

UNITED STATES PATENT OFFICE

2,467,326

PRODUCTION OF BRANCHED CHAIN HYDROCARBONS CATALYZED BY FRIEDEL-CRAFTS CATALYSTS MODIFIED BY BORIC ACID

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No Drawing. Application September 29, 1945, Serial No. 619,431

12 Claims. (Cl. 260—671)

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This invention relates to the treatment of organic compounds in the presence of a particular type of catalyst to produce compounds of branched carbon structure. The invention is more particularly concerned with the production of branched chain hydrocarbons by processes which utilize a catalyst prepared by reacting boric acid and a metal halide of the Friedel-Crafts type.

The production of branched chain hydrocarbons may involve the isomerization of less branched into more branched hydrocarbons, such as the isomerization of normal butane to isobutane, the isomerization of more branched into less branched hydrocarbons, such as the conversion of dimethylcyclopentane into methylcyclohexane or the conversion of methylcyclopentane into cyclohexane, the alkylation of paraffins, naphthenes, and aromatics, the dealkylation of cyclic hydrocarbons including naphthenic and aromatic hydrocarbons, the polymerization of olefins, and the like.

In one embodiment the present invention relates to a process for producing hydrocarbons of branched carbon structure which comprises subjecting a reactive hydrocarbon under conversion conditions to the action of a catalyst prepared by reacting boric acid and a metal halide of the Friedel-Crafts type with the evolution of hydrogen halide.

The hydrocarbons which may be utilized as starting materials for the process of the present invention comprise paraffinic, olefinic, naphthenic, and aromatic hydrocarbons. The paraffins and olefins include both normal and branched chain isomers, and the naphthenes and aromatics comprise cyclic and alkylated cyclic hydrocarbons. The different types of hydrocarbons which may be converted into branched and more highly branched chain hydrocarbons according to the process of the present invention are hereinafter referred to more completely.

Aromatic hydrocarbons, such as benzene, toluene, other alkyl benzenes, naphthalene, alkyl naphthalenes, other poly-nuclear aromatics, etc., which are alkylated by olefinic hydrocarbons as hereinafter set forth, may be obtained from any source such as by distillation of coal, by the dehydrogenation of naphthenic hydrocarbons, by the dehydrogenation and cyclization of aliphatic hydrocarbons, etc.

Naphthenic hydrocarbons which may be alkylated or isomerized according to the present process occur generally in admixture with paraffins and aromatics in different crude petroleum,

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Of the different naphthenic hydrocarbons, also referred to as cycloparaffins, the cyclopentane, cyclohexane, alkyl cyclopentane and alkyl cyclohexane hydrocarbons are generally those which are isomerized or alkylated in the presence of a catalyst of the type herein described to produce naphthenic hydrocarbons of more highly branched chain structures, which are utilizable as constituents of high antiknock gasoline or for other purposes.

Normal paraffinic hydrocarbons which may be converted into isoparaffinic hydrocarbons by the present process comprise normal butane and higher boiling paraffinic hydrocarbons of straight-chain structure. Similarly, mildly branched liquid paraffins may be isomerized into more highly branched chain paraffinic hydrocarbons with substantially higher antiknock value than the less branched compounds charged to the process.

Isobutane is the isoparaffin commonly subjected to alkylation although higher molecular weight isoparaffins also react with olefinic hydrocarbons under similar or modified conditions of operation to produce branched chain paraffinic hydrocarbons of higher boiling point than the isoparaffinic hydrocarbons charged to the process.

Olefinic hydrocarbons utilizable in the present process comprise mono-olefins having one double bond per molecule and poly-olefins having more than one double bond per molecule. Mono-olefins which may be polymerized or be utilized for alkylating isoparaffinic, naphthenic, or aromatic hydrocarbons in the presence of the catalyst herein described are either normally gaseous or normally liquid and include ethylene, propylene, butylenes, amylenes, and higher normally liquid olefins, the latter including various polymers of normally gaseous olefins. Cyclic olefins such as cyclohexene may also be utilized, but generally not under the same conditions of operation as those employed with non-cyclic olefins. Other olefinic hydrocarbons utilizable in the present process include conjugated diolefins such as butadiene and isoprene and also non-conjugated diolefins and other poly-olefinic hydrocarbons containing more than 2 double bonds per molecule.

Alkylation of saturated hydrocarbons, including isoparaffinic, naphthenic and aromatic hydrocarbons may also be effected in the presence of the catalyst hereinafter described, by reacting with the saturated hydrocarbons a substance capable of producing olefinic hydrocarbons under

the conditions of operation chosen for the process. Such olefin-producing substances include alcohols, ethers, and esters capable of undergoing dehydration or splitting to form olefinic hydrocarbons containing at least 2 carbon atoms per molecule which may be considered to be present in the reaction mixture even though possibly only as transient intermediate unsaturates which react further with the saturated hydrocarbons to produce desired reaction products. Olefinic hydrocarbons and the above mentioned olefin-producing substances are herein referred to as olefin-acting compounds. Alkyl halides are also olefin-acting compounds and may be considered as esters of halogen acids.

Organic compounds other than hydrocarbons which may be utilized in the process of the present invention include such alkylatable compounds as the phenols and heterocyclic compounds such as indole. Examples of isomerizable organic compounds are halogenated paraffins containing at least two and preferably three carbon atoms and certain halogenated aromatics, such as ortho chloroethyl benzene.

I have found that catalysts useful in promoting the formation of more-highly branched hydrocarbons from less highly branched hydrocarbons may be made by interacting boric acid with a metal halide of the Friedel-Crafts type under such conditions that limited amounts of hydrogen halide are evolved, which amounts generally are from about 0.5 to about 2.0 molecular equivalents based upon the metal halide. It is apparent that since there are a number of Friedel-Crafts type metal halides which may be interacted, a considerable number of alternative catalysts may be made although such catalysts will not necessarily be equivalent in their action in any particular hydrocarbon conversion reaction to produce more-branched chain hydrocarbons.

Friedel-Crafts type metal halides which may be reacted with boric acid to form catalysts useful in the present process include aluminum chloride, aluminum bromide, zinc chloride, zirconium chloride, ferric chloride, antimony chloride, bismuth chloride, and others. Substantially anhydrous aluminum chloride is the Friedel-Crafts type catalyst usually employed in hydrocarbon conversion reactions of the types mentioned herein. However, disadvantages accompany its use in some instances on account of its high degree of activity. Thus it has a tendency to form undesirable complexes with unsaturated and aromatic hydrocarbons. However, by reacting proportioned mixtures of an aluminum halide, such as aluminum chloride, and boric acid in accordance with the present invention, catalysts of modified activities are obtained which may be utilized for promoting the formation of more highly branched chain hydrocarbons as herein set forth. These catalysts do not form substantial amounts of complexes with unsaturated and aromatic hydrocarbons and, accordingly, they may be used in continuous processes over long periods of time with relatively little contamination by such complexes that in many instances the catalyst life is considerably longer than the life of the corresponding aluminum halide in similar types of hydrocarbon conversion reactions. An additional advantage of these catalysts is that their solubility in the products of the reaction is considerably less than that of metal halides, such as aluminum chloride and aluminum bromide, and thus the usual step of recovering dissolved catalyst from the reaction products can be eliminated.

In the isomerization, alkylation, and polymerization reactions with the type of catalysts herein described, either batch or continuous operation may be employed. In a simple batch procedure, proportionate amounts of the organic compound and catalyst together with minor amounts of hydrogen halide may be added to a vessel capable of withstanding mildly superatmospheric pressure and the contents heated for a time adequate to cause the desired degree of conversion. After a period of heating, the reaction vessel may be cooled, the contents discharged, and a separation effected between the organic compound and the catalyst.

In continuous operations the granular catalyst, either alone or on carriers, may be placed in reaction chambers and preheated mixtures of the organic compounds along with hydrogen halide may be passed through the catalyst bed. The products from such a treatment may be continuously fractionated to separate the hydrogen halide from the organic compounds.

The reactions described herein are carried out at temperatures of from about -20° to about 150° C. and under a pressure of from substantially atmospheric to approximately 100 atmospheres. In the hydrocarbon mixtures subjected to alkylation it is preferable to have present from about 2 to about 40 molecular proportions of the alkylatable hydrocarbon per one molecular proportion of olefinic hydrocarbon.

The following examples are given to illustrate the method of preparing the catalyst and the character of results obtained by the use of the present process although the data presented are not introduced with the intention of unduly restricting the generally broad scope of the invention.

EXAMPLE I

A catalyst was prepared as follows: 20.64 g. ($\frac{1}{2}$ mole) of C. P. boric acid and 133.3 g. (1 mole) of anhydrous aluminum chloride were intimately mixed by rotating in a ball mill for 20 hours. The bulk of this mixture was transferred to glass liner and heated for two hours at 200° C. and then for two more hours at 250° C. in a rotating bomb. The product was recovered in two parts as follows:

	Grams
In lower part of liner.....	95.3
In upper part of liner.....	2.0

The material in the upper part of the liner appeared to be sublimed aluminum chloride and was discarded. The material in the lower part of the liner was a hard, brittle, granular, yellow-gray solid which was designated as the catalyst. It was noted that hydrogen chloride was evolved during the mixing in the ball mill and during the heating in the bomb.

EXAMPLE II

Part of the catalyst prepared as described in Example I was used to isomerize n-pentane in an Ipatieff rotating autoclave. The charge stock consisted of 90 volume per cent of C. P. normal pentane and 10 volume per cent of cyclohexane. The operating conditions and results are shown in the following table.

TABLE 1

Isomerization of normal pentane

Operating conditions:	
Temp.	$^{\circ}$ C. 100
Time	hours 4
Max. press.	kg./cm. ² 30

Charged, g.:	
Catalyst	8.2
HCl	3.7
Normal pentane	68.2
Cyclohexane	7.6
Recovered hydrocarbon	g. 71.2
Analysis of recovered hydrocarbons, mol per cent:	
Butane	7.1
Isopentane	52.2
Normal pentane	30.1
C ₆ +	10.6

The results show that over 50% of the normal pentane was converted to isopentane.

EXAMPLE III

A portion of the catalyst prepared as described in Example I was used in the batch alkylation of benzene with propylene with the following results.

TABLE 2

Alkylation of benzene with propylene

Operating conditions:	
Temp.	°C. 100
Time	hours 4
Charged, grams:	
Catalyst	17.8
HCl	10.0
Benzene	156.0
Propylene	15.4
Recovered hydrocarbons:	
Non-condensable gas	cc. 1140
Liquid	grams 170

Distillation of liquid product

Cuts	Bolling Range, °C.	cc.	Grams	n _D ²⁰
1-5	80-82	128		1.5002
6	82-100	9.7		1.5003
7	100-145	1.4		1.4941
8	145-148	1.4		1.4905
9	148-152.5	8.4	7.1	1.4900
10	152.5-154	9.8	8.2	1.4907
11	154-158	8.1	7.0	1.4911
12	158-165	2.8	2.2	1.4912
13	165-190	2.7	2.3	1.4918
Residue	>190		2.9	1.4987

Cuts 8 through 12 represent monoprolylated benzene. These cuts were water white and saturated to potassium permanganate.

EXAMPLE IV

Propylene was polymerized in a batch experiment using still another portion of the catalyst prepared as described in Example I. The operation conditions and results are shown in Table 3.

TABLE 3

Polymerization of propylene

Operating conditions:	
Temp.	°C. 75
Time	hours 6
Charged, g.:	
Catalyst	20.0
HCl	3.7
Propylene	30.4
Recovered hydrocarbon:	
Condensable gas	cc. 16
Liquid outside bomb liner	cc. 5
Polymer	g. 15.5

Distillation of liquid product

Cut No.	Bolling Range, °C.	Weight percent of Distillation Charge	n _D ²⁰
1	140-200	10	1.4224
2	200-300	23	1.4474
Residue	>300	59	1.4598
Loss		8	

Cuts 1 and 2 decolorized potassium permanganate immediately, which shows that they were unsaturated. The residue was very viscous and was unsaturated to bromine in carbon tetrachloride.

I claim as my invention:

1. A process for producing hydrocarbons of branched carbon structure which comprises subjecting a reactive hydrocarbon under conversion conditions to the action of a catalyst prepared by reacting boric acid and a metal halide of the Friedel-Crafts type with the evolution of hydrogen halide.

2. A process for producing hydrocarbons of branched carbon structure which comprises subjecting a reactive hydrocarbon under conversion conditions to the action of a catalyst prepared by reacting boric acid and aluminum chloride with the evolution of hydrogen chloride.

3. A process for producing alkylated aromatic hydrocarbons which comprises contacting an aromatic and an olefin under alkylating conditions with a catalyst prepared by reacting boric acid and aluminum chloride with the evolution of hydrogen chloride.

4. The process of claim 3 further characterized in that said process is carried out at a temperature of from about -20° C. to about 150° C.

5. A process for producing alkylated benzene which comprises contacting about 2 to about 20 molecular proportions of benzene and one molecular proportion of an olefin at a temperature of from about -20° to about 150° C. with a catalyst prepared by reacting boric acid and aluminum chloride with the evolution of hydrogen chloride.

6. A process for the isomerization of isomerizable hydrocarbons which comprises subjecting said hydrocarbon to the action of a catalyst prepared by reacting boric acid and aluminum chloride with the evolution of hydrogen chloride.

7. A process for the isomerization of straight chain and mildly branched paraffins to more highly branched paraffins which comprises subjecting said paraffin at a temperature of from about -20° to about 150° C. to the action of a catalyst prepared by reacting boric acid and aluminum chloride with the evolution of hydrogen chloride.

8. A process for the isomerization of n-butane to isobutane which comprises subjecting n-butane at a temperature of from about -20° to about 150° C. to the action of a catalyst prepared by reacting boric acid and aluminum chloride with the evolution of hydrogen chloride.

9. A process for the polymerization of olefinic hydrocarbons which comprises subjecting said olefin to polymerization in the presence of a catalyst prepared by reacting boric acid and aluminum chloride with the evolution of hydrogen chloride.

10. A process for the polymerization of normally gaseous olefinic hydrocarbons which comprises subjecting said hydrocarbons to polymerization at a temperature of from about -20° to

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about 150° C. in the presence of a catalyst prepared by reacting boric acid and aluminum chloride with the evolution of hydrogen chloride.

11. A process for the alkylation of alkylatable hydrocarbons which comprises contacting said hydrocarbon and an olefin under alkylating conditions with a catalyst prepared by reacting boric acid and aluminum chloride with the evolution of hydrogen chloride.

12. A process for the alkylation of alkylatable hydrocarbons which comprises subjecting said hydrocarbon and an olefin to contact at a temperature of from about -20° to about 150° C. with a catalyst prepared by reacting boric acid

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and aluminum chloride with the evolution of hydrogen chloride.

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