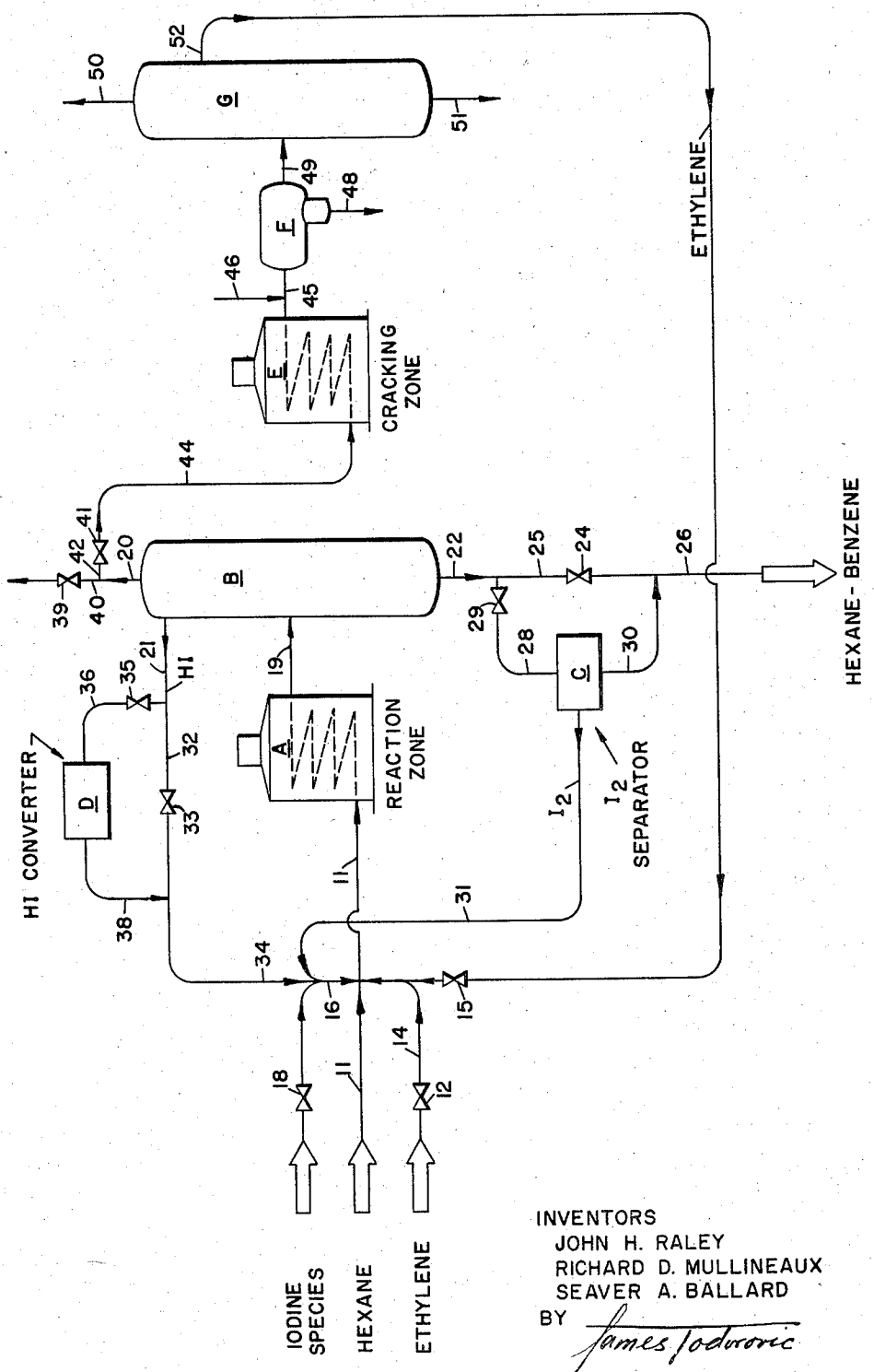
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HYDROCARBON CONVERSION PROCESS

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HYDROCARBON CONVERSION PROCESS

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

It is a principal object of this invention to provide an improved process for the conversion of hydrocarbons containing at least three 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. Another object is to provide an improved process for the formation of one or more new or different carbon-to-carbon bonds between contiguous carbon atoms in a given molecule to produce an olefinic, acetylenic, or aromatic bond. Specific objects of the invention are to dehydrogenate aliphatic saturated hydrocarbons to aliphatic olefins and diolefins, alicyclic saturated hydrocarbons to cyclic olefins and aromatics, and alkyl aromatics having side chains of two or more carbon atoms to the corresponding aromatics with olefinic side chains, 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 having at least three carbon atoms per molecule 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 in the presence of a hydrogen accepting olefin.

The invention will be described by reference to the accompanying drawing wherein the single figure thereof is a schematic representation of a mode 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. Heating of the compound at an elevated temperature in the presence of free iodine effects C-to-H bond cleavage in the molecule, with the resultant formation of one or more new or different C-to-C linkages to produce, 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.

In the presence of iodine as reactant the breaking of a C-to-H bond normally occurs with the reaction of an atom of iodine with the hydrogen atom to form a molecule of hydrogen iodide. To convert one aliphatic to a corresponding olefinic bond in accordance with the above-described process it is necessary to remove two hydrogen atoms, and 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 in the conversion of hydrocarbons having at least three carbon atoms per molecule the amount of iodine required to be charged with the hydrocarbon to be converted can be substantially reduced by adding to the mixture of charge hydrocarbon and iodine species a substantial amount of a hydrogen accepting olefin. Said olefin ultimately is converted to a saturated hydrocarbon by addition of the hydrogen removed from the charge hydrocarbon while the latter is converted in the process to a compound having a higher carbon-to-hydrogen ratio. In the absence of hydrogen accepting olefin, substantially all hydrogen removed from the hydrocarbon adds to the iodine to form HI. In the presence of said olefin at least part of the hydrogen adds to the olefin, thus reducing the amount of hydrogen that must be accepted by iodine for a given total removal of hydrogen from the charge. The present invention, therefore, reduces the iodine requirement of the process or, conversely, permits the production of a greater amount of the desired product per unit weight of iodine employed.

The process of the present invention has wide application in the conversion of various types of hydrocarbons to related hydrocarbons having at least one different carbon-to-carbon linkage and a higher carbon-to-hydrogen ratio. Thus, alkanes of at least three carbon atoms can be dehydrogenated to alkenes, alkadienes and acetylenes. For example, isobutane can be dehydrogenated to isobutene, n-butane to butene-1, butene-2 and butadiene-1,3 and n-pentane and isopentane to the corresponding pentenes and pentadienes. Various hydrocarbons may be coupled through acyclic carbon atoms. For instance, propylene can be dehydrocoupled to give di-allyl and isobutylene dehydrocoupled to give di-methallyl. Acyclic hydrocarbons containing 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 in-

volved 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; ortho-methylpropylbenzene 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 use of a hydrogen accepting olefin, according to the present invention, 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 merely in the presence of iodine theoretically requires 11.8 pounds of iodine. Under practical conditions somewhat more iodine 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 is required to apply the process on a commercial scale; or, in the alternative, to avoid a large iodine inventory, a low conversion per pass must 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, thus substantially reducing the amount of free iodine which must be charged to obtain substantially complete conversion of the charge hydrocarbon or, conversely, permitting increased conversion per pass when charging a relatively small proportion of iodine.

It is believed that in the present process the hydrogen does not pass directly from the feed hydrocarbon to the hydrogen accepting olefin, but rather that hydrogen is abstracted from the feed hydrocarbon by an iodine atom to form HI, and HI interacts with the hydrogen accepting olefin to produce the corresponding saturated hydrocarbon and elemental iodine. Therefore, it is possible to carry out the present process by adding the major amount of iodine to the reaction zone in the form of HI, but at least a small amount of I_2 is preferably present in the initial reaction mixture. The present invention is not to be construed as limited by the above-described reaction mechanism.

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 well as iodine compounds which liberate iodine under the reaction conditions. Such compounds are, for example, the alkyl iodides, including polyiodides, aralkyl iodides, and the like.

The suitability of any particular olefin for use as hydrogen acceptor in a reaction in accordance with the present invention is readily determined as follows:

A compound "A" is to be converted by reaction in the presence of iodine into a compound "B" having a higher carbon-to-hydrogen ratio, i.e., the reaction involves dehydrogenation; an olefin "R" is to be employed as hydrogen acceptor, being converted in the reaction to a hydrogenated compound "RH_2." The reactions involved may be written as shown in Equations 1 and 2 below, where "(g)" signifies that the component is in the gaseous state.

(1) $A(g) \rightarrow B(g) + xH_2(g)$ $\Delta F_1 = m$

(2) $xR(g) + xH_2(g) \rightarrow xRH_2(g)$ $\Delta F_2 = n$

ΔF_1 is the standard free energy change of the reaction of Equation 1 and ΔF_2 the standard free energy change of the reaction of Equation 2. This may be expressed, for example, in kilogram calories per gram mole; for most common compounds this value is found in, or readily calculated from, thermodynamic tables, e.g., the tables published by the American Petroleum Institute (API), Research Project 44, entitled "Selected Values of Properties of Hydrocarbons and Related Compounds," Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa., October 31, 1954. If the algebraic sum of ΔF_1 and ΔF_2 is a negative number (i.e., $m+n<0$), then the olefin "R" is suitable as a hydrogen acceptor in the reaction. Since the free energy for a given reaction varies with the temperature, ΔF_1 and ΔF_2 must be taken at the desired reaction temperature. In cases where compound "A" in Equation 1 is a non-aromatic compound and compound "B" is an aromatic one, the standard free energy change ΔF_1 is a large negative number at temperatures suitable for the present reaction. For most commonly occurring olefins, ΔF_2 at the same temperature is a relatively small positive or negative number. Therefore, in reactions where an aromatic is produced, the algebraic sum of the standard free energies generally is negative regardless of the particular olefin employed as hydrogen acceptor. In those cases where Reaction 1 represents the conversion of a paraffin to an olefin or diolefin or the conversion of a monoolefin to a diolefin, ΔF_1 will generally be a relatively small negative number and the choice of the olefine "R" is, therefore, more limited. It will usually be an olefin having a lower number of carbon atoms than compound "A" and of no greater degree of branching than compound "A."

To illustrate the above relationship and calculations, assume that it is desired to determine whether or not ethylene is suitable as hydrogen acceptor in the conversion of propane to propylene by means of iodine at a temperature of 527° C. (800° K.). The equations are set up as follows:

(1) $C_3H_8(g) \rightarrow C_3H_6(g) + H_2(g)$

(2) $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

To determine the standard free energy change of the Reaction 1, i.e., ΔF_1, the standard free energies of formation of the several compounds are read from the appropriate API Project 44 tables as follows (taking the values at 800° K.):

$\Delta F_f°$ of C_3H_8 = +30.45 Kcal.

$\Delta F_f°$ of C_3H_6 = +34.81 Kcal.

$\Delta F_f°$ of C_2H_4 = +24.49 Kcal.

$\Delta F_f°$ of C_2H_6 = +15.92 Kcal.

$\Delta F_f°$ of H_2 = 0 Kcal. (by definition).

The ΔF of an equation is the algebraic sum of the $\Delta F_f°$ values of the products minus the algebraic sum of the $\Delta F_f°$ values of the reactants. Hence

$\Delta F_1 = 34.81 - 30.45 = +4.36$ Kcal.

$\Delta F_2 = 15.92 - 24.49 - 0 = -8.57$ Kcal.

and $\Delta F_1 + \Delta F_2 = -4.21$ Kcal.

Thus, the above-described condition is met, namely, the sum of the standard free energy changes is a negative

value, and it is concluded that ethylene is a suitable hydrogen acceptor in the conversion of propane to propylene. When charge compounds of greater numbers of carbon atoms are to be converted, a separate equation is written for each compound formed as product of the reaction, and the criterion of summing the ΔF values is separately applied to each of these equations as Equation 1.

For convenience of terminology, the term "hydrogen accepting olefin" is employed herein to designate an olefin suitable for accepting hydrogen in the conversion of a particular compound, as determined by the above-stated criteria.

Ethylene is the preferred hydrogen accepting olefin for use in the present invention. Thermodynamically, it is the most suitable one because at any given temperature the free energy change of the conversion of ethylene to ethane is a lower positive or greater negative number than that for the corresponding conversion of any other olefin. Ethylene has further considerable advantages for use in the present invention in that it and its hydrogenation product, ethane, are less subject to cracking than the olefins of higher molecular weight. Similarly, ethylene is less subject to ready conversion by any other reaction in the presence of iodine than higher molecular weight olefins which may be converted into more highly unsaturated compounds by reaction with iodine under the reaction conditions normally employed.

Propylene is a suitable olefin for use in many reactions in accordance with the present invention, particularly where compound "B" in Equation 1, supra, is an aromatic hydrocarbon. The ΔF_2 for propylene is about 4 kilocalories greater (i.e., more positive) than for ethylene, at temperatures in the range employed in the present invention. Next to ethylene, propylene is preferably employed, but any other olefin, such as butene-1, butene-2, isobutene, a normal or branched pentene, hexene, or higher olefin may be employed, always provided that it meets the criterion set out supra.

The olefin employed as hydrogen acceptor need not be charged in pure form. Mixtures of olefins, e.g., a mixed ethylenepropylene stream, may be employed. The olefin may also be charged in admixture with hydrocarbons which are relatively inert under reaction conditions, e.g., ethylene may be charged in admixture with methane and/or ethane. Since the effectiveness of the olefin as hydrogen acceptor depends on the equilibrium between the olefin and the corresponding paraffin, the presence of the corresponding paraffin in the feed will tend to suppress this reaction and such paraffin is therefore preferably held to a relatively low concentration in the olefin charge stream.

The olefin employed as hydrogen acceptor in the present process may be derived from any convenient source. Thermal and catalytic cracking of petroleum hydrocarbons furnishes large amounts of olefins in most petroleum refineries. Ethylene may be recovered from cracked gases or it may be produced and recovered by any of numerous known processes, e.g., those discussed in "Petroleum Refiner," vol. 20, No. 9, pp. 220–225 (September 1951).

The olefin employed as hydrogen acceptor may desirably be regenerated from the corresponding paraffin recovered from the total reaction products. For example, when ethylene is employed as the hydrogen accepting olefin, a C_2 stream comprising ethylene and ethane is recovered by distillation or separation from the other reaction products and this stream may then be charged to an ethane cracking zone operating, e.g., at temperatures in the range from 700° to 850° C., preferably between 760° and 820° C., at pressures ranging from subatmospheric to about 50 p.s.i., and at contact times of less than one second. A C_2 stream comprising a high concentration of ethylene is separated from heavier byproducts of the cracking reaction and may be directly charged back to the conversion step of the present invention, or the ethylene may be further purified and concentrated prior to being recycled.

The conditions for carrying out the conversion step 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 depend on the particular compound to be converted, on the hydrocarbon which it is desired to obtain as principal product, and on the compound selected as hydrogen accepting olefin.

In the conversion of hydrocarbons to corresponding olefins, diolefins and aromatics by reaction with iodine, the temperature required is at least 300° C., generally being at least about 350° C. and usually preferably in the range between 400° and 600° C., although higher temperatures may be utilized, e.g., up to 700° C. or higher where the molecular weight of the hydrocarbons in the system is relatively low, e.g., up to C_4. The 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 suitable dehydrogenation or dehydrocyclization in the presence of iodine and hydrogen accepting olefin. In the case of less thermally stable charge substances, such as hydrocarbons having six or more carbon atoms per molecule, the temperature is suitably adjusted in the range between 400° and 575° C. The higher temperatures, e.g., between 450° and 575° C. may be employed when ethylene is the hydrogen accepting olefin and somewhat lower temperatures, e.g., between 400° and 550° C. when another olefin is the hydrogen acceptor. With feeds of lower molecular weight, e.g., C_3 through C_5, the hydrogen accepting olefin employed will generally be ethylene and the preferred temperature range for these systems is between 500° and 600° 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 reactor effluent stream make a superatmospheric pressure more desirable in some cases. 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 proportions of iodine and hydrogen accepting olefin 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 not be over about 1 minute, but it may be as much as 3 to 5 minutes. With most common reactants the dehydrogenation is very rapid so that a residence time from 0.1 to 10 seconds suffices and is preferred.

The ratio of hydrogen accepting olefin to the hydrocarbon to be converted in the present reaction, which may be designated as hydrogen donor, may be varied over a wide range. This ratio may be expressed in theoretical equivalents of the hydrogen accepting olefin; one theoretical equivalent, commonly referred to, for convenience, as one "theory," is the number of moles required to accept the hydrogen liberated in the conversion of one mole of the hydrogen donor. The ratio employed may suitably vary from 0.1 to 10 theories of hydrogen accepting olefin, and is preferably in the range between 1 and 5 theories. In selecting the ratio of hydrogen accepting olefin to hydrogen donor it is generally preferred not to exceed a volume ratio of olefin to donor

of about 20:1. For example, in the complete conversion of n-hexane to benzene:

(1) $C_6H_{14} \rightarrow C_6H_6 + 8H$

(2) $4C_nH_{2n} + 8H \rightarrow 4C_nH_{2n+2}$

one theory of olefin is four moles per mole of hexane. In vapor phase, the volume ratio is the same as the mole ratio; hence a volume ratio of 20:1 (the maximum referred to above) equals 20 moles of olefin per mole of hexane, or 20/4=5 theories of olefin.

The amount of iodine employed may also, for convenience, be expressed in theories. The "theory" or theoretical equivalent of iodine is calculated on the basis of iodine acting as hydrogen acceptor, i.e., ignoring the hydrogen accepting olefin in the system. For example, to convert one gram molecular weight of n-hexane to benzene requires eight gram atomic weights, or four gram molecular weights, of elemental iodine (I_2); one theory of iodine in that reaction is, therefore, four moles per mole of n-hexane. The number of theories of iodine species charged in the present reaction is suitably in the range from 0.01 to 0.8, and preferably from 0.1 to 0.6 theory. When less than one theory of hydrogen accepting olefin is employed the amount of iodine species required is in the higher part of the range; whereas, when the amount of hydrogen accepting olefin is two or more theories the amount of the iodine may be selected in the lower part of the suitable range. 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.

Advantage may be taken in the present invention of the catalytic decomposition of hydrogen iodide to iodine and hydrogen within the reaction zone, as disclosed in detail in copending patent application Serial No. 563,660, of the present applicants, filed on February 6, 1956. Suitable catalysts are the noble metals, e.g., platinum or rhodium, either unsupported or on a suitable porous support, such as silica gel. By virtue of such decomposition the amount of iodine required to be charged is reduced and may be within the lower part of the ranges stated above.

The present invention will be illustrated by means of the drawing, which shows a schematic flow scheme of one method of operating the process. For the sake of illustration, n-hexane is assumed to be the charge hydrocarbon, to be converted into benzene by reaction with iodine in the presence of ethylene as hydrogen accepting olefin. Hexane is charged through line **11**, from a source not shown. Ethylene is added to line **11** by opening valve **12** in line **14** or valve **15** in line **52**, the former supplying ethylene from an outside source, not shown, and the latter supplying it from a source described below. Two theories of ethylene are suitably added in this manner, i.e., 8 moles of ethylene per mole of hexane. Active iodine species is added to line **11** through line **16**. This may include elemental iodine added through line **31** from a source described below, HI or elemental iodine added through line **34** from another source described below and makeup elemental iodine, HI, or alkyl iodide added to line **16** by opening valve **18**. The mixture of hexane, ethylene and iodine species in line **11** may be vaporized and preheated by separate equipment, not shown, and is then introduced into reaction zone A, which may be a heated vessel or coil, in which the mixture is maintained at a temperature in the range between 500° and 550° C. for from 2 to 10 seconds. The reactor effluent is withdrawn through line **19** and then passed to fractionator B, which may be a conventional packed column or bubble plate distillation column with the conventional associated equipment including a reboiler and reflux condenser. Prior to entering distillation column B, the mixture may be cooled somewhat by indirect heat exchange in a heat exchanger, not shown, in line **19**. In fractionator B the reactor effluent is separated to withdraw as overhead, through line **20**, a stream comprising essentially ethane and ethylene, as distillate, through line **21** a stream comprising essentially hydrogen iodine, and as bottoms through line **22** the total liquid hydrocarbons including hexane, benzene produced in the reaction and other hydrocarbon products which may have been produced to a small extent, including hexene. The liquid hydrocarbon bottoms also may contain elemental iodine present in the effluent in line **19**. If the stream in line **22** contains substantially no iodine, valve **24** in bypass line **25** is opened and the total hydrocarbon withdrawn through line **26** for further work-up, including separation of unconverted hexane from the reaction products. The hexane may be recycled to line **11**. If the stream in line **22** contains elemental iodine it is passed to line **28** by closing valve **24** and opening valve **29** and is introduced by line **28** into iodine separator C in which the iodine is separated from the hydrocarbon stream by suitable means, e.g., by fractional distillation. Hydrocarbon is then returned to line **26** via line **30**. The iodine recovered in the separator is returned to the process via lines **31** and **16**.

The hydrogen iodide in line **21** may be returned for use in the process in the form of hydrogen iodide by lines **21, 32, 34** and **16** on opening valve **33**, or the hydrogen iodide may be passed to HI converter D by closing valve **33** and opening valve **35** in line **36**. In HI converter D, elemental iodine is recovered from the HI by suitable means, e.g., by oxidation of the HI with chlorine to regenerate elemental iodine, which is then returned to the process via lines **38, 34** and **16**.

The C_2 stream in line **20** may be discarded from the system by opening valve **39** in line **40** or it may be returned for reuse by opening valve **41** in line **42** to pass the ethane through line **44** into cracking zone E which is operated at a temperature of approximately 820° C. with a very short contact time to produce a mixture of ethane and ethylene. Effluent from cracking zone E has its temperature rapidly reduced by direct heat exchange with a suitable quench, such as water, introduced via line **46** and is then passed through line **45** into phase separator F where an aqueous layer is separated and withdrawn via line **48** and the hydrocarbon via line **49**. From line **49** the hydrocarbon stream is passed to separator G which may represent fractional distillation, adsorption or absorption equipment in which lighter material than ethylene is removed by line **50**, heavier material by line **51** and an ethylene stream by line **52** for return to line **11**. The ethylene may be highly purified in separator G, but a substantial amount of ethane may be retained in it without seriously affecting the effectiveness of the ethylene as hydrogen accepting olefin.

In the drawing and description of the process, much necessary auxiliary equipment such as valves, pumps, heat exchangers, and the like has not been shown in order to simplify presentation of the process. The location of such equipment will be apparent to those skilled in the art.

The description of the process given above in connection with the drawing is for illustrative purposes only and not to be considered a limitation on the process of the present invention. Different methods of recovering the reactor effluent and separating hydrogen iodide, iodine and reaction products therefrom may be employed.

The invention will be further illustrated by means of the following example: Two runs were made in which normal butane, diluted with a small amount of helium, was charged to a reaction zone in the presence of ele-

mental iodine and ethylene. The reaction conditions for the runs, designated runs 1 and 2, and the essential results obtained are presented in Table I.

Table I

Run No.	1	A	2	B
Temperature, °C	550	550	600	600
Pressure, mm. Hg	950	760	1,000	760
Residence time, seconds	2.2	2.2	2	2
Diluent Mole/mole feed (C_4)	He 0.063		He 0.066	
I_2/C_4H_{10} Mole ratio	0.215	0.215	0.36	0.36
Theories of I_2[a]	0.215	0.215	0.36	0.36
C_2H_4/C_4H_{10} Mole ratio	0.48	0.0	0.53	0.0
Theories of C_2H_4[b]	0.48	0.0	0.53	0.0
Conversion of C_4H_{10}, Percent mole to:				
C_4H_8	16.0	19.0	43.8	34.0
C_4H_6	0.9	0.2	4.7	1.2
C_1–C_3 (C_4 equivalents)	2.3	0.0	7.3	0.0
Coke	0.0	0.0	<0.01	0.0
Loss	3.2	0.0	5.1	0.0
Total	22.4	19.2	60.91	35.2
Selectivity, percent mole	75–88	100	80–87	100
Conversion of C_2H_4 to C_2H_6, percent	~9.3		between 20 and 40	
Conversion of I_2, percent	100		99	

[a] Based on $C_4H_{10}+I_2 \rightarrow C_4H_8+2HI$.
[b] Based on $C_4H_{10}+C_2H_4 \rightarrow C_4H_8+C_2H_6$.

Run No. 1 was carried out at 550° C. with an iodine-to-butane mole ratio of 0.215 and an ethylene-to-butane mole ratio of 0.48. Run No. 2 was made at 600° C. with an iodine-to-butane mole ratio of 0.36 and ethylene-to-butane ratio of 0.53. Residence time was approximately two seconds in each run. The ratios of iodine and of ethylene-to-butane, expressed as theories, are based on the stoichiometric requirement for conversion of the butane to butylene, and are, therefore, numerically equal to the respective mole ratios. For purposes of comparison, Table I also shows runs A and B which represent the calculated maximum conversion obtainable in the absence of hydrogen accepting olefin at the reacting conditions of runs 1 and 2, respectively, as determined by thermodynamic equilibrium, assuming an inert diluent to be present in an amount equal to the ethylene employed in runs 1 and 2, respectively. In numerous actual experiments carried out in the absence of hydrogen accepting olefin, it has been found that the conversion actually obtained is on the order of 80% of thermodynamic equilibrium conversion at the condition of these runs.

The effectiveness of ethylene as hydrogen accepting olefin is indicated by the results shown for conversion of C_4H_{10} to C_4H_8 and C_4H_6. In run No. 1, 16.0% of butylenes was recovered compared to the theoretical maximum of 19.0% and compared to the normally obtainable 16%. Additional butylene produced is included in the 3.2% loss. Butadiene yield was increased to 0.9% from the theoretical maximum 0.2%. Under the somewhat more severe conditions of run No. 2, the normal butylenes yield substantially exceeded the yield theoretically possible with the amount of iodine charged in the absence of hydrogen accepting olefins; the actual yield was 43.8%, compared with a theoretical of 34.0%. Similarly, the butadiene yield exceeded very substantially the theoretical, being 4.7% compared with a theoretical, 1.2%, or nearly 400% of the theoretical butadiene yield.

The use of the small amount of helium diluent in these runs is for reasons not connected with the use of ethylene. Substantially identical results are obtained, in suitable equipment, when the helium diluent is omitted.

We claim as our invention:

1. A process for converting a first hydrocarbon containing at least three carbon atoms per moluecule and containing non-aromatic carbon-to-hydrogen bonds into at least a second hydrocarbon having a higher carbon-to-hydrogen ratio which comprises subjecting a vapor mixture comprising said first hydrocarbon, a hydrogen accepting olefin having a lower carbon number than said first hydrocarbon and a reactant iodine species in sufficient amount to furnish at least 0.05 mole of iodine per mole of said first hydrocarbon to a temperature of at least 300° C. to effect a C-to-H bond cleavage in said first hydrocarbon and conversion of at least part of said olefin to the corresponding paraffin, and recovering said second hydrocarbon.

2. A process according to claim 1 in which said first hydrocarbon is an aliphatic compound and said second hydrocarbon is an aliphatic compound having at least one more olefinic double bond.

3. A process according to claim 1 in which said first hydrocarbon is aliphatic and said second hydrocarbon is aromatic.

4. A process according to claim 1 in which said hydrogen accepting olefin is ethylene.

5. A process for converting a first hydrocarbon containing at least three carbon atoms per molecule and containing non-aromatic carbon-to-hydrogen bonds into at least a second hydrocarbon having a higher carbon-to-hydrogen ratio which comprises contacting a vapor mixture comprising said first hydrocarbon, at least 0.1 theory of a hydrogen accepting olefin having a lower carbon number than said first hydrocarbon and no less than 0.05 mole per mole of said first hydrocarbon but no more than 0.8 theory of elemental iodine at an elevated temperature in the range between 300° and 600° C. to effect a C-to-H bond cleavage in the molecule of said first hydrocarbon and conversion of at least part of said olefin to the corresponding paraffin, and recovering said second hydrocarbon.

6. A process according to claim 5 in which the temperature is in the range between 400° and 575° C., the contact time in the range between 0.1 and 10 seconds, the proportion of iodine in the range between 0.1 and 0.6 theory, and the proportion of said hydrogen accepting olefin in the range between 1 and 5 theories.

7. A process for converting normal butane into butylenes and butadiene which comprises contacting a mixture comprising butane, ethylene and at least 0.05 mole of iodine per mole normal butane at a temperature in the range between about 500° and 600° C. for a time in the range between 0.1 and 10 seconds and recovering from the reaction product at least butylenes and butadiene.

8. A process for converting acyclic hydrocarbons containing at least six contiguous nonquaternary carbon atoms to aromatics which comprises contacting a mixture of at least one of said hydrocarbons, ethylene and at least 0.2 mole of iodine per mole of acyclic hydrocarbon at a temperature in the range between 300° and 575° C. for a time in the range between 0.1 and 10 seconds whereby said acyclic hydrocarbons are converted to aromatic hydrocarbons and said ethylene to ethane.

9. A process for converting hydroaromatic cyclic hydrocarbons into aromatics which comprises contacting a mixture of at least one of said hydrocarbons, ethylene and at least 0.2 mole of iodine per mole of hydroaromatic cyclic hydrocarbon at a temperature in the range between 300° and 575° C. for a time in the range between 0.1 and 10 seconds whereby said hydroaromatic hydrocarbons are converted to aromatic hydrocarbons and ethylene to ethane.

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