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OLEFIN ISOMERIZATION PROCESS

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This invention relates to the isomerization of olefins having at least four carbon atoms per molecule and deals more particularly with a method of converting such olefins into isomeric olefins in which the double bond occupies a different position in the molecule. In one of its specfic embodiments, the invention is directed to the treatment of mixtures of isomeric olefins of at least four carbon atoms or hydrocarbin mixtures predominating in or containing such olefinic mixtures to obtain high yields of a single olefin or of less complex mixtures of olefins.

The cheapest and most readily available sources of olefins are the products of cracking, dehydrogenation or other pyrolytic treatment of hydrocarbons derived from petroleum, shale oil, coal and the like. These cracking products are highly complex mixtures, however, and are of little use for anything except fuel unless some separation of their components can be made. The first important step in the segregation of these mixtures was the isolation of fractions containing predominantly hydrocarbons having the same number of carbon atoms per molecule. The use of the olefinic content of such fractions was further improved by the discovery that the more reactive tertiary olefins, i. e. iso-olefins having an unsaturated tertiary carbon atom, could be selectively reacted or removed leaving the secondary olefins, i. e. olefins which form secondary derivatives by normal addition at the double bond, in a more suitable condition for subsequent separate reaction. This procedure is entirely satisfactory for the production of many valuable products but it does not make available individual olefins of four or more carbon atoms per molecule but yields mixtures of olefins having double bonds at different positions in the molecule. Thus, for example, after selective removal of isobutylene from the butane-butylene fraction of petroleum cracking gases, hydrocarbons containing both normal, alpha and beta-butylenes are obtained and from higher fractions even more complex olefinic mixtures result. For many purposes these olefinic mixtures are much less desirable than hydrocarbons containing only one olefin as beta-butylene or alpha-butylene instead of mixtures thereof. In particular, it has been found that for the production of butadiene, whether by direct catalytic or non-catalytic dehydrogenation or by chlor-substitution followed by dehydrochlorination, beta-butylene is preferred as feed since it gives higher yields under comparable reaction conditions and less undesirable by-products than when its isomers or mixtures containing substantial amounts of such isomers are used. Likewise, in the alkylation of isoparaffins and in interpolymerization with butadiene, beta olefins give better results than olefinic mixtures comprising the corresponding isomeric olefins. While the invention is not limited thereto, it has as an important object the provision of a process for making available more desirable olefins from olefinic mixtures. It is a further object to convert the less desirable olefins in such mixture into more desirable isomers without substantial loss of olefins.

It has already been proposed to isomerize olefins in various ways, particularly by converting them into a suitable derivative such, for example, as the corresponding alcohol or ester, which may be decomposed to yield the desired isomeric olefin. Such procedures involve high costs for reagents, equipment and labor, and efforts have been made to find less expensive catalytic procedures. However, the catalytic methods heretofore suggested have not been entirely satisfactory. One of the drawbacks of previous catalytic methods has been the high temperatures involved which have made the processes hard to control and have tended to produce undesirable by-products. Such methods have the further disadvantage that the equilibrium between alpha and beta isomers favors the alpha olefin as the temperature rises. An object of the present invention is to overcome the disadvantages of the prior art methods and to provide a method of isomerizing olefins which is not only economical but also gives high yields of more desirable products. Other objects and advantages of the invention will be apparent from the following description.

For the purpose of making the invention more clear it will be described with more particular reference to the production of beta butylene from fractions of cracking products predominating in olefins and paraffins having four carbon atoms per molecule. This application of the invention has been chosen as an illustration because it is not only of particular commercial importance but also involves fewer components than analogous higher boiling hydrocarbon mixtures. It will be understood, however, that the same procedure may be applied to such higher boiling hydrocarbon mixtures, it being only necessary to modify the reaction conditions in accordance with the difference in reactivity, if any, of the olefins involved. Furthermore, instead of fractions composed of or predominating in compounds having the same number of carbon atoms per molecule, hydrocarbon mixtures of wider boiling range may be used and mixtures of homologous olefins thereby obtained.

Also, instead of olefinic fractions of cracking products, pure or substantially pure olefins or olefins admixed with other compounds may be employed, the invention being independent of the source or purity of the olefin or olefins isomerized.

It has now been discovered that alpha butylene may be readily converted to beta butylene by contact with an aqueous inorganic acid solution, preferably aqueous sulfuric acid, under carefully controlled conditions of operation at which the isomerization is effected catalytically and the cost of acid is very low. For the production of beta butylene from a C_4 fraction of cracking gases containing isobutylene and butanes as well as alpha and beta butylenes, it is desirable that the isobutylene content be first removed or at least substantially reduced in order that the loss of olefin through interpolymerization be kept low in the process. The removal of isobutylene may be effected by selectively absorbing the isobutylene in a suitable solvent, for example a dilute acid solution at low temperatures as described in United States Patents 2,007,159 and 2,133,732. Alternatively, selective polymerization of the isobutylene at higher temperatures as disclosed, for example, in United States Patents 2,007,160, 2,101,857 or 2,156,718 may be used for its removal. Still other methods of selectively removing tertiary olefins from the corresponding secondary olefins may also be used. Thus, the isobutylene may be selectively esterified or may be chlorinated, for example, as described in United States Patent 2,030,938, or other suitable removal methods may be used. It is not essential that the separation of the isobutylene from the secondary butylenes be complete, although it is preferred to reduce the isobutylene content as completely as possible as the yield of beta butylene in the process is improved by reducing the isobutylene content prior to isomerization.

When the removal of isobutylene is effected by conversion to derivatives such, for example, as polymers, etc., it is not necessary to separate the isobutylene derivative or derivatives from the unreacted secondary butylenes before treating the latter for conversion to beta butylene; however, such products are preferably removed, as by distillation or the like, as the capacity of the isomerization unit may thus be increased.

For the isomerization step of the process it is preferred to use sulfuric acid as the catalyst. The olefin or olefin-containing hydrocarbon may be used in either the liquid or gaseous phase. Any suitable method of contacting the olefin with the catalyst may be employed. Thus, for example, the catalyst may be deposited on a porous support or may be present in the form of a film on non-porous packing in a tower or a horizontal tube through which the olefin-containing hydrocarbon is flowed. Alternatively, the catalyst acid may be flowed concurrently, or preferably countercurrently to the flow of olefin, through a tower containing suitable packing, baffles, trays or the like. Jet mixer or mechanically stirred contact vessels may also be used. For continuous operation with the olefin at least partly in the liquid phase it is advantageous to use mixing by means of a pump which is in communication with a separator wherein olefin-containing hydrocarbons may be separated at least in part from the catalyst acid and the latter returned to the reaction. A preferred method of operation which is more fully described and claimed in United States Patent 2,232,674 comprises circulation of an emulsion of olefin-containing hydrocarbon and sulfuric acid into which the olefin to be isomerized is fed at one point while taking off at another point in the circuit emulsion which is fed to a decantation tank or other means for separating product from catalyst acid. The latter may be returned to the circuit after suitable adjustment of its concentration, for example, by replacing a part with fresh acid. The separated hydrocarbon phase, after further settling or neutralization, if necessary, may be distilled or otherwise treated for recovery of the isomerized olefin-containing hydrocarbons. It is also feasible to carry out the isomerization step by bubbling the olefin or olefins through a column containing acid solution maintained under suitable conditions. The process may be carried out batchwise or intermittently instead of continuously. Reduced olefin concentration tends to reduce losses through polymerization and suitable diluents may be added for this purpose.

When employing sulfuric acid as the catalyst it is preferred to maintain a concentration of acid between about 50% and about 85% on a hydrocarbon-free basis. The exact choice of acid concentration within this range depends upon the temperature of operation adopted. For the isomerization of alpha butylene to beta butylene it is preferred to employ sulfuric acid of about 65% to 75% concentration at about 170° F. to 180° F. With acid of lower concentration higher temperatures up to about 250° F. are used, while with stronger acids lower temperatures, preferably above about 120° F., are employed. For the isomerization of other olefins somewhat different combinations of acid concentration and temperature may be more advantageous, depending upon whether the olefin or olefins involved are more or less reactive than the secondary butylenes. In any case it is preferred to operate under conditions at which substantial polymerization, particularly interpolymerization of isomeric secondary olefins, does not take place.

It is preferred, in liquid phase operations, to maintain a substantial volume of acid in contact with the hydrocarbon undergoing treatment. About 0.3 to about 1.5, preferably 0.7 to 1.3, volumes of acid per volume of hydrocarbon may be used. While frequently short times of contact of the olefin to be isomerized with the catalyst acid is sufficient and contact times of less than five minutes may be used when employing strong acid at the higher temperatures, in liquid phase operations with sulfuric acid of about 65% to 80% concentration longer periods of contact of the order of about 5 to 60 minutes, preferably about 10 to 30 minutes, are advantageous. Under these conditions space velocities of about 0.1 to about 2.5 volumes of liquid olefin per volume of acid phase per hour may be advantageously used.

The following example illustrates one application of the process of the invention to the production of beta butylene from a butane-butylene fraction having a composition approximately as follows:

	Per cent by weight
Isobutylene	17.4
Alpha and beta butylenes	30.0
Butanes	52.6

This hydrocarbon mixture was contacted with sulfuric acid of 65% concentration at about 100° F. to selectively extract the isobutylene. The extraction was carried out in countercurrent using two cooled contact vessels, through each of which an emulsion of hydrocarbon and acid was con-

tinuously circulated. For the extraction about 0.86 mols of sulfuric acid per mol of isobutylene were used.

After removal of isobutylene the hydrocarbon mixture had the following composition:

	Per cent by weight
Isobutylene	2.7
Alpha and beta butylenes	33.5
Butanes	63.8

This mixture was treated in a single stage continuous reactor with a mixture of sulfuric acid and disodium phosphate corresponding to 85.7% H_2SO_4 and 1.2% H_3PO_4 in an amount equivalent to about 0.6 mol of acid per mol of olefin. The reaction temperature was 153° F. and the contact time was 5.5 minutes. Under these conditions the alpha butylene was substantially completely converted to beta butylene and the loss of olefin through polymerization was very low, there being only 8.8% polymer in the product.

In another run in which the hydrocarbon feed to the isomerization unit contained 50% of alpha butylene, the remainder being normal pentane, and 70% sulfuric acid was used as catalyst at 185° F., it was found that less than 3% of the olefin was unchanged after a contact time of 15 minutes. By fractionation of the hydrocarbon product substantially pure beta butylene could be recovered. Similar results were obtained with pure alpha butylene using 59.7% sulfuric acid at 220° F. and 30 minutes contact time, the butylene recovered in this case being over 95% beta butylene.

Catalyst acid which has lost its effectiveness for isomerization of olefins in part or completely as a result of the accumulation of organic impurities, particularly absorbed olefin, in repeated use in the process, may advantageously be employed in the preliminary step of tertiary olefin removal. Such acid may also be regenerated, for example by vacuum distillation, and reused in the isomerization step. Thus a portion of the acid phase separated from the isomerization products may be heated under vacuum to effect removal of beta olefin therefrom and returned along with another portion of said separated acid phase to contact with alpha olefin containing hydrocarbon.

It will be apparent that the process of the invention offers many advantages over prior methods of olefin isomerization, not only with respect to the high yields of olefins which may be obtained but also in regard to the substantial savings in reagent and operating costs which may be effected thereby. While the rearrangement of alpha-unsaturated secondary mono-olefins such, for example, as butene-1 and higher homologues has been emphasized in the foregoing discussion, it is to be understood that other non-tertiary olefins may be analogously treated to produce olefins having the double bond further removed from the end of the chain. The invention is of wide scope, not only with regard to the olefinic compounds which may be treated but also with respect to the methods of operation which may be employed. Thus, for example, instead of treating the entire paraffin-olefin mixture as described in foregoing illustrative examples, it is feasible to separate the olefins from the paraffins as by treatment with cuprous chloride before carrying out the isomerization step of the process, although for the production of pure beta butylene it is generally preferable to make such separation after isomerization. Also, instead of using acids for the preliminary separation of the tertiary olefin from the olefins to be isomerized, extraction with a mixture of cresols and a small amount of disecondary butyl sulfate or the like as described in United States Patent 2,265,583 may be employed. Isobutylene may also be separated from mixtures of alpha and beta butylenes by extractive distillation for example. Still other changes may be made and the invention is not limited to the details of operation disclosed by way of illustration nor by any theory advanced in explanation of the improved results obtained.

I claim as my invention:

1. A process of producing beta butylene from a hydrocarbon mixture comprising isobutylene, alpha and beta butylenes and butanes which comprises extracting said mixture with sulfuric acid of less than 70% concentration to remove isobutylene therefrom without substantial polymerization, intimately mixing the remaining alpha and beta butylenes with about 0.3 to 1.5 volumes of sulfuric acid of about 70% to 75% concentration per volume of liquid hydrocarbon, at about 170° F. to 180° F. for about 5 to 30 minutes, separating the resulting mixture into a beta butylene-containing hydrocarbon phase and an acid phase without substantially reducing the concentration, on a hydrocarbon-free basis, of said acid, heating a portion of the separated acid phase under vacuum to effect removal of beta butylene therefrom, returning at least a part of the thus heated acid and another portion of said separated acid phase to contact with alpha and beta butylene-containing hydrocarbon, and distilling the separated hydrocarbon phase to recover beta butylene in a more concentrated form.

2. A process of producing a normal beta olefin from the corresponding alpha olefin of at least four carbon atoms per molecule which comprises intimately contacting said alpha olefin in the substantial absence of tertiary olefin with sulfuric acid of about 50% to 85% concentration at a temperature between about 120° F. and 250° F. at which isomerization of said alpha olefin to said beta olefin takes place, separating the resulting mixture into a beta olefin-containing hydrocarbon phase and an acid phase without substantially reducing the concentration, on a hydrocarbon-free basis, of said acid, heating a portion of the separated acid phase under vacuum to effect removal of beta olefin therefrom, returning at least a part of the thus heated acid and another portion of said separated acid phase to contact with said alpha olefin and recovering beta olefin from the separated hydrocarbon phase.

3. A process of producing a normal beta olefin from a hydrocarbon mixture comprising the corresponding alpha olefin of at least four carbon atoms per molecule and a tertiary olefin, which comprises contacting said mixture with sulfuric acid to selectively remove tertiary olefin therefrom, intimately mixing the remaining alpha-olefin-containing hydrocarbon with sulfuric acid of about 50% to 85% concentration at a temperature between about 120° F. and 250° F. at which isomerization of said alpha olefin to said beta olefin takes place, separating the resulting mixture into a beta-olefin-containing hydrocarbon phase and an acid phase without substantially reducing the concentration, on a hydrocarbon-free basis, of said acid, heating a portion of the separated acid phase under vacuum to effect removal of beta olefin therefrom, returning at

least a part of the thus heated acid to contact with said alpha-olefin-containing hydrocarbon and using another part of said separated acid in effecting said tertiary olefin removal.

4. A process of producing a normal beta olefin from a hydrocarbon mixture comprising the corresponding alpha olefin of at least four carbon atoms per molecule and a tertiary olefin, which comprises contacting said mixture with sulfuric acid to selectively remove tertiary olefin therefrom, intimately mixing the remaining alpha-olefin-containing hydrocarbon with sulfuric acid of about 50% to 85% concentration at a temperature between about 120° F. and 250° F. at which isomerization of said alpha olefin to said beta olefin takes place, separating the resulting mixture into a beta-olefin-containing hydrocarbon phase and an acid phase containing absorbed olefin without substantially reducing the concentration, on a hydrocarbon-free basis, of said acid, continuously returning at least a substantial part of said separated acid phase to contact with said alpha-olefin-containing hydrocarbon until the acid is at least partly spent with respect to its effectiveness for isomerizing olefins as a result of the accumulation of organic impurities therein, and using said at least partly spent acid in effecting said tertiary olefin removal.

5. A process of producing beta butylene from a hydrocarbon mixture comprising isobutylene, alpha and beta butylenes and butanes which comprises extracting said mixture with sulfuric acid to remove isobutylene therefrom without substantial polymerization, intimately mixing the remaining alpha and beta butylenes with about 0.3 to 1.5 volumes of sulfuric acid of about 70% to 75% concentration per volume of liquid hydrocarbon, at about 170° F. to 180° F. for about 5 to 30 minutes, separating the resulting mixture into a beta butylene-containing hydrocarbon phase and an acid phase without substantially reducing the concentration, on a hydrocarbon-free basis, of said acid, distilling the separated hydrocarbon phase to recover beta butylene in a more concentrated form, continuously returning at least a part of said separated acid phase to contact with alpha and beta butylene-containing hydrocarbons until the acid is at least partly spent with respect to its effectiveness for isomerizing olefins as a result of the accumulation of organic impurities therein, and feeding at least a part of said spent acid to said isobutylene extraction.

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