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ISOMERIZATION OF SATURATED HYDROCARBONS

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This invention relates to the catalytic isomerization of isomerizable saturated hydrocarbons and is more specifically concerned with an improved process wherein these hydrocarbons are isomerized under carefully selected conditions of operation in the presence of a mono-cyclic aromatic containing more than 8 carbon atoms.

The isomerization of saturated hydrocarbons has assumed considerable importance at the present time, particularly in the isomerization of paraffinic hydrocarbons boiling within the gasoline range such as pentane, hexane, heptanes, etc., which upon isomerization produce compounds which have very desirable antiknock properties when included in aviation gasoline blends. Further, these isomerized products may be alkylated with an alklating agent such as an olefin, alcohol, etc., to produce alkylated derivatives which have very desirable antiknock qualities and which may be included in aviation gasoline blends.

It is well known that saturated hydrocarbon may be isomerized using catalysts of the Friedel-Crafts type such as aluminum halides, zinc halides, zirconium halides or mixtures thereof in the presence of a hydrogen halide. The primary difficulty which arises in these isomerization operations is the excessive catalyst consumption due to the formation of hydrocarbon-metallic halide complexes from the products of decomposition reactions which occur simultaneously with the isomerization reaction.

Various methods have been employed to prevent the decomposition of the saturated hydrocarbon thereby preventing the excessive catalyst consumption. For example, it has been proposed to introduce hydrogen in the reaction zone to suppress decomposition and to hydrogenate fragmental hydrocarbons formed by decomposition to avoid the formation of the hydrocarbon-metallic halide complex. The use of hydrogen as a decomposition suppressor has been found to be very expensive and entails the use of a considerable amount of auxiliary equipment such as compressors, separators, etc., to provide a means for recycling the hydrogen to the reaction zone.

It is an object of the present invention to provide a method for suppressing the decomposition of the isomerizable hydrocarbons which is economical and practical and which obviates the difficulties which are inherent in the use of hydrogen.

In one broad embodiment, the present invention comprises a process for isomerizing a saturated hydrocarbon by contacting said hydrocarbon with an isomerizing catalyst under isomerization conditions in the presence of a minor amount of a mono-cyclic aromatic hydrocarbon having more than 8 carbon atoms.

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I have discovered that the addition of these aromatic hydrocarbons selectively suppresses the decomposition reaction and permits the isomerization of the saturated hydrocarbons to a degree previously considered unattainable. The exact mechanism as to how the presence of these aromatic compounds suppresses decomposition reaction is not known but it is probable that it involves the alkylation of the aromatic with a small amount of the initial decomposition products, said alkylation producing hydrogen in situ which prevents further decomposition of the saturated hydrocarbon.

One class of aromatic compounds having more than 8 carbon atoms which is effective in the process of the present invention is di-substituted aromatics such as para-cymene, di-ethyl benzene, para-methyl secbutyl benzene and similar compounds.

Another class of mono-cyclic aromatic hydrocarbons are mono-substituted aromatics in which a branched chain alkyl group is attached to the aromatic nucleus such as isopropyl benzene, secondary butyl benzene and tertiary butyl benzene.

These aromatics may be derived from any source such as, for example, by the precise fractionation of gasoline fractions or by alkylation of benzene with various olefins to produce the alkylated aromatic derivative. A particular suitable charging stock for the operation is a carefully separated gasoline fraction which contains the desired amounts of the aromatic and saturated hydrocarbons. The aromatic concentration desired is of the order of about 0.1 to about 10 per cent by volume and more preferably about 0.2 to about 3 per cent.

I have found that some aromatic fractions, particularly those obtained by precise fractionation of gasoline boiling range mixtures at times contain impurities which prevent or decrease the effect of the mono-cyclic alkyl aromatic as a decomposition suppressor. However, these aromatics may be subjected to a preliminary treatment with alkali-acting materials such as magnesia, alumina, calcium oxide or aqueous solutions of sodium hydroxide or other alkali agents, sulfur dioxide, sulfuric acid or other well-known treating agents to remove the impurities. The products obtained from this preliminary treatment have been found to be entirely satisfactory in the process of this invention.

The operating conditions such as temperature and pressure will vary somewhat depending upon the alkylated aromatic and catalyst employed. Ordinarily temperatures within the range of about 50 to 350° F. and more preferably between the approximate range of about 120 to 250° F. and pressures varying from substantially atmospheric to about 500 pounds or more are desirable.

Any of the well-known Friedel-Crafts type isomerization catalysts may be employed. It is desirable that hydrogen halides such as hydrogen chloride and hydrogen bromide be used in conjunction with these catalytic materials. The ordinary concentration of these hydrogen halides is within the range of about 1 to 40 mol per cent of the charge and preferably 5 to 20 mol per cent. These catalysts comprise the chlorides and bromides of aluminum, zinc, zirconium, iron, either alone or in admixture with one another. These compounds may be employed in the solid granular state or upon inert supporting materials such as alumina, silica, thoria, crushed firebrick, quartz, activated clays and activated chars.

It is also within the scope of this invention to employ mixtures of these compounds and in particular the aluminum halides with the halides of antimony, bismuth, arsenic, to form low-melting compounds which are molten under the conditions of operation.

The isomerization operation may be conducted in various ways; for example, the heated hydrocarbon mixture either in the liquid, vapor or mixed phase may be passed through a reaction zone containing a bed of solid granular catalysts either supported or unsupported, and the reaction product being separated into the desired isomers and unconverted material which can be recycled to the reaction zone.

Another method of operation consists of employing a catalyst supply chamber containing a bed of granular catalyst through which a stream of the hydrocarbon mixture in liquid phase is introduced to dissolve the required amount of catalyst. This catalyst-containing stream is introduced into a reaction zone along with a regulated amount of the hydrogen halide and a substantial portion of the hydrocarbons isomerized therein. This reaction zone may comprise a large vessel which will provide sufficient time for the reaction to occur or may be filled with a retaining material such as molten salts, metallic halide-hydrocarbon complexes or solid packing materials such as bauxite, Raschig rings, berl saddles, granulated quartz and other materials well known to those skilled in the art.

The following examples illustrate in a general way the effectiveness of the mono-cyclic alkyl aromatics disclosed herein in suppressing decomposition reactions during the isomerization operation. It is not intended that these examples unduly limit the generally broad scope of this invention to the numerical values indicated since the invention is broadly applicable to the ranges hereinbefore specified.

In the following experiments, 85 grams of normal pentane was placed in an electrically heated autoclave equipped with a stirrer. Weighed amounts of aromatics, substantially anhydrous aluminum chloride and HCl were added to the pentane. The autoclave was sealed and maintained at 167° F. for a period of 6 hours. A blank run without aromatic addition was also made. The results of these experiments are shown in the table below.

Table

	Test No.—							
	1	2	3	4	5	6	7	8
Charge, grams:								
N. Pentane	←			85				→
$AlCl_3$	←			15				→
HCl	←			2.8				→
P. Cymene			1.7					
P. Methyl sec-butyl benzene				1.7				
Di-ethyl benzene					1.7			
Iso-propyl benzene						1.7		
Sec-butyl benzene							1.5	
Tertiary butyl benzene								1.7
Analysis of prod., mol per cent:								
i C_4H_{10}	54.1		1.1	1.4	1.1	1.8	2.0	Trace
n C_4H_{10}	8.1			1.9		0.5	1.6	
i C_5H_{12}	19.2		65.6	61.6	33.3	47.0	43.5	71.9
n C_5H_{12}	11.8		30.4	31.3	64.7	48.2	50.1	25.4
Higher boiling	6.8		2.9	3.8	0.9	1.5	2.8	2.7

I claim as my invention:

1. A process for isomerizing an isomerizable saturated hydrocarbon which comprises subjecting said hydrocarbon to contact with an isomerizing catalyst of the Friedel-Crafts type in the presence of a minor amount of a mono-cyclic aromatic hydrocarbon having more than 8 carbon atoms.

2. A process for isomerizing an isomerizable saturated hydrocarbon which comprises subjecting said hydrocarbon to contact with an isomerizing catalyst of the Friedel-Crafts type in the presence of a branched chain alkyl mono-cyclic aromatic.

3. A process for isomerizing an isomerizable saturated hydrocarbon which comprises subjecting said hydrocarbon to contact with an isomerizing catalyst of the Friedel-Crafts type in the presence of a di-substituted mono-cyclic aromatic hydrocarbon having more than 8 carbon atoms.

4. A process for isomerizing an isomerizable saturated hydrocarbon which comprises subjecting said hydrocarbon to contact with an isomerizing catalyst of the Friedel-Crafts type in the presence of a minor amount of a straight chain alkyl mono-cyclic aromatic having more than 8 carbon atoms.

5. The process of claim 1 further characterized in that said isomerizable saturated hydrocarbon comprises a paraffin hydrocarbon.

6. The process of claim 2 further characterized in that said branched chain mono-cyclic alkyl aromatic comprises tertiary butyl benzene.

7. The process of claim 3 further characterized in that said di-substituted mono-cyclic aromatic hydrocarbon comprises para-cymene.

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