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ISOMERIZATION OF PARAFFIN HYDROCARBONS BY CONTACT WITH CATALYST COMPRISING ALUMINUM CHLORIDE AND FERRIC CHLORIDE

Vladimir N. Ipatieff and Herman Pines, Chicago, Ill., assignors to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

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This is a continuation in part of our co-pending application Serial No. 325,193, filed March 21, 1940, now abandoned.

This invention relates to the treatment of paraffin hydrocarbons of normal or mildly branched structure.

In a more specific sense the invention is concerned with a process whereby a paraffin hydrocarbon such as normal butane is converted into its isomer or isomers, the process involving the use of special catalysts and particular conditions of operation which favor the isomerization reactions so that relatively high yields of the iso-compounds are produced.

Since the invention is concerned with the transformation of normal paraffin hydrocarbons into their isomers and thus includes the transformation of normal butane into iso-butane, the following table is introduced to indicate the structure and principal physical characteristics of normal and iso-butane.

Name	Structure	B. P., °C.	Critical Temperature, °C.	Critical Press. Atmospheres
n-butane...	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	+0.5	151	36
i-butane...	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	-10.5	134.5	37

Butanes are produced in considerable quantities in the oil refining industry. They occur in substantial amounts in natural gases (in which the normal compound usually predominates), in refinery gases which are evolved from crude petroleum storage tanks, and in the primary distillation of crudes, and they are also present in considerable percentages in the gases produced incidental to cracking heavy petroleum fractions for the production of gasoline. In the case of cracked gas mixtures the relative proportions of iso and normal butanes vary, but the ratio of the iso to the normal compound is as a rule considerably higher than in natural gas.

Butanes may be considered as more or less marginal compounds in respect to their desirability in ordinary gasoline, that is, a certain percentage of them is essential for sufficient vapor pressure to insure ease in starting, while an excess tends to produce vapor lock. For these reasons

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the total percentage of 4-carbon atom hydrocarbons is commonly adjusted in conjunction with the boiling range and vapor pressure of the other gasoline components to produce a gasoline of desirable starting characteristics according to seasonal demands.

The butanes at the present time bear a further important relationship to oil refining in that their excess production is being utilized as a source of gasoline either by ordinary thermal cracking or by special catalytic dehydrogenation processes followed by polymerization in which catalysts may or may not be used. Isobutane has been found to be much more readily alkylated with olefins in the presence of catalysts than normal butane. Considering the corresponding mono-olefins, the normal butenes are considerably more difficult to polymerize, either thermally or catalytically, than isobutene, and it is found also that the octenes representing the dimers of the isobutene are of higher antiknock value than those from n-butenes which holds also for the octanes produced by hydrogenation. It is therefore, of considerable importance at the present time to convert as much as possible of the normal butane production into isobutane, and the present invention is especially concerned with a process for accomplishing this object.

In one specific embodiment the present invention comprises the isomerization of normal paraffin hydrocarbons by contacting them with composite catalysts comprising essentially aluminum chloride and ferric chloride in regulated proportions.

While the essential components of the catalysts which are preferred for use in the process of the invention are aluminum chloride and ferric chloride, it is comprised within the scope of the invention to employ other halides of aluminum and iron such as the bromides and iodides alone or in admixture and it is further comprised within the scope of the invention to add other metal halides than those of aluminum and iron although these latter additions are usually in minor amounts. The efficiency of the present process in converting normal paraffins into isoparaffins and particularly normal butane into iso-butane depends upon the moderating effect of ferric chloride admixtures with aluminum chloride so that undesirable side reactions are suppressed and there is thus made possible a higher ultimate yield of any desired isomer.

We have found that there is a definite critical range in the amounts of ferric chloride in mixtures of aluminum chloride and ferric chloride which corresponds to optimum isomerizing activity with a greatly reduced tendency toward undesirable side reactions the molar ratios of aluminum chloride and ferric chloride being smaller than 95:5 and greater than 25:75. If composites are used in which the molar ratios of these components fall within this range, there is an increased production of isomers with greatly decreased production of fixed gases and lighter and heavier products than the desired isomers, showing that there is much less cracking. The use of catalyst composites in which aluminum chloride and ferric chloride are present in these critical ratios in isomerization reactions is the principal feature of the present invention.

In accordance with the process of the present invention the preferred mixtures of halides may be alternatively utilized on various types of granular adsorptive supports such as, for example, activated chars or carbons, aluminas, various forms of porous silica, such as Kieselguhr, certain types of clays including fuller's earth, montmorillonite, bentonite, etc., and in general refractory supports having a requisite degree of porosity, firebrick, for example, being included in this category. As a rule the weight of total halides in the granular composites is less than 50% of the total weight of the composite. Obviously the activity of various composite catalysts can be varied by varying the relative amounts of the more active aluminum chloride and the amounts of the less active ferric chloride so that it is not to be inferred that catalysts of widely varying composition will have exactly the same effect in isomerizing normal butane or other paraffin hydrocarbon. The use of adsorptive supports makes possible the use of aluminum chloride in granular form under temperatures and pressures which might otherwise cause an undesirable degree of volatilization of the aluminum chloride and hence a decrease of catalytic activity of the composites. Apparently there is very little formation of the types of sludges ordinarily encountered in catalyzing reactions with aluminum chloride so that the supported materials may sometimes be used in continuous processes over relatively long periods of time compared with the periods of operation when using the mixed halides along without supports. The presence of hydrogen chloride is essential to the success of the reactions, this being preferably added as such since the addition of water to generate hydrogen chloride gradually consumes the metal halides and ultimately renders the catalyst composites ineffective.

We have determined that by the use of the class of catalysts described, and particularly by the concurrent use of considerable superatmospheric pressure, normal butane may be converted into isobutane with a yield of as high as 40 to 50% in a single pass. In continuous operation yields as high as 90% may be obtained by fractionating the products and recycling unconverted butane. Temperatures employed when using the present types of catalysts may vary from about 25° C. to about 300° C. and superatmospheric pressures may be employed to increase the capacity of reactors. In the case of some higher molecular weight and readily decomposable hydrocarbons or hydrocarbon mixtures, as well as in the case of normal butane, advantages are sometimes gained by conducting the isomerization reactions at temperatures of about 50 to about 175° C. in

the presence of added hydrogen. The presence of hydrogen chloride is essential and up to a certain point the activity of the catalyst composites depends upon the amount of hydrogen chloride present although excesses beyond the critical amount are seldom desirable.

A preferred procedure in the manufacturing of supported catalysts of the present invention consists in, first, impregnating a selected absorbent support with a required amount of ferric chloride by heating the granular support with ferric chloride in a pressure vessel at a temperature of about 300° C. in the presence of some hydrogen chloride and hydrogen. After this the same procedure is repeated with the aluminum chloride so that in the prepared composites, the aluminum chloride and ferric chloride are intimately associated, since they have gone through either a fused or a sublimed state. While there is a possibility of the presence of definite complexes of the two components, it is not known exactly whether such complexes actually exist. However, as later examples will show, the results obtained when utilizing mixtures of granular supports separately impregnated with aluminum chloride and ferric chloride are not at all of the same character as those obtained when the two salts have been successively added to the same supporting granules.

The process may be operated under batch or continuous conditions. Batch operations may be conducted by adding a granular prepared catalyst to a paraffin hydrocarbon such as normal butane contained in a pressure vessel, after which the vessel is sealed and agitated or the contents stirred mechanically while the temperature and pressure are raised by the application of external heat to produce a temperature corresponding to maximum production of the iso-compound. Hydrogen or other gas may be added at this point, hydrogen being preferred since it has been observed that the presence of hydrogen further tends to depress side reactions and give higher yields of isomers. This type of operation is better adapted to small scale production, and plants of considerable capacity are best operated in a continuous manner. In continuous operations the butane may be pumped along with regulated amounts of hydrogen and hydrogen chloride through a tubular heating element until it reaches a given temperature and pressure within the approximate ranges previously specified and reaction is then brought about by passing the preheated and prepressured mixture through a stationary body of a composite catalyst such as, for example, aluminum chloride and ferric chloride on activated carbon. In the absence of moisture there will be substantially no corrosion when using these substances. After completion of the desired isomerization the total products are subsequently fractionated to recover catalysts and separate the normal and isobutanes, after which the normal compound may be recycled for further treatment. Details of such operations will be more or less familiar to those skilled in the art.

The following illustrative data are introduced to indicate in a general way the nature of the results obtainable by the use of the process, though they are not introduced with the intention of correspondingly limiting the scope of the invention.

A series of composite supported catalysts were prepared in which the molar ratios of aluminum chloride to ferric chloride were varied and these catalysts were used to isomerize normal butane.

The total weight of the metal chlorides in each of the composite catalysts was 35 per cent.

In the first series of tests results of which are tabulated in Table 1 an amount of composite catalyst containing 10 parts by weight of metal halides was placed in a pressure vessel, the composites in all cases consisting of 35 parts by weight of metal halides and 65 parts by weight of granular charcoal. 58 parts by weight of normal butane and 6 parts by weight of hydrogen chloride were added and the pressure vessel contents were maintained at a temperature of 125° C. for a period of 4 hours, after which the products were released and analyzed.

Table 1

Experiment No.	1	2	3	4	5
Catalyst:					
AlCl ₃ , parts by wt.	10	9.2	7.1	4.5	2.2
AlCl ₃ , Mol. per cent of metal halides	100	90	75	50	25
FeCl ₃ , parts by wt.	0	0.8	2.9	5.5	7.9
FeCl ₃ , Mol. per cent of metal halides	0	10	25	50	75
Analyses of Products:					
C ₃ H ₈	35.2	32.7	3.7	0.8	0.1
i-C ₄ H ₁₀	16.3	34.5	54.0	38.8	13.8
n-C ₄ H ₁₀	40.0	24.0	38.8	57.9	86.1
C ₅ H ₁₂ +	8.5	8.8	3.5	2.5	0

It will be observed that, from the results of the above experiments, the best composition of catalyst was that used in experiment No. 3 which gave a yield of 54.0 parts of isobutane with a low production of propane and substances heavier than normal butane designated as C₅H₁₂+. Obviously the pure aluminum chloride used in experiment No. 1 gave more decomposition than isomerization as evidenced by the fact that more propane was produced than isobutane. Experiment No. 5 indicated that the lower limit of aluminum chloride percentage had been reached since there was a low production of both iso-butane and products of decomposition.

In the second series of tests the same series of catalysts was used at a temperature of 175° C. and a time of reaction of 2 hours. The results of this series are shown in Table 2 which also includes special experiment No. 2 wherein the amount of aluminum chloride in relation to hydrocarbons was lowered and experiment No. 7 in which use was made of a mixture of catalyst composite comprising, on the one hand, particles of activated carbon impregnated with aluminum chloride and, on the other hand, particles impregnated with ferric chloride. This series of tests shows substantially the same type of results as shown in the first series and indicates that the best molar ratio of aluminum chloride to ferric chloride was about 3 to 1 and that there was a relatively large amount of side reactions when using the mechanical mixture of catalysts in run 7 as compared with run 5 in which aluminum chloride and ferric chloride in the same relative proportion had been impregnated on the same support.

Table 2

Experiment	1	2	3	4	5	6	7
Catalyst:							
AlCl ₃ , parts by wt.	10.0	4.5	9.2	7.1	4.5	2.2	4.5
AlCl ₃ , Mol. Per Cent of metal halides	100	100	90	75	50	25	50
FeCl ₃ , parts by wt.	0	0	0.8	2.9	5.5	7.9	5.5
FeCl ₃ , Mol. Per Cent of metal halides	0	0	10	25	50	75	50
Analyses of Products:							
C ₃ H ₈	37.7	16.3	38.6	18.1	5.2	---	23.6
i-C ₄ H ₁₀	30.2	42.2	28.8	41.1	33.8	8.0	35.9
n-C ₄ H ₁₀	24.3	34.3	19.5	32.4	59.4	91.1	32.8
C ₅ H ₁₂	7.8	7.2	13.1	8.4	1.6	0.9	7.7

The data in the above two tables show that when aluminum chloride was employed alone there was a relatively large formation of by-products both lighter and heavier than the desired isobutane and that improved results were obtained when 10 mole per cent of ferric chloride was present. On the other hand, when the mole per cent of aluminum chloride was as low as 25 per cent the isomerization began definitely to decline so that the isobutane produced was no greater than in the case of 100 per cent aluminum chloride although there was a much lower production of by-products due to cracking.

We claim as our invention:

1. A method for isomerizing a normal paraffinic hydrocarbon which comprises contacting it with a mixture of aluminum chloride and ferric chloride containing at least 20 mol per cent of the latter at a temperature of the order of 250° F. for a period of time sufficient to effect the desired isomerization.

2. A process for isomerizing a normal paraffinic hydrocarbon which comprises contacting said hydrocarbon, at isomerizing temperature and for a period of time sufficient to effect the desired isomerization, with a catalyst comprising a mixture of aluminum chloride and ferric chloride, the ferric chloride constituting at least 20 mol per cent of said mixture.

VLADIMIR N. IPATIEFF.
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