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ISOMERIZATION OF NORMAL BUTANE

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This invention relates particularly to the treatment of butane of normal or straight-chain structure.

In a more specific sense, the invention is concerned with a process whereby normal butane is converted into iso-butane, 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-compound are produced.

Since the invention is concerned principally with the two 4-carbon atom paraffin hydrocarbons and their transformation, one into the other, the following table is introduced to indicate the structure and the principal physical characteristics of these two compounds:

Properties of butanes

Name	Structure	B. P.	Critical temperature	Critical pressure
n-Butane.....	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	$^{\circ}\text{C.} +0.5$	$^{\circ}\text{C.} 151$	Atmospheres 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 the total percentage of 4-carbon atom hydrocarbons is commonly adjusted in conjunction with the boiling range and vapor pressure of the other gasoline compounds 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. Investigations have shown that iso-butane is considerably more amenable to cracking and dehydrogenation, both with and without catalysts, than the normal compound. Considering the corresponding monoolefins, the normal butenes are considerably more difficult to polymerize, either thermally or catalytically, than iso-butene, 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 iso-butane, and the present invention is especially concerned with a process for accomplishing this object.

In one specific embodiment the present invention comprises the treatment of normal butane for the isomerization thereof into iso-butane with catalysts comprising essentially metallic halides at elevated temperatures and superatmospheric pressures.

In a preferred embodiment the catalysts comprise essentially heavy metal chlorides and hydrogen halides.

We have determined that by the use of the class of catalysts mentioned, and particularly by the convenient use of considerable superatmospheric pressure normal butane may be converted into iso-butane with a yield of as high as 60% to 65%. Evidently the use of super atmospheric pressures of the order of 10 to 50 atmospheres at temperatures of 150°C. and higher, besides depressing the volatilization of granular catalysts tends also to depress numerous undesirable side reactions which would result in the formation of hydrogen and low molecular weight hydrocarbons, so that the reaction proceeds more or less in one direction until an equilibrium is established.

There are several alternative catalysts which may be employed in accomplishing the present isomerization reaction and, while they may be used more or less interchangeably, some are more effective than others and it is not intended to infer that they are equivalent. Among the compounds which may be employed may be mentioned aluminum chloride, zinc chloride, iron

chloride, zirconium chloride, stannic chloride and boron fluoride. Experiments have indicated that best results are obtained when a minor percentage of a hydrogen halide is present in the reactions along with these compounds. Some of the compounds may be employed either in the dry state or in aqueous solution with suitable modifications of operating conditions. In the case of such compounds as aluminum chloride, which readily sublimes, stannic chloride, which boils at 114° C., and boron fluoride, which is normally gaseous, these are most conveniently employed in the anhydrous condition, the hydrogen halides, such as for example hydrogen chloride or hydrofluoric acid, being separately introduced in the gaseous state. There will be some variations in the relative amounts of metal salts and hydrogen halides used at optimum treating conditions, but the determination of the best ratios is somewhat a matter of experiment.

The process may be operated under batch or continuous conditions. Choosing aluminum chloride and hydrogen chloride as example of jointly used catalytic materials, batch operations may be conducted by separately adding aluminum chloride, hydrogen chloride and normal butane to a closed pressure container, after which the container is 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. 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 operation the butane may be pumped through a tubular heating element at a given temperature and pressure within the approximate ranges previously specified and reaction brought about along the line of flow by the separate or joint injection of proportioned amounts of metal salts and hydrogen halides, the best example of this type of operation being the combination of aluminum chloride and hydrogen chloride or boron fluoride and hydrogen fluoride. In the absence of moisture there will be substantially no corrosion when using these substances. After passage through the heating element the reactants may be passed to enlarged insulated chambers for the completion of the desired isomerization and the total products subsequently fractionated to recover catalysts and separate the normal and iso-butaness, after which the normal compound may be recycled for further treatment.

Continuous operations may also be conducted by passing normal butane mixed with a hydrogen halide through beds of heated, granular catalyst, which may comprise any of the solid salts mentioned, either alone or mixed with carrying or spacing materials of a relatively inert character. This type of operation is readily utilizable in the case of such compounds as zinc chloride, iron chloride and stannic chloride. Treatment of the products in these cases will involve merely the condensation of the hydrocarbon products and the recycling of the hydrogen halides for further use.

The following examples 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.

Example I

100 parts by weight of normal butane, 20 parts by weight of aluminum chloride and 2 parts by weight of hydrogen chloride were introduced under a pressure of about five atmospheres into a pressure vessel, which was then rotated and heated for twelve hours at an average temperature of 150° C., the maximum pressure developed being about 30 atmospheres. After the bomb was cooled the hydrocarbons were released and fractionated and it was found that they consisted of 66.5% of iso-butane and 31.9% of normal butane. This indicates that the equilibrium under these conditions is considerably in favor of iso-butane.

Example II

In this operation normal butane was passed through a tubular heating element and then into an enlarged reaction chamber, into which sublimed aluminum chloride and hydrogen chloride gas were introduced. A pressure of about 25 to 30 atmospheres and a temperature of 160° C. were maintained on the reaction vessel, after which the reaction products were separated and it was found that the hydrocarbons consisted of about 63% iso-butane and 32% normal butane. This indicates a selective conversion of the normal butane into iso-butane under these conditions.

Example III

In this case the catalyst employed was a composite consisting of about 50 parts by weight of ground pumice and 50 parts by weight of substantially anhydrous zinc chloride. This material was placed in a vertical cylindrical reaction chamber which was insulated to conserve heat and the normal butane was preheated to a temperature of approximately 200° C. and passed downwardly through the contact mass under a pressure of approximately 30 atmospheres. Approximately 60% iso-butane and 30% normal butane were found in the reaction products, the remaining 10% comprising lighter fixed gases and other reaction products.

Example IV

The catalytic materials employed in this case consisted of boron fluoride and hydrogen fluoride. Normal butane was preheated to a temperature of approximately 180° C. and passed into an insulated reaction chamber at the same time as boron fluoride and hydrogen fluoride were injected. The reaction chamber was nickel-lined, as this was found to further accelerate the isomerization reactions. An analysis of the hydrocarbon products showed that they consisted of approximately 62% by weight of iso-butane and 32% by weight of normal butane, the remaining products being lighter gases and some heavier polymerized products.

The character of the present invention and its value commercially have been shown respectively by the foregoing specification and examples introduced although the proper scope of the invention is not limited in exact correspondence with the descriptive or numerical sections.

We claim as our invention:

1. A process for producing isobutane which comprises subjecting normal butane, in the substantial absence of polymerizable olefins, to the action of a metallic halide catalyst of the Friedel-Crafts type and a relatively small amount of a hydrogen halide, under conditions such that iso-

merization of normal butane constitutes the principal reaction in the process, whereby to convert a major portion of the normal butane into isobutane.

2. A process for producing isobutane which comprises subjecting normal butane, in the substantial absence of polymerizable olefins, to the action of a metallic halide catalyst of the Friedel-Crafts type and a relatively small amount of a hydrogen halide at temperatures of the order of about 150 to 200° C. and under pressures of the order of about 10 to 50 atmospheres, whereby to effect isomerization of normal butane into isobutane as the principal reaction in the process.

3. The process as described in claim 1 further characterized in that said catalyst comprises zirconium chloride.

4. The process as described in claim 1 further characterized in that said catalyst comprises zinc chloride.

5. A process for producing isobutane which comprises subjecting normal butane to the action of a metallic halide catalyst of the Friedel-Crafts type under conditions and in the presence of an amount of a hydrogen halide such that isomerization of normal butane constitutes the principal reaction in the process.

6. A process for producing isobutane which comprises passing normal butane and a hydrogen halide through a reaction zone maintained under isomerizing conditions and containing a metallic halide catalyst of the Friedel-Crafts type, said conditions and the amount of said hydrogen halide being such that isomerization of normal

butane constitutes the principal reaction in the process.

7. A process for producing isobutane from normal butane which comprises adding a gaseous hydrogen halide to the normal butane, and passing the resultant mixture under isomerizing conditions through a bed of solid carrier material containing a metallic halide catalyst of the Friedel-Crafts type, said conditions and the amount of said hydrogen halide being such that isomerization of normal butane constitutes the principal reaction in the process.

8. A process for producing isobutane from normal butane which comprises adding a substantially anhydrous hydrogen halide to normal butane, and contacting the resultant mixture under isomerizing conditions with a substantially anhydrous metallic halide catalyst of the Friedel-Crafts type supported on a solid carrier material, said conditions and the amount of said hydrogen halide being such that isomerization of normal butane constitutes the principal reaction in the process.

9. The process as defined in claim 5 further characterized in that the hydrogen halide and the metallic halide are substantially anhydrous.

10. The process as defined in claim 5 further characterized in that the metallic halide catalyst comprises zinc chloride.

11. The process as defined in claim 7 further characterized in that the metallic halide catalyst comprises zinc chloride.

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