at conditions suitable for such conversion, and permitting the resulting elemental iodine to convert additional portions of the charge hydrocarbon by subjecting the new mixture to suitable conversion conditions.

The process of the present invention has wide application for the conversion of various types of hydrocarbons to related hydrocarbons having at least one different carbon-to-carbon linkage. Thus, alkanes of at least two carbon atoms can be dehydrogenated to alkenes. For example, ethane can be dehydrogenated to ethene; propane to propene; isobutane to isobutene, and the like. Alkanes having a chain of at least three carbon atoms can be dehydrogenated to alkadienes. For instance, propane can be dehydrogenated to allene, n-butane to butadiene-1,3, and n-pentane and isopentane to the corresponding penta-dienes. Various hydrocarbons may be dehydrocoupled through acyclic carbon atoms. For instance, propylene can be dehydrocoupled to give di-allyl, and isobutylene to give di-methallyl. Acyclic hydrocarbons containing in a chain at least six contiguous non-quaternary carbon atoms, whether saturated or unsaturated, can be cyclized, often with aromatization. For example, n-hexane can be dehydroaromatized to benzene; n-heptane to toluene; n-octane to o-xylene and ethylbenzene; 2,5-dimethylhexane to p-xylene; hexadiene-1,3 to benzene; hexene-1 to cyclohexane; and the like. As disclosed and claimed in copending U.S. application Serial No. 489,303 of J. H. Raley and R. D. Mullineaux, filed February 18, 1955, acyclic hydrocarbons containing at least six carbon atoms, one of which is a quaternary carbon atom, can be structurally isomerized and/or dealkylated to change the quaternary C-atom to a non-quaternary C-atom. For example, 2,2,5-trimethylhexane can be demethylated and dehydroaromatized to give p-xylene and also dehydroisomerized with demethylation and aromatization to give m-xylene. Instead of all of the carbon atoms being acyclic, as in the preceding illustrative examples, the acyclic carbon atoms which are involved in the conversion and the formation of a new carbon-to-carbon bond, as already indicated, can be in one or more acyclic hydrocarbon radicals attached to a cyclic nucleus, such as an aromatic nucleus. In that case, one or more of the cyclic carbon atoms may be involved in the conversion when it involves the formation of a new ring, such as an aromatic ring. For example, ethylbenzene can be dehydrogenated to styrene; toluene dehydrocoupled to dibenzyl and stilbene; o-diethylbenzene dehydroaromatized to naphthalene; orthomethylpropylbenzene dehydroaromatized to naphthalene; o-methylethylbenzene dehydrogenated to o-methylstyrene; n-butylbenzene dehydrogenated to 4-phenylbutadiene-1,3, and dehydroaromatized to naphthalene; 2,3-diethylnaphthalene to anthracene; butylcyclohexane to naphthalene; and butylcyclopentane to indene. Further, the reaction with iodine is suitably employed in the dehydrogenation of hydroaromatic cyclic hydrocarbons, e.g. the conversion of cyclohexane to

cyclohexene or benzene, of methylcyclohexane to toluene and the like.

The conversion to iodine of hydrogen iodide present in the total reaction mixture containing some unconverted hydrocarbon charge as well as some hydrocarbon conversion product is particularly useful for those reactions having high theoretical iodine requirements, e.g. the dehydrocyclization of paraffins and the dehydrogenation of naphthenes to aromatics. Thus, to convert one pound of normal hexane to benzene theoretically requires 11.8 pounds of iodine. Under practical conditions somewhat more diiodine may be required. The price of iodine being well in excess of one dollar per pound, it is seen that, even when completely efficient recovery of the resulting hydrogen iodide from the products, reconversion thereof to iodine and reuse of the iodine is accomplished, an expensive inventory of iodine would be required to apply the process on a commercial scale; in the alternative, to avoid a large iodine inventory, a low conversion per pass would have to be used and large amounts of unconverted feed hydrocarbon separated from the products and recycled.

By operating in accordance with the present invention, each atom of iodine charged serves to remove more than one atom of hydrogen from the original hydrocarbon charge without intermediate separation of hydrogen iodide, thus substantially reducing the amount of free iodine which must be charged to obtain substantially complete conversion of the charge hydrocarbon or, conversely, permitting greatly increased conversion per pass when charging a relatively small proportion of iodine.

The conditions for carrying out the process of this invention may be selected such that in the absence of the iodine there would be only a relatively low rate and amount of dehydrogenation. The conditions, of course, depend on the particular compound being converted, as well as upon the hydrocarbon which it is desired to obtain as principal product. Thus, the temperature required for the dehydrogenation or dehydrocyclization of hydrocarbons is at least about 300° C., generally being at least about 350° C., and usually preferably in the order of about 400 to 600° C., although higher temperatures may be utilized up to about 800° C. Higher temperatures are not objectionable so long as other undesirable changes are not effected. However, excessively high temperatures are not required in order to effect reaction in the presence of the substantial proportion of iodine. In the case of less thermally stable substances, the temperature is more suitably adjusted within the lower range of values, such as about 350° to 500° C., and in some cases it may be as low as about 300° to 350° C. Conversely, in the case of more thermally stable substances, such as the lower molecular weight hydrocarbons, such as ethane and propane, the temperature is more suitably adjusted at the higher range of values, such as about 550–600° C., and it can even be as high as 600–800° C.

The process is suitably carried out at various pressures, from subatmospheric to superatmospheric pressures in vapor phase. Although atmospheric pressure is suitable and is advantageous in most cases, other considerations, such as factors which are involved in the separation and recovery of the hydrogen iodide and hydrocarbon products from the product stream, in some cases make a superatmospheric pressure more desirable. Thus, the pressure can be at any value at which the reactants are sufficiently vaporized at a temperature at which the hydrocarbon is substantially thermally stable. The pressure employed is preferably in the range between 1 and 10 atmospheres, absolute, but may be as high as 30 atmospheres and even higher.

The residence time of the reactants at the selected reaction conditions depends upon the particular hydrocarbon reactant, the proportion of iodine in the reaction mixture, the temperature and pressure, and the nature of the dehydrogenation product. In general it should be at

least about 0.01 second, and usually at least about 0.1 second, while usually it should be not over about one minute, but it may be as much as 3 to 5 minutes. In some instances the dehydrogenation is very rapid, so that a minimum residence time suffices.

An important factor in the practice of the invention is the carrying out of the conversion in the presence of a substantial proportion of free iodine. Although it is generally preferable to employ elemental iodine as the iodine species charged to the reaction zone with the hydrocarbon feed, the iodine may also be employed in the form of certain of its compounds. Hydrogen iodide may suitably be employed as at least a part of the charge, since it will be converted to iodine by the catalyst. Iodine compounds which liberate iodine under the reaction conditions, e.g. alkyl iodides; including polyiodides, aralkyl iodides, and the like, may also be employed.

The amount of iodine stoichiometrically required to convert a given amount of reactant entirely into the corresponding desired product is referred to as the theoretically required amount and will be designated "one theory" of iodine. Thus, in the conversion of one gram mol of C_4H_{10} to C_4H_6 by means of iodine, one theory of iodine is one gram mol of I_2 . In the conversion of one gram mol of C_4H_{10} to C_4H_8 , one theory of iodine is two gram mols of I_2 .

The conversion of a charge hydrocarbon may be carried substantially to completion or conversion may be held to a relatively low value, e.g. 10 to 20% in a single pass through the reaction zone.

The amount of elemental iodine charged with the feed to the reaction zone should be at least about 0.05 mole of iodine per mole of hydrocarbon to be converted. At the more severe reaction conditions, e.g. higher temperatures and longer residence times and with the higher molecular weight hydrocarbon feeds, the amount of iodine to be charged should be at least 0.1 to 0.2 mole per mole of hydrocarbon. By maintaining such a minimum ratio, undesirable side reactions such as thermal cracking are substantially completely avoided.

In those reactions in which aromatics are produced, it is not ordinarily necessary to provide more than one theory of iodine for the overall reaction, and a preferred range of total elemental iodine applied is between 0.025 and 1.0 theory. A substantially greater proportion of elemental iodine is desirable, e.g., up to 3 or 4 theories, in the reactions involving dehydrogenation without aromatization, in which excess iodine tends to suppress the reverse reaction of hydrogen iodide with the dehydrogenated product.

By virtue of the internal or "in situ" reconversion of HI to I_2 , the amount of elemental iodine which is required to be charged with the feed to the reaction zone is substantially less than the amount which would be required for the same conversion of charge hydrocarbon in the absence of said reconversion. The percentage of the stoichiometric iodine requirement which is charged as elemental iodine with the feed to the reaction zone is determined by the efficiency of the internal reconversion of HI to iodine. This can be affected at will, to a considerable extent, by the choice of the type and amount of catalyst and by the manner in which the catalyst is arranged in the reaction zone. Economic factors are considered in balancing the various conditions.

In the preferred mode of carrying out the present invention the conversion of the charge stock by means of elemental iodine and the reconversion of hydrogen iodide to elemental iodine and hydrogen are both carried out in a single vessel maintained at a single set of reaction conditions of temperature and pressure. The temperatures and pressures given above which are suitable for the conversion of a compound by dehydrogenation or dehydrocyclization in the presence of elemental iodine are also suitable for the catalytic conversion of hydrogen iodide

5

6

to elemental iodine and hydrogen. It is pointed out below, by means of examples, that different catalysts vary in their effectiveness in converting HI to I_2 and H_2 . The amount of conversion with a given catalyst may be increased by choosing a longer contact time at a given temperature or a higher temperature at a given contact time, within the ranges stated.

Suitable catalysts for use in the present invention for the conversion of HI to I_2 and H_2 are metals and metal iodides which are stable under the reaction conditions. The catalysts can be employed without support or they can be supported on a suitable porous solid of high surface area. The support should preferably have no appreciable hydrocarbon cracking activity in order to avoid converting the charge hydrocarbon to undesired by-products. Suitable supports are high surface area silica and high surface area alumina. In general, solids of substantially no surface acidity are suitable catalyst supports. Some solids of high surface area and substantially no acidic cracking activity may also be employed as catalysts without any added catalytic metal or metal compound. High surface area alumina exhibits appreciable catalytic activity, but high surface area silica shows only little catalytic activity. Suitable metals, which can be employed either supported on a porous solid or unsupported in suitable forms such as wire gauze, wire, strip, filings, shavings, and the like, include the noble metals, especially platinum, palladium, and rhodium. Substantial catalytic activity is exhibited by an alloy of nickel, molybdenum, iron and chromium, commercially available under the designation "Hastelloy C." Metal iodides which may suitably be employed as catalyst are FeI_2 , Cu_2I_2 , PbI_2 , VI_2 , CrI_2 , and MnI_2 .

A preferred catalyst for use in the present invention is platinum, either unsupported in the form of platinum wire or gauze or the like, or supported in concentrations, e.g., between 0.1 and 1% by weight and suitably between 0.2 and 0.5%, on a porous solid of high surface area, e.g., between 80 and 500 square meters per gram, which exhibits essentially no cracking activity, such as substantially pure alumina or substantially pure silica.

During the course of reaction, small amounts of carbonaceous decomposition product of the hydrocarbon reactants may be deposited on the catalyst, thus gradually reducing catalyst activity. When this occurs, the flow of feed is temporarily interrupted and the catalyst is reactivated by "burning off" the carbonaceous deposit by means of a free oxygen containing gas, e.g. air, or an inert gas such as nitrogen or flue gas to which a controlled amount of oxygen is added. Regeneration temperatures are suitably maintained between 500° and 900° C., conveniently at or near the temperature at which the conversion reaction is carried out. Some catalysts, e.g. those employing a porous alumina support, deteriorate at excessively high regeneration temperatures whereas others, e.g. platinum gauze, are readily regenerated, without damage, at very high temperatures.

The present invention will be further illustrated by means of Figs. 1, 2 and 3 which illustrate suitable modes for practicing the invention.

Referring to Fig. 1, the chosen feed compound, for example, n-hexane to be converted to benzene, is charged through line 101. Elemental iodine is added to the feed from an outside source through line 102 if desired, and from a source to be described below through line 111, if desired. The amount of elemental iodine added is suitably 0.4 theory, i.e. 1.6 moles of I_2 per mole of hexane charged (calculated on the reaction $C_6H_{14} \rightarrow C_6H_6 + 8H$). The mixture of iodine and normal hexane then enters reactor 103. The mixture entering the reactor is in vapor phase at a temperature, suitably, of 500° C., having been heated and vaporized by means not shown. The temperature in reactor 103 is maintained at about 500° C. The mixture first enters reaction zone 104, which is an empty space in which a partial conversion of hexane to benzene

takes place, thus producing a mixture comprising unconverted hexane, benzene, and hydrogen iodide, which may still contain some unconverted elemental iodine. This mixture then enters zone 105 of reactor 103 which is packed with a fixed bed of catalyst, suitably pellets of 0.25% by wt. platinum supported on silica-free alumina having a surface area of about 100 sq. meter/gram. In zone 105, part of the hydrogen iodide produced previously is reconverted to elemental iodine which then reacts with additional portions of the hexane feed to produce additional benzene. Additional hydrogen iodide may be introduced into zone 105 through valved lines 117, 118, 119 and 120 from a source described below. If this is done, the amount of elemental iodine added through lines 102 and/or 111 is adjusted downward so that the total amount of iodine species remains at the desired value, i.e. about 0.4 theory. The reaction mixture leaves reactor 103 through line 106 where it may be cooled somewhat by means not shown, and then enters distillation vessel 107 which may be a conventional distillation column, such as a packed column, bubble plate column or the like.

From column 107 an overhead stream comprising essentially hydrogen iodide may be taken through line 109 and a bottoms stream comprising benzene product, unconverted hexane feed, other hydrocarbon products if produced, and elemental iodine in solution, may be taken through line 108 and passed to a separator 110 in which iodine is separated from the hydrocarbons by suitable means e.g., fractional distillation. The iodine free hydrocarbon stream is then passed through line 112 to further separating means, not shown, to recover benzene product, unconverted hexane which may be returned to line 101, and other hydrocarbon products if formed. Elemental iodine from separator 110 may be returned to line 101 through line 111. The hydrogen iodide taken off in line 109 may be discarded or sent to regeneration and iodine separating means, not shown, via line 113 by opening valve 114, or it may be returned to reactor 103 by passing it through line 115 to manifold 116 which is connected to valved lines 117, 118, 119 and 120.

Since the overhead from column 107 contains hydrogen formed in the reaction zone as well as HI, it will be necessary to remove at least a bleed stream by line 113, periodically or continuously, to separate the hydrogen and discard it from the system in order to avoid build-up of an excessive concentration of hydrogen. Alternatively, a means for separating hydrogen from HI may be included in line 115. The separation of hydrogen from HI can be carried out by dissolving HI in a solvent, e.g. water, by distillation, by adsorption of HI on a solid, e.g. calcium oxide, or in other suitable manner; the HI is recovered by regeneration of the solvent or adsorbent.

A different arrangement of the reactor and of the product recovery system is shown in Fig. 2, which represents a schematic flow diagram of another mode of operating in accordance with the present invention. A feed to be converted which may be, for example, butane to be converted to butenes and 1,3-butadiene is charged through line 201. Elemental iodine is added to line 201 via line 202. The mixture of butane and iodine from line 201 is then passed into reactor 203. The mixture enters the reactor in vapor form at an elevated temperature, suitably 550° C. Reactor 203 is a vessel, e.g. a cylindrical vessel or pipe, lined internally with a catalytic metal, e.g. "Hastelloy C." The vessel is shown, in this example, to contain an internal baffling arrangement, such as disc and donut contactors, to provide added turbulence to force the reaction mixture against the catalytic surface of the reactor. The proportion of elemental iodine added is suitably about 0.6 theory (for conversion of butane to butadiene), i.e., 1.2 moles of iodine per mole of n-butane.

In reactor 203 the iodine and butane are maintained

at about 550° C. by heating means not shown and react to produce butenes, butadiene and HI. The HI reacts at the catalytic surface of the reactor to form I₂ and H₂, and the I₂ so formed converts further amounts of butane or butenes. The mixture leaving reactor 203, entering line 206, contains butenes, butadiene and butane and may contain HI and I₂ in varied proportions. This mixture is promptly contacted with a liquid to remove at least the HI. A suitable liquid, added through line 207, is, for example, 30% aqueous solution of HI. The total mixture enters separating vessel 208 from which an aqueous phase containing HI and I₂ is withdrawn through line 209 and a hydrocarbon phase containing butane, butenes, and butadiene and other reaction products, if formed, is withdrawn through line 210. Hydrogen formed in the reaction zone is withdrawn through

regeneration, or "burning," of catalyst is conventional in numerous catalytic processes and methods of carrying it out are well known.

The methods of recovering product and iodine-containing material from the reactor effluent, illustrated in Figs. 1 and 2, are merely presented as examples of suitable ways of operating. Other methods of product work-up may be employed.

EXAMPLE I

The catalytic activity of a number of materials for the conversion reaction: $\text{HI} \rightarrow \text{I}_2 + \text{H}_2$ was determined by passing hydrogen iodide gas through a tube maintained at an elevated temperature and containing a portion of the material to be tested. The results of eleven runs on a variety of materials are summarized in Table I.

Table I

Run No.	Metal	Form	Porous Solid	Surface Area of Porous Solid, m. ² /g.	Temperature, ° C.	Time of Contact, Seconds	Conversion $\text{HI} \rightarrow \text{I}_2 + \text{H}_2$, Percent	Percent of Equilibrium conversion at same conditions
1	None		None		485	10	0.1	.45
2	None		SiO ₂	331	485	16	1.8	8
3	None		Al ₂ O ₃	109	485	4	9	41
4	Pt.	Supported	SiO ₂	331	485	<0.9	22	100
5	Pt.	do.	Al ₂ O ₃	109	485	<0.9	22	100
6	Rh.	do.	Al ₂ O ₃	109	485	<0.9	22	100
7	Pt.	Strip			485	4	9	41
8	Pd (1st run)	do.			485	5	12	55
9	Pd (Later run)	do.			485	16	6	27
10	Au.	do.			485	6	0.7	3
11	Ag.	do.			555	6	2	8

line 211 and discarded from the system. The aqueous solution from line 209 can be worked up to recover HI and I₂ therefrom, which may be returned for further use. The hydrocarbon mixture in line 210 is worked up in a system not shown, e.g., by distillation, to recover the desired product and unconverted feed which may, if desired, be returned to line 201.

A further modification of the reactor suitable for use in the present invention is shown in Fig. 3. A suitable feed, for example, cyclohexane to be converted to benzene, is added through line 301 and iodine is added through line 302. One half theory of iodine, i.e., 1.5 moles per mole of cyclohexane, is employed. The mixture of feed and iodine in vaporized form enters reactor 303 in which the catalyst is arranged in the form of a metal gauze, e.g., platinum gauze, stretched across the reactor at intervals. Thus, reaction takes place between the feed and iodine in the first reactor space, 304, HI produced in the first space is converted to I₂ and H₂ by platinum gauze 305, further reaction takes place in the next empty reactor space 306, and further conversion of HI to I₂ and H₂ takes place on the second platinum gauze 307 and so forth. The mixture of reaction product, HI, I₂ and unconverted feed, if any, leaves the reactor through line 308 for suitable workup in accordance, for example, with one of the methods shown in Figs. 1 and 2.

Figs. 1, 2 and 3 are schematic representations of suitable flow arrangements. Necessary equipment such as valves, pumps, heaters, coolers, and the like have not been shown and their placement will be readily apparent to those skilled in the art. Other equivalent methods of arranging the catalyst in the reaction zone may be employed. For example, wire gauze 305, 307, etc. in Fig. 3 may be replaced by a packed section containing supported catalyst. It is not necessary that the catalyst be present in a fixed bed, but it may suitably be employed as a fluidized bed of finely divided particles or as a moving bed of pelleted particles in accordance with methods well known to the art.

To simplify presentation, the separate lines and valves, etc. required in catalyst regeneration are not shown. Such

All of these runs, except run 11 were carried out at a temperature of 485° C. At this temperature the conversion of HI to elemental iodine and hydrogen reaches an equilibrium of 22%.

Equilibrium conversion was attained in a contact time of less than nine-tenths of a second in runs Nos. 4, 5 and 6 in which the catalytic material, respectively, was 0.25 weight percent platinum supported on silica, 0.25 weight percent platinum supported on alumina, and 0.25 weight percent rhodium supported on alumina. Alumina with no catalytic metal added was a quite effective catalyst as shown in run 3 where 41% of equilibrium conversion was reached in 4 seconds. Of the non-supported metals, platinum gave 41% of equilibrium conversion in 4 seconds, palladium, in run 9, showed 55% of equilibrium conversion in 5 seconds. In a later run however, run 10, the activity of the same palladium had declined substantially. A very small amount of conversion was caused by silica gel of high surface area in run 2 and by unsupported silver in run 12. In the later run, made at 555° C., it was observed that the silver was gradually converted to silver iodide which melted in the reaction zone. Theoretical equilibrium at 555° C. is 24%. Unsupported gold gave only 3% of equilibrium conversion in 6 seconds. All of the above runs are compared with run No. 1, the non-catalytic reaction in an empty tube, in which only 0.45% of equilibrium conversion was attained in 10 seconds.

EXAMPLE II

In Table 2 are presented the reaction conditions employed and the results obtained in runs Nos. 12, 13 and 14 in which normal heptane was charged as the hydrocarbon, admixed with 0.47 theory, 0.39 theory and 0.46 theory of iodine, respectively. The theory is calculated on the reaction $\text{C}_7\text{H}_{16} + 4\text{I}_2 \rightarrow \text{C}_7\text{H}_8 + 8\text{HI}$. In run No. 12 the reaction zone was an unobstructed space. In run No. 13 the reaction zone was packed with a catalyst of 0.25% wt. platinum oxide supported on silica having an overall surface area of 295 sq. meters/gram. The arrangement of catalyst in the reactor was approximately as shown in Fig. 1. In run No. 14 the catalyst was a mixture of platinum gauze, platinum wire, and platinum strip. This was

arranged in two separate packed sections in the reactor, each preceded and followed by an empty reaction zone, the four sections being of approximately equal volume.

Table 2

Run No.	12	13	14
Temperature, °C.	507	488	498
Pressure, mm. Hg.	760	760	760
Residence Time, Seconds	8.5	12.5	20.5
Catalyst	none	Platinum on Silica gel	Pt, unsupported
Surface area, m. ² /g.		295	<<1
I ₂ /C ₇ H ₁₆ mole ratio	1.89	1.56	1.83
Theory of iodine ^a	0.47	0.39	0.46
Conversion:			
C ₇ H ₁₆ , percent	55.6	66.2	73.7
I ₂ , percent	99.8	93.8	95.6
Product, moles/100 moles C ₇ H ₁₆ fed:			
Toluene	43.4	48.7	51.8
Benzene	5.8	7.6	8.8
Total aromatics	49.2	56.3	60.6
C ₇ olefin	0.8	3.2	2.4
C ₁ -C ₅ (C ₇ equivalent)	1.7	3.0	3.4
H ₂	1.8	90.5	59.8
Residue (C ₇ equivalent)	0.7	2.0	0.2
Coke (C ₇ equivalent)	0.0	0.9	
Loss (C ₇ equivalent)	4.0	2.0	6.8
Aromatics yield, basis I ₂ reacted, percent ^b	104	154	139
Aromatization efficiency, percent ^c	88.6	85.0	82.3

^a Based on reaction $C_7H_{16} + 4I_2 \rightarrow C_7H_8 + 8HI$.

^b 100% yield corresponds to 1 mole aromatics/4 moles I₂ reacted.

^c Moles aromatic/100 moles C₇H₁₆ reacted.

From the results of runs 12 through 14 it is seen that in the check run No. 12, without the use of catalyst, approximately 50% of aromatics was produced; in run No. 14, in which the theory of iodine employed was approximately the same as in No. 12, the amount of aromatics produced was in excess of 60%, the increase amounting to 20% of the aromatics produced in the former run. In run No. 13 the theory of iodine employed was appreciably less, but the amount of aromatics produced was still in excess of 56%. The aromatics yield in check run No. 12, calculated on the basis of the amount of iodine reacted, was 104%; in run No. 13 the aromatics yield was 154%, showing that on the average one atom of iodine removed 1.5 atoms of hydrogen; and in run No. 14 the aromatics yield was 139%, showing that on the average one atom of iodine removed approximately 1.4 atoms of hydrogen. By suitable choice of reaction conditions, catalyst and reactor geometry, the efficiency of iodine utilization can be further substantially improved over the results shown in these runs.

In a blank run, employing the same conditions as run No. 14 including the same arrangement of unsupported platinum metal in the reactor, but excluding iodine, no significant amount of the feed was converted to aromatic hydrocarbons.

We claim as our invention:

1. A process for converting a first hydrocarbon containing at least two carbon atoms and containing non-aromatic carbon-to-hydrogen bonds into at least a second different hydrocarbon containing a new carbon-to-carbon linkage and having a higher carbon-to-hydrogen ratio which comprises contacting in a reaction zone a mixture comprising said first hydrocarbon and hydrogen iodide in vapor phase at a temperature in the range from 300° to 800° C. with a catalyst capable of converting hydrogen iodide to elemental iodine and hydrogen, said catalyst being selected from the group consisting of platinum, palladium, rhodium and nickel-molybdenum-iron-chromium alloy to produce a mixture comprising said first hydrocarbon and iodine and subjecting the later mixture in at least one reaction zone which may comprise the aforementioned reaction zone to conditions including a temperature in the range from 300° to 800° C. suitable for conversion of said first hydrocarbon and iodine to at least said second hydrocarbon and hydrogen iodide

whereby the ultimate yield of said second hydrocarbon is at least about 140% of the stoichiometric amount based on the amount of originally charged iodine reacted.

2. A process according to claim 1 in which the first-mentioned mixture comprising said first hydrocarbon and hydrogen iodide is the product of contacting said first hydrocarbon with iodine at conditions suitable for conversion thereof to at least said second hydrocarbon and hydrogen iodide.

3. A process according to claim 1 in which the steps of conversion of the mixture comprising said first hydrocarbon and iodine and conversion of hydrogen iodide are repeated in succession.

4. A process according to claim 1 in which said first said hydrocarbon is an alkane.

5. A process according to claim 1 in which said first hydrocarbon is an alkene of at least 3 carbon atoms.

6. A process according to claim 1 in which said first hydrocarbon is an arylalkane.

7. A process according to claim 1 in which said first hydrocarbon is a cycloparaffin.

8. A process according to claim 1 in which said catalyst comprises a catalytic amount of platinum.

9. A process according to claim 1 in which said catalyst comprises essentially platinum supported on a non-acidic porous support of substantially no cracking activity.

10. A process according to claim 1 in which said catalyst comprises a catalytic amount of palladium.

11. A process according to claim 1 in which said catalyst comprises a catalytic amount of rhodium.

12. A process according to claim 1 in which said catalyst comprises a catalytic amount of a nickel-molybdenum-iron-chromium alloy.

13. A process for converting a first hydrocarbon containing at least two carbon atoms and containing non-aromatic carbon-to-hydrogen bonds into at least a second different hydrocarbon containing a new carbon-to-carbon linkage and having a higher carbon-to-hydrogen ratio which comprises contacting in a reaction zone a mixture comprising said first hydrocarbon and between 0.05 and 0.8 theory of elemental iodine, the amount of the elemental iodine in said mixture also being at least 0.1 mole of iodine per mole of hydrocarbon, at an elevated temperature in the range from 300° to 800° C. in vapor phase to convert at least a substantial proportion of said mixture into at least said second hydrocarbon and hydrogen iodide, subjecting the resulting mixture comprising both said first and said second hydrocarbon and hydrogen iodide to contact with a catalyst capable of converting hydrogen iodide in a separate reaction zone to elemental iodine and hydrogen, said catalyst being selected from the group consisting of platinum, palladium, rhodium and nickel-molybdenum-iron-chromium alloy, at a temperature in the range from 300° to 800° C. in vapor phase, to produce a new mixture comprising said first and second compound and elemental iodine and subjecting said new mixture in at least one reaction zone which may comprise said second-named reaction zone to conditions including a temperature in the range from 300° to 800° C. for further conversion of said first compound and iodine to at least said second compound and hydrogen iodide whereby the ultimate yield of said second hydrocarbon is at least about 140% of the stoichiometric amount based on the amount of originally charged iodine reacted.

14. A process according to claim 13 in which said catalyst comprises a catalytic amount of platinum.

15. A process for converting a first hydrocarbon containing at least two carbon atoms and containing non-aromatic carbon-to-hydrogen bonds into at least a second different hydrocarbon containing a new carbon-to-carbon linkage and having a higher carbon-to-hydrogen ratio which comprises contacting in a reaction zone containing a catalyst selected from the group consisting of platinum, palladium, rhodium and nickel-molybdenum-iron-chro-

mium alloy in vapor phase at a temperature in the range from 300° to 800° C. a mixture comprising at least said first hydrocarbon and at least 0.1 mole of elemental iodine per mole of hydrocarbon whereby said first hydrocarbon is converted to said second hydrocarbon and hydrogen iodide and whereby in said same reaction zone hydrogen iodide resulting from said reaction is converted to elemental iodine and hydrogen and said elemental iodine reacts with further amounts of said first hydrocarbon, the conversion of the mixture comprising said first hydrocarbon and iodine and the conversion of hydrogen iodide to elemental iodine and hydrogen taking place simultaneously in said reaction zone, and recovering from said reaction zone a product comprising said second hydrocarbon in an amount at least equivalent to about 140% of the stoichiometric equivalent of the amount of elemental iodine originally converted.

16. A process for converting an alkane containing at least two carbon atoms per molecule into a second hydrocarbon having a higher carbon-to-hydrogen ratio which comprises passing into a reaction zone containing a catalyst containing as its essential catalytic ingredient platinum supported on a non-acidic porous support of substantially no cracking activity a mixture comprising said alkane and between 0.05 and 0.8 theory of elemental iodine and subjecting the mixture in vapor phase to a temperature in the range from 300° to 800° C. to convert said alkane and iodine to at least said second hydrocarbon and hydrogen iodide and to convert hydrogen iodide to elemental iodine and hydrogen in the presence of

said catalyst and withdrawing from said reaction zone the resulting reaction mixture comprising said second hydrocarbon in an amount which is at least 140% of the stoichiometric equivalent of the amount of elemental iodine.

17. A process in accordance with claim 16 in which said alkane contains six contiguous non-quaternary carbon atoms in a chain and said second hydrocarbon is an aromatic hydrocarbon.

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