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ISOMERIZATION OF HYDROCARBONS

Wilhelm Carel Brezesinska Smithuysen, Amsterdam, Netherlands, assignor to Shell Development Company, San Francisco, Calif., a corporation of Delaware

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This invention relates to the catalytic isomerization of hydrocarbons, and it particularly relates to the catalytic isomerization of the saturated paraffin hydrocarbons.

An object of the invention is to provide a practical and economical process, adapted to operation on a commercial scale, for the production of the commercially more valuable branched or more highly branched chain paraffin hydrocarbons from the corresponding normal or less branched chain paraffin hydrocarbons.

Another object of the invention is to provide a process for the catalytic isomerization of the normal and slightly branched chain paraffin hydrocarbons to the corresponding iso- or more highly branched chain hydrocarbons which is characterized by the use of a selective and particularly active isomerization catalyst which permits selective isomerization of the treated hydrocarbon or mixture of hydrocarbons under such conditions that practical conversions to the desired branched or more branched chain isomers are obtained while undesirable side reactions such as cracking, dehydrogenation, etc., are reduced to a practical minimum.

The process of the invention is of great technical importance in that it provides a simple and effective method for converting the less valuable, because less reactive, normal paraffin hydrocarbons to the corresponding more reactive and more valuable iso or branched chain paraffin hydrocarbons. The branched chain paraffin hydrocarbons which boil within the gasoline boiling range are, because of their relatively much higher anti-knock value, of greater value and in more demand than the normal hydrocarbons of the same number of carbon atoms for use as internal combustion motor fuel or as constituents of such fuel compositions. The process of the invention can be applied to the individual normal or only slightly branched chain paraffin hydrocarbons to increase their anti-knock value, or it may be applied directly to hydrocarbon fuel mixtures containing relatively high percentages of normal or only slightly branched paraffin hydrocarbons to isomerize said hydrocarbons and thus increase the total anti-knock value of the fuel mixture with a minimum of treatment and with substantially no loss of the treated material.

The lower boiling isoparaffin hydrocarbons such as isobutane, isopentane, the isohexanes, etc., are relatively much more valuable than the normal compounds of the same number of carbon atoms because of their greater activity per se and because of the much greater reactivity of

the corresponding olefines. The isoparaffin hydrocarbons can be easily dehydrogenated to the corresponding tertiary olefines which in turn are valuable starting materials in the production of tertiary alcohols, tertiary alcohol derivatives, unsaturated tertiary carbon atom-containing alcohols, etc., as well as in the production of high anti-knock motor fuels and motor fuel constituents via copolymerization, or interpolymerization with ethylene or secondary olefines, followed by hydrogenation of the resulting polymer product. The isoparaffin hydrocarbons are also much more suitable than the normal paraffin hydrocarbons as starting material in the production of motor fuels by alkylation, that is, by reaction of the paraffin hydrocarbon with an olefine in the presence of a suitable catalyst.

The process of my invention comprises contacting the hydrocarbon to be isomerized, or a mixture of such hydrocarbons, or one or more of such hydrocarbons in the presence of an inert diluent material incapable of isomerization such as aromatic hydrocarbons, substantially completely isomerized paraffin hydrocarbons, nitrogen, hydrogen, etc., with a catalyst consisting of or essentially comprising a double compound of an acid-acting metallic halide with an aromatic compound at a temperature at which the isomerization proceeds at a practical rate but at a temperature below 150° C., the material to be isomerized being contacted with the catalyst for a time sufficient to effect the desired isomerization but insufficient to effect any substantial decomposition such as cracking or dehydrogenation of the treated material.

By use of the special catalyst herein defined, the desired degree of isomerization can be effected while undesirable side reactions are reduced to a practical minimum, and, in some cases, substantially completely obviated. The special catalyst is, when used under the conditions herein specified, a selective isomerization catalyst, it accelerates substantially only the isomerization reaction and permits the isomerization to be effected rapidly and to the desired extent under conditions at which the occurrence of undesirable side reactions can be substantially obviated. It is known that aluminum chloride is a catalyst for the isomerization of paraffin hydrocarbons. However, this knowledge has failed to provide any technically feasible process for the isomerization of the normal paraffin hydrocarbons, particularly those which are normally liquid, to the isoparaffin hydrocarbons because of the fact that aluminum chloride per se is not

at all selective as regards the isomerization reaction. It is, under the conditions at which it acts as an isomerization catalyst, also an excellent cracking and dehydrogenation catalyst, and very frequently, its activity as a decomposition catalyst exceeds its activity as an isomerization catalyst with the result that only a minor amount of the treated material is isomerized, the remainder being converted to undesired decomposition products.

The treatment of hydrocarbons in accordance with the process of the invention has the apparent effect of displacing the end groups of the hydrocarbon molecule toward the center of the carbon chain; consequently the process can be advantageously applied to the treatment of any hydrocarbon possessing a structure capable of modifications in such a way as to result in a hydrocarbon molecule containing the same number of carbon atoms but being of a more condensed type. The process can be applied to the isomerization to an isoparaffin of any of the normal paraffin hydrocarbons higher than propane. The class of suitable normal paraffin hydrocarbons starts with normal butane, which is normally gaseous, and includes the normally liquid normal paraffin hydrocarbons such as normal pentane, normal hexane, normal heptane, normal octane, normal nonane and the like. Suitable already branched chain hydrocarbons which can be isomerized to still more branched chain hydrocarbons in accordance with the process of the invention may be pentanes, hexanes, heptanes, octanes, nonanes, etc. The hydrocarbons or hydrocarbon mixtures treated are preferably those which boil at a temperature not greater than about 100° C. and thus comprise the hydrocarbons with from four to seven carbon atoms inclusive.

For purposes of convenience and clearness of description only, the process will hereinafter be described with reference to its use to convert a normal paraffin hydrocarbon containing at least four carbon atoms to the corresponding isoparaffin hydrocarbon.

The process may be applied to the treatment of a pure or substantially pure normal paraffin hydrocarbon, or to a hydrocarbon mixture comprising one or more normal paraffin hydrocarbons. For example a suitable starting material may comprise, besides a substantial amount of a normal paraffin hydrocarbon, one or a plurality of other hydrocarbons which may not be capable of isomerization under the conditions of the operation, or the treated mixture may comprise one or more normal paraffin hydrocarbons and a substantially inert diluent material such as hydrogen, nitrogen and the like. The invention provides means for converting to isoparaffin hydrocarbons the normal paraffin hydrocarbon content of cracked gasolines and other commercial hydrocarbon mixtures such as are obtained by the cracking of higher molecular weight hydrocarbons and hydrocarbon mixtures such as petroleum oils, shale oils, petroleum products, animal and vegetable oils, waxes and the like. Conveniently treated normal paraffin hydrocarbon-containing mixtures are the so-called alkane-alkylene fractions such as the butane-butylene fraction, the pentane-pentylene fraction, etc. from which the olefines have preferably been removed. Treatment of such mixtures results in materially increasing their isoparaffin hydrocarbon content.

The catalysts used in the process essentially

comprise a double compound of an acid-acting halide and an aromatic compound. The term "acid-acting halide" is used herein and in the appended claims to designate those metallic or non-metallic halides (other than the hydrogen halides) which will give an acid reaction in water. Representative acid-acting halides are the boron halides, the halides of aluminum, zinc, iron, zirconium, tin, beryllium, and the like. The acid-acting halide is present in the catalyst as a double compound with an aromatic compound. These double compounds may be regarded as the additive compound of an acid-acting halide with an aromatic compound.

A preferred group of catalysts for use in the process of the invention comprises the double compounds of the aluminum halides (aluminum chloride, aluminum bromide, aluminum iodide and aluminum fluoride) with an aromatic hydrocarbon, particularly an aromatic hydrocarbon which has been substituted by one or more alkyl groups. Representative catalysts of this preferred group are the double compounds of an aluminum halide, preferably aluminum chloride, with an aromatic hydrocarbon such as toluene, dimethyl benzene, trimethyl benzene, ethyl benzene, triethyl benzene, propyl benzene, dipropyl benzene, the isopropyl benzenes, the normal butyl benzenes, the tertiary butyl benzenes, the amyl benzenes, the mixed alkyl benzenes such as ethyl toluene, dipropyl toluene, etc., the mono- and polymethyl naphthalenes, the mono- and polyethyl, propyl, butyl and the like alkyl naphthalenes, the mixed alkyl naphthalenes, the alkyl anthracenes, the alkenyl benzenes, naphthalenes, anthracenes, etc., the mixed alkyl-alkenyl benzenes, naphthalenes, anthracenes and the like, and their homologues, analogues and suitable substitution products.

The aluminum halide-aromatic hydrocarbon double compounds may, in general, be regarded as the additive compounds of two mols of the aluminum halide with one mol of the aromatic hydrocarbon which may or may not be alkyl and/or alkenyl substituted. A representative catalyst, namely, the double compound of an aluminum halide with a dialkyl benzene, may be represented by the formula $2Al(Hal)_3.C_6H_4(R)_2$, wherein R represents an alkyl radical.

The aluminum halide-aromatic hydrocarbon double compound catalysts may be prepared in any suitable manner. A convenient method of preparing the aluminum halide-alkylated aromatic hydrocarbon double compound catalysts comprises adding the preferably anhydrous aluminum halide to the liquid non-alkylated aromatic hydrocarbon such as benzene and adding to the mixture in a regulated amount the desired quantity of the alkyl halide corresponding to the alkyl radical which it is desired to substitute into the aromatic hydrocarbon. The alkyl halide is preferably added slowly while intensively agitating the reaction mixture, as by mechanical stirring, and while maintaining the reaction mixture at or below about 20° C. The aromatic hydrocarbon and the aluminum halide are preferably employed in excess of the alkyl halide. When all of the alkyl halide has been added, and the reaction is substantially complete, the excess of the aluminum halide and the unreacted aromatic hydrocarbon are separated. The resulting aluminum halide-alkylated aromatic hydrocarbon compound may then be used alone or in admixture with a dissimilar compound of the

same type in any suitable manner as hereinafter described.

The aluminum halide-alkylated aromatic hydrocarbon double compounds are in most cases more or less heavy liquid substances, and as such they can, when operation of the process in the liquid phase is desired, be easily added to and intimately contacted with the hydrocarbon material to be treated under the desired conditions of treatment. The catalyst material is quite stable and can be used at temperatures as high as 150° C. with substantially no decomposition or loss of activity. The catalysts are, however, unstable in the presence of water and consequently the presence of water during their preparation, storage and use should be avoided.

The process of the invention is executed at temperatures below 150° C. and preferably at temperatures of from 20° C. to 140° C. A favorable conversion of the treated hydrocarbon material is often obtained at room temperature or only slightly elevated temperatures. In general, temperatures equal to or higher than 150° C. are not suitable because at about this temperature the catalysts used in the process lose their selective isomerization power and begin to accelerate cracking and other decomposition reactions.

The process may be executed with the hydrocarbon compound to be treated in either the gaseous or the liquid phase. When operation in the liquid phase is desired, the hydrocarbon material to be treated and the catalyst may be charged to a suitable reaction vessel in the desired relative amounts and the mixture maintained at the desired temperature for a time necessary to effect the desired extent of isomerization. The relative proportions of the catalyst and the hydrocarbon material to be treated may vary over a comparatively wide range, and will, in general, depend upon the particular hydrocarbon material to be treated, upon the particular catalyst used, and upon the specific temperature and contact time employed. In general, the hydrocarbon to be treated is present in relatively great excess over the catalyst. If desired, the gaseous hydrocarbon or hydrocarbon mixture may be contacted with the catalyst. This may be done in a variety of suitable manners. For example, when the catalyst is a liquid, it may be maintained at the desired temperature, with stirring if desired, while the gaseous hydrocarbon material is bubbled through it at the desired rate. If desired, the liquid or solid catalyst may be adsorbed on or supported on the surface of a suitable solid carrier material such as clay, charcoal, alumina, pumice, diatomaceous earth. The gaseous or liquid hydrocarbon material may be contacted with the solid or adsorbed catalyst in the conventional manners.

The presence in the reaction system of a hydrogen halide or substance capable of yielding a hydrogen halide under the conditions existing in the reaction system, in some cases, has a beneficial effect upon the life and activity of the catalyst. Thus, a hydrogen halide, such as hydrogen chloride and hydrogen bromide, may be added to the reaction mixture or separately added to the reaction zone in the desired amount in any convenient manner, intermittently or continuously. In lieu of a hydrogen halide per se, a controlled amount of a compound, such as propyl chloride, tertiary butyl chloride, propyl bromide, tertiary butyl bromide and the like alkyl halides, which will decompose under the reac-

tion conditions to yield a hydrogen halide, may be intermittently or continuously added.

The process may be executed under atmospheric, subatmospheric or superatmospheric pressure. Since pressure, in general, favors the isomerization reaction, the process is preferably executed at atmospheric or at a superatmospheric pressure. When operation under pressure is resorted to, pressures up to about 30 atmospheres are generally sufficient. If desired, relatively inert diluent materials such as hydrogen, nitrogen, methane, ethane, propane, etc., may be added to the material treated or separately introduced into the reaction zone to aid in establishing and/or maintaining the desired operating pressure. For example, the process may be executed with a substantial partial pressure of hydrogen in the reaction zone. Such added hydrogen or other inert gas may have the beneficial effect of acting as a heat conductor to maintain a substantially constant temperature throughout the reaction zone, or it may serve as a means of introducing heat into the reaction zone.

The process may be executed in a batch, intermittent or continuous manner. When separation of isomerized hydrocarbon from the unreacted material is desired, such separation may be effected in any suitable manner as by fractional distillation, selective absorption, selective reaction, etc.

The following examples illustrate suitable modes of executing the process of the invention. The invention is not to be regarded as restricted to the particular catalysts, the particular modes of operation, the particular hydrocarbons treated, or the particular operating conditions specified in the examples.

Example I

The catalyst was prepared in the following manner: About 2.5 mols of anhydrous aluminum chloride were suspended in about 3.0 mols of benzene. This mixture was stirred and maintained at a temperature of about 0° C. while a total of about 2.0 mols of tertiary butyl chloride was added slowly, a small quantity at a time. When all of the tertiary butyl chloride had been added, and the reaction was apparently complete, the unreacted aluminum chloride was separated from the liquid by decantation. The liquid was then heated to about 80° C. under reduced pressure to remove the unreacted benzene. The residue was an oily liquid consisting of the complex double compound of aluminum chloride and tertiary butyl benzene, and containing about 66% by weight of aluminum chloride.

About 40 cc. of the liquid catalyst were added to about 100 gm. of normal pentane and the mixture maintained at a temperature of about 35° C. for about 2.5 hours and later allowed to stand for some time at about room temperature. The hydrocarbon material was then separated from the catalyst material, washed with water, dried and analyzed. It was found that about 18.3% of the treated normal pentane had been isomerized to isopentane, with no appreciable amount of decomposition. About 73% of the applied normal pentane was recovered unchanged.

Example II

By use of procedures similar to that described in the preceding example, a variety of different aluminum chloride-alkylated aromatic hydrocarbon double compound catalysts was prepared.

Among the catalysts of this group prepared and used to effect the isomerization of normal pentane to isopentane were the complex double compounds: aluminum chloride-ethyl benzene, aluminum chloride-n-butyl benzene, aluminum chloride-isopropyl benzene and aluminum chloride-isobutylene benzene.

All of these catalysts, when used at temperatures of from about 35° C. to 100° C. were active in converting normal pentane to isopentane with no appreciable loss of the pentane due to the occurrence of decomposition reactions. For example, with the aluminum chloride-normal butyl benzene catalyst, about 15.5% of the normal pentane was converted to isopentane in a single treatment, and with the aluminum chloride-isopropyl benzene catalyst about 13.5% of the normal pentane was converted to isopentane in a single treatment.

Example III

100 gm. of normal pentane were heated with 30 cc. of the complex catalyst prepared as described in Example I and with 30 gm. of hydrogen chloride during 120 hours at a temperature of 120° C. in a closed vessel of 1 liter capacity. After separation from the catalyst material the reaction product was proved to contain 40 gm. isopentane, 44 gm. non-converted normal pentane, 12 gm. isobutane, 2 gm. normal butane and 2 gm. propane.

While I have described my invention in a detailed manner and provided specific examples illustrating suitable modes of executing the same, it is to be understood that modifications may be made and that no limitations other than those imposed by the scope of the appended claims are intended.

I claim as my invention:

1. A process for the production of isopentane which comprises contacting a saturated hydrocarbon fraction consisting essentially of normal pentane in the liquid phase in the presence of hydrogen chloride with a preformed complex compound of aluminum chloride and an alkylated aromatic hydrocarbon in which the aluminum chloride is present in the greater mol ratio in the substantial absence of solid aluminum chloride and at a temperature of from 20° C. to 140° C. whereby there is effected as the predomi-

nating reaction the isomerization of normal pentane to isopentane.

2. A process for the conversion of a normal paraffin hydrocarbon to a branched chain paraffin hydrocarbon containing the same number of carbon atoms which comprises contacting a saturated hydrocarbon fraction consisting essentially of a normal paraffin hydrocarbon having four to nine carbon atoms in the liquid phase in the presence of hydrogen chloride with a preformed complex compound of aluminum chloride and an alkylated aromatic hydrocarbon in which the aluminum chloride is present in the greater mol ratio in the substantial absence of solid aluminum chloride and at a temperature of from 20° C. to 140° C. whereby there is effected as the predominant reaction the isomerization of said normal paraffin hydrocarbon to a corresponding branched chain isomer.

3. A process for the isomerization of saturated hydrocarbons which comprises contacting a saturated hydrocarbon fraction consisting essentially of saturated hydrocarbons having between four and nine carbon atoms in the presence of hydrogen chloride with a preformed complex compound of aluminum chloride and an alkylated aromatic hydrocarbon in which the aluminum chloride is present in the greater mol ratio in the substantial absence of solid aluminum chloride and at a temperature of from 20° C. to 140° C. whereby there is effected as the predominant reaction the isomerization of the saturated hydrocarbons of said fraction.

4. A process for the isomerization of saturated hydrocarbons which comprises contacting a saturated hydrocarbon fraction consisting essentially of saturated hydrocarbons having between four and nine carbon atoms in the presence of a hydrogen halide with a preformed complex compound of an aluminum halide and an alkylated aromatic hydrocarbon in which the aluminum halide is present in the greater mol ratio in the substantial absence of solid aluminum halide and at a temperature of from 20° C. to 140° C. whereby there is effected as the predominant reaction the isomerization of the saturated hydrocarbons of said fraction.

WILHELM CAREL BREZESINSKA

SMITHUYSEN.