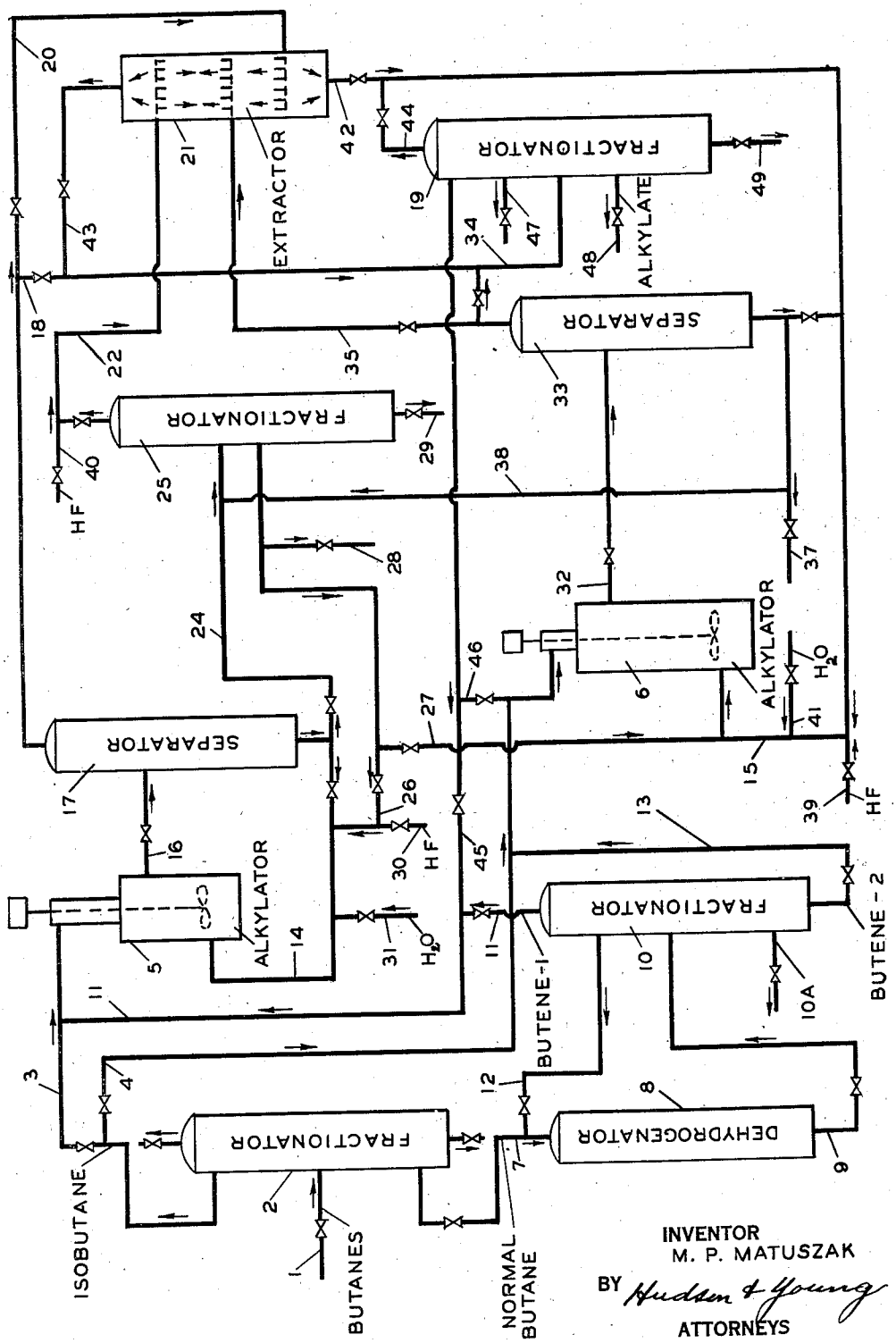
Aug. 26, 1947. M. P. MATUSZAK 2,426,559

ALKYLATION OF ISOPARAFFINS BY MEANS OF NORMAL OLEFINS IN THE PRESENCE OF HYDROFLUORIC ACID

Filed Aug. 21, 1944



INVENTOR
M. P. MATUSZAK
BY Hudson & Young
ATTORNEYS

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UNITED STATES PATENT OFFICE

2,426,559

ALKYLATION OF ISOPARAFFINS BY MEANS OF NORMAL OLEFINS IN THE PRESENCE OF HYDROFLUORIC ACID

Maryan P. Matuszak, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

Application August 21, 1944, Serial No. 550,447

2 Claims. (Cl. 260—683.4)

1

This invention relates to the conversion of hydrocarbons in the presence of hydrofluoric acid. In a particular embodiment of this application it relates to the alkylation of low-boiling isoparaffin hydrocarbons by reaction with low-boiling normal olefins such as propylene, butene-1, butene-2, pentene-1, pentene-2, and the like. Particular advantages result from the specific embodiment wherein isobutane is alkylated by reaction with butene-1.

At present, one important commercial method of converting low-boiling hydrocarbons into motor-fuel hydrocarbons is alkylation of isoparaffins with olefins in the presence of catalysts such as hydrofluoric acid and sulfuric acid. In present commercial processes using hydrofluoric acid the hydrofluoric acid is preferably anhydrous, and the presence of water is generally considered, on the basis of results obtained in the hydrofluoric acid alkylation of isobutane with isobutylene, to be highly undesirable because it increases corrosion of equipment, decreases alkylate yield and quality, and increases formation of organic fluorine compounds, which must be removed from the alkylate at considerable trouble and expense.

Contrary to the teachings of the prior art, I have made the surprising and unexpected discovery that, in the hydrofluoric acid alkylation of isobutane with a normal butylene, especially butene-1, the presence of a minor amount of water in the hydrofluoric acid leads to the production of an alkylate so superior in octane rating that the disadvantages attendant upon the presence of water are much more than counterbalanced. It may be emphasized at the outset that the advantages of the present invention attendant upon the presence of water in the hydrofluoric acid are obtained only when the olefin is a normal olefin and are obtained in the highest degree when the olefin is butene-1; they are not obtained when the olefin is an isoolefin, such as isobutylene.

Among the objects of this invention is to provide an improved process for the conversion of hydrocarbons.

Another object is to provide an improved process for alkylating isobutane with a normal butylene, whereby the alkylate obtained has an octane rating higher than that of the alkylate obtained under comparable conditions by conventional hydrofluoric acid alkylation.

A further object of my invention is to alkylate low-boiling isoparaffins.

Another object is to provide a process for utilizing hydrofluoric acid containing a limited proportion of water as a relatively superior catalyst for the alkylation of isobutane with butene-1.

Other objects and advantages will be apparent

2

from the accompanying description and disclosure.

This invention has resulted from a continuation of the experimental and inventive activity evidenced by my copending applications, Serial Number 467,872, now Patent 2,399,368, issued April 30, 1946, Serial Number 467,873, and Serial Number 467,874, now Patent 2,387,162, issued October 16, 1945, all of which were filed December 4, 1942, and of which this application is considered to be a continuation-in-part insofar as any common subject matter is concerned. The last-mentioned copending application is a continuation-in-part of my application Serial Number 395,282, filed May 26, 1941, now Patent 2,320,629, issued June 1, 1943.

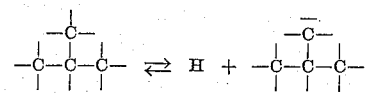
As was pointed out in these copending applications, in present-day acid-catalyzed alkylation processes for reacting paraffins with olefins to produce heavier paraffins, the principal or major constituents of the alkylate produced are those which would be formed if one olefin molecule added to one paraffin molecule by a mechanism termed paraffin-olefin juncture. In such juncture, apparently a hydrogen or a methyl group from the original paraffin becomes attached to one of the two double-bond carbon atoms of the original olefin, and the rest of the original paraffin becomes attached to the other double-bond carbon atom. The number of carbon atoms per molecule of the major components of the product is accordingly equal to the sum of the numbers of carbon atoms per molecule of the paraffin and the olefin reactants. Only a limited number of the many possible paraffin isomers characterized by this number of carbon atoms per molecule are formed as primary products of simple paraffin-olefin junctures. However, other isomers may be formed by secondary and side reactions, such as isomerization of the primary alkylate, isomerization of the original olefin prior to the alkylation reaction, dimerization of the original olefin accompanied or followed by hydrogenation of the dimer, and the like.

Heretofore, those skilled in the art of alkylation have directed their efforts mainly towards increasing the extent of the simple paraffin-olefin juncture and towards decreasing the extent of side reactions, especially polymerization of the olefin. However, in many instances, specific side reactions other than polymerization produce constituents in the alkylate that are more desirable and valuable than those produced by the juncture of the initial paraffin with the initial olefin. Such a desirable side reaction is believed to be promoted in the process of the present invention, whereby apparently a relatively increased proportion of one or more relatively high-octane-number octanes, particularly 2,2,4-trimethyl pentane, is produced in the alkylate.

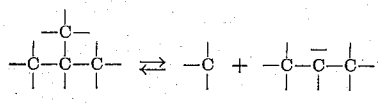
This particular octane is the primary alkylate formed by paraffin-olefin juncture in the hydrofluoric acid alkylation of isobutane with isobutylene. Although it is also formed to a small extent in the hydrofluoric acid alkylation of isobutane with a normal butylene, no fully satisfactory explanation of its formation from these particular reactants has been available, and no economical and readily practicable means for promoting or increasing its formation has thus far been proposed.

The following theoretical explanation or mechanism for the formation of 2,2,4-trimethylpentane in the acid-catalyzed alkylation of an isoparaffin with an olefin is offered solely for the purpose of aiding an understanding of some aspects of the present invention.

In the presence of an alkylation catalyst such as hydrofluoric acid, the isoparaffin appears to "ionize" in at least two ways, each yielding a positive ion and a negative ion, which for convenience may be designated and differentiated from each other by adding to the root form of the corresponding radical the terminations ium and ide, respectively. For example, isobutane ionizes to either hydrium (proton or positive hydrogen ion) and isobutide or methium and isopropide, as follows:



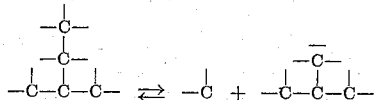
Isobutane Hydrium Isobutide



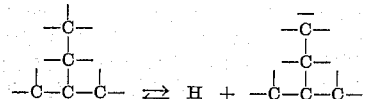
Isobutane Methium Isopropide

The dashes perpendicular to an atom represent bonds or shared pairs of electrons between two carbon atoms or between a carbon atom and a hydrogen atom, and the dashes parallel to an atom represent unshared or "lone" pairs of electrons. For simplicity, the hydrogen atoms are not written, except for the one directly involved in the reaction.

The first type of ionization may be characterized as hydrium-forming ionization, and the second type may be characterized as methium-forming ionization. For isopentane, the methium-forming ionization appears to predominate over the hydrium-forming ionization to an extraordinarily high degree:



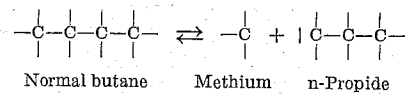
Isopentane Methium Isobutide



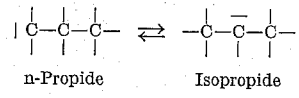
Isopentane Hydrium Isopentide (or isoamide)

This predominance of methium-forming ionization in the case of isopentane is of exceedingly great significance because it indicates an

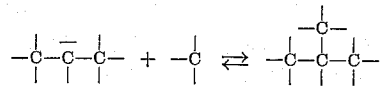
exceptionally strong tendency for the ethyl group to undergo methium-forming ionization. That is, any hydrocarbon possessing an ethyl group has a strong tendency to lose the methyl group in this ethyl group by liberation of methium. This tendency naturally increases with the size and the complexity of the hydrocarbon molecule, with the possible exception of hydrocarbons having the structure of 2,3-dimethylpentane, such as 2,3,3-trimethylpentane, in which it is apparently internally counterbalanced to some extent. It is almost undetectable in propane, but it increases in normal butane to the extent that advantageous isomerization to isobutane can occur by an over-all succession of methium-forming ionization, hydrogen shifting (which may involve hydrium-forming ionization), and recombination of ions:



Normal butane Methium n-Propide



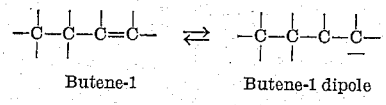
n-Propide Isopropide



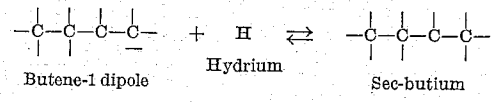
Isopropide Methium Isobutane

This strong tendency for an ethyl group to undergo methium-forming ionization appears to account for the fact that the alkylation of isopentane can give the high yields of concomitantly formed isobutane and isohexane that are indicated in my aforementioned copending application, Serial Number 467,872; for the isobutide for the methium-forming ionization of one isopentane molecule can unite with the hydrium from the hydrium-forming ionization of another isopentane molecule to yield a molecule of isobutane, and, similarly, the methium and the isopentide can unite to form a molecule of isohexane. In similar fashion, in the alkylation of isobutane, the formation of propane and of isopentane can be accounted for by the combination of hydrium with isopropide and of methium with isobutide, respectively; however, it does not necessarily follow that such propane and such isopentane are formed in molecularly equivalent amounts, for the hydrium and the isopropide corresponding to the methium and the isobutide that unite to form isopentane may be selectively consumed in other reactions.

The ionization of paraffins in hydrofluoric acid and recombination of ions to form either the original or new paraffins is apparently promoted by the presence of an olefin. The reason for the promotion appears to be that the olefin has a strong tendency to acquire a positive ion, such as hydrium, by the following mechanism, exemplified for butene-1, which forms principally secondary butium:

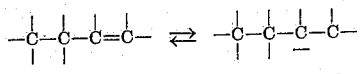


Butene-1 Butene-1 dipole

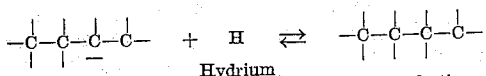


Butene-1 dipole Hydrium Sec-butium

In similar fashion, but to a relatively minor extent, butene-1 can yield primary butium:

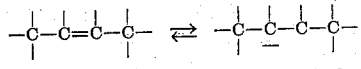


Butene-1 Butene-1 dipole

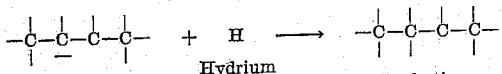


Butene-1 dipole Hydrium Primary butium

In similar fashion, butene-2 yields substantially only secondary butium:



Butene-2 Butene-2 dipole

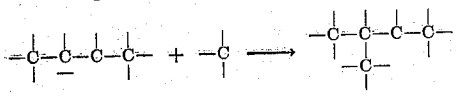


Butene-2 dipole Hydrium Sec-butium

By this mechanism methium may be added similarly, instead of hydrium, but the resulting positive ion differs for butene-1 and butene-2:

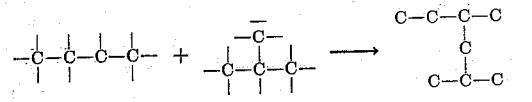


Butene-1 dipole Methium Diethylmethium

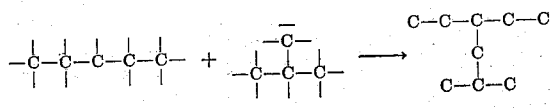


Butene-2 dipole Methium Methylisopropylmethium

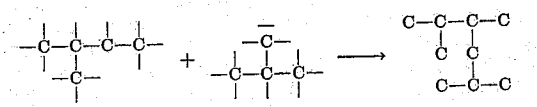
The resulting positive ion logically can combine with any of the negative hydrocarbon ions present to form a primary-alkylate paraffin (for simplicity the carbon-hydrogen bonds in the product may be omitted):



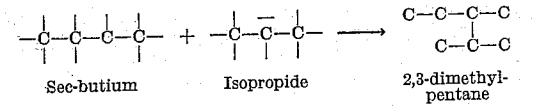
Sec-butium Isobutide 2,4-dimethylhexane



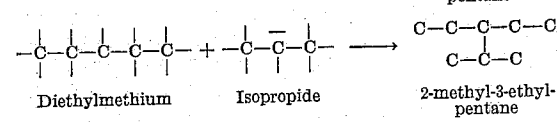
Diethylmethium Isobutide 2-methyl-4-ethylhexane



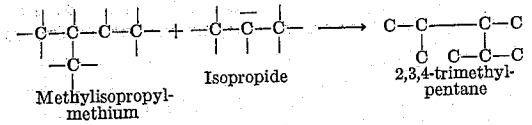
Methylisopropylmethium Isobutide 2,3,5-trimethylhexane



Sec-butium Isopropide 2,3-dimethylpentane



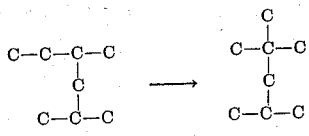
Diethylmethium Isopropide 2-methyl-3-ethylpentane



Methylisopropylmethium Isopropide 2,3,4-trimethylpentane

The identity and the relative proportion of any particular primary-alkylate paraffin produced in this matter depends on the identity and the relative proportions of the ions that unite to form the paraffin.

Certain of the theoretical primary-alkylate products contain, just as does isopentane, one or more ethyl groups. In consequence, these products have a relatively high tendency to undergo methium-forming ionization, and the resulting negative ion then may undergo reactions like those already exemplified. For example, 2,4-dimethylhexane, which is theoretically a major primary product in the alkylation of isobutane with a normal butylene, may undergo an isomerization similar in mechanism to that already shown for the isomerization of normal butane (but far more facile because of the relatively larger size and complexity of the molecule):



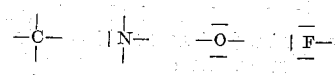
2,4-dimethylhexane 2,2,4-trimethylpentane

If, instead of undergoing a hydrogen shift and then recombining with methium, the negative ion preliminarily formed by methium-forming ionization acquires hydrium, 2,4-dimethylpentane is formed. Similarly, from 2-methyl-4-ethylhexane may be formed 2,4,4-trimethylhexane or 2,4-dimethylhexane, depending on whether the negative ion formed by the methium-forming ionization eventually combines with methium or with hydrium; inasmuch as each of these products still contains an ethyl group, further reaction may occur, to form such final product paraffins as 2,2,4-trimethylpentane and 2,4-dimethylpentane. Similarly, other primary-alkylate paraffins containing ethyl groups are converted, at least in part, to other paraffins that do not contain ethyl groups. In consequence, such a paraffin as 2-methyl-3-ethylpentane, which is formed only in relatively small proportion and which contains at least one ethyl group, is practically absent from the final alkylate, whereas such a paraffin as 2,3,4-trimethylpentane, which also is formed in relatively small proportion but which does not contain as ethyl group, survives and can be isolated from the final alkylate.

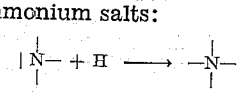
The foregoing simple but far-reaching theoretical explanation or mechanism of acid-catalyzed alkylation presents a clear, logical picture of the reactions that take place. It appears to account remarkably well for most if not all of the experimental facts known at present in the field of acid-catalyzed alkylation. For present purposes, it need not be made exhaustive, so that no attempt need be made herein to account explicitly for the presence or the absence of each and every alkylate product.

In this mechanism, a limited proportion of water can play a role that is apparently similar to the initial role of the olefin, that of promoting the ionization of various paraffins by acting as a hydrium or methium acceptor. Understanding of this theoretical conception may be facilitated by a consideration of the nature of hydrofluoric acid, particularly strong or substantially anhydrous hydrofluoric acid as distinguished from a dilute aqueous solution. The nature of this material is most simply comprehended by a realization that it is the fourth member of the series: methane, ammonia, water, hydrofluoric acid.

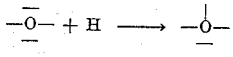
Electronically, these compounds may be represented as follows:



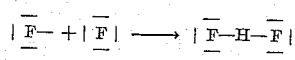
In this series, each member has one more "lone" electron pair than the preceding member. Each member has a tendency to acquire the structure present in methane, that is, to have four hydrogen atoms each bound to the central atom by an electron pair. This tendency is obviously strongest in ammonia, which unites or coordinates with hydrium to form the positive ammonium ion present in ammonium salts:



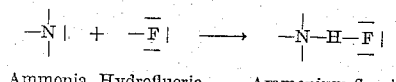
This tendency is relatively less strong in water, which however, does form the positive hydronium (hydroxonium) ion:



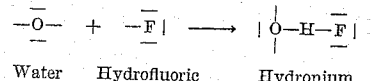
Understandably, this tendency is least strong in hydrofluoric acid, which in fact attracts fluoride rather than hydrium, forming a complex negative ion containing a hydrogen bridge:



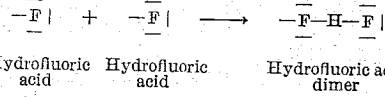
Although this last equation appears to indicate a difference in kind rather than a difference in degree between hydrofluoric acid on the one hand and ammonia and water on the other, the fact is that the difference is only one of degree, as may be readily realized from the consideration that hydrofluoric acid polymerizes and that both ammonia and water combine with hydrofluoric acid to form salts. Of these salts, the salt from ammonia, ammonium fluoride, is quite stable and is well known in solid form, whereas the corresponding salt from water, hydronium (or hydroxonium) fluoride, is relatively less stable, so that it is known chiefly in solution, although it undoubtedly can be isolated as a solid at low temperatures; corresponding to these two salts is the relatively still less stable dimer of hydrofluoric acid. The gradation among these three substanances is readily seen from the following electronic equations for their formation:



Ammonia Hydrofluoric acid Ammonium fluoride



Water Hydrofluoric acid Hydronium fluoride



Hydrofluoric acid Hydrofluoric acid Hydrofluoric acid dimer

It appears from the foregoing that, on passing from ammonia to hydrofluoric acid, there is a definite gradation in the tendency to form ions or salts corresponding to the ammonium ion or the ammonium salt. In water this tendency is of an intermediate strength that is highly suited for the purposes of the present invention, whereby the reactions leading to relatively high-octane-number motor-fuel paraffins are promoted and expedited, possibly through facilitating ionization of paraffins by the acceptance or acquisition of hydrium or methium to form the corresponding positive oxonium ion. However, the proportion of water present must be limited, for too large a proportion changes the system from one in which hydrofluoric acid is the solvent to one in which water is the solvent, and the nature of the reactions that can take place is correspondingly greatly changed. Apparently, when the proportion of water is gradually increased, the solubility of the paraffin is correspondingly decreased, wherefore the ionization of the paraffin is likewise decreased, and the alkylation reactions are correspondingly hindered. Concurrently, ionization of hydrofluoric acid into hydrogen and fluoride ions is correspondingly increased, so that any positive ion formed by the union of an olefin molecule and a hydrogen ion is caused to unite with a fluoride ion rather than with a negative hydrocarbon ion of the type of isobutide, isopropide, or the like. In consequence, the olefin is largely consumed in the formation of the corresponding alkyl fluoride instead of undergoing juncture with a paraffin.

In accordance with one aspect of this invention, the formation of molecules of hydrocarbons having high octane numbers is promoted by the presence of a minor, or limited, proportion of water in the hydrofluoric acid. From the results of extensive experimentation, it has been found that the proportion of water in the hydrofluoric acid should be between approximately 2 and approximately 10 per cent by weight of the hydrogen fluoride, exclusive of any dissolved organic material, when normal butenes are the alkylating olefins. The optimum proportion for any particular set of selected alkylation conditions may be readily determined by trial; usually the optimum proportion in alkylating isobutane with butene-1 is between 4.0 and 6.0 per cent by weight, so that the proportion is preferably adjusted to approximately 5.0 percent. This proportion is rather critical from the point of view of obtaining an alkylate of the highest possible octane rating. If too little water is present, the alkylation degenerates into the conventional alkylation; if too much is present, the olefin is consumed in formation of the corresponding alkyl fluoride, accompanied by considerable polymerization, and the resulting product is inferior in both yield and octane rating and contains an excessive proportion of organic fluorine compounds. However, the critical limits of the proportion of water in hydrofluoric acid alkylation with butene-2 appear to differ somewhat from those found for butene-1, under otherwise substantially identical alkylation conditions. That is, in alkylation of isobutane with butene-2, the optimum proportion of water appears to be between approximately 2.0 and approximately 4.0 per cent by weight of the hydrogen fluoride in the catalyst, so that the proportion is preferably maintained at approximately 3.0 per cent. For alkylating an isoparaffin with a mixture of normal butylenes, the preferred proportion of water may be calculated in accordance with the proportions of these butylenes in the olefin feed; for example, for an olefin feed containing approximately equal proportions of butene-1 and of butene-2, the preferred proportion of water is approximately 4.0 per cent by weight of the hydrogen fluoride in the catalyst. In alkylating with solely isobutylene, however, no water preferably should be present in the catalyst; hence, when the alkylation is being made with a mixture containing one or both normal butylenes

and isobutylene, the proportion of water should be adjusted in accordance with the proportions of the specific butylenes present. For example, for alkylating with a mixture containing approximately equal proportions of butene-1, butene-2, and isobutylene, the proportion of water should preferably be adjusted to approximately 3.0 per cent by weight of the hydrogen fluoride. It will be understood that adjusting the proportion of water in this manner is in the interest of obtaining the optimum octane rating for the over-all alkylate produced.

A detailed explanation of one embodiment of this invention may be made with reference to the accompanying drawing, which is a schematic flow-diagram exemplifying a preferred manner of converting four-carbon paraffins to motor-fuel paraffins.

A mixture of isobutane and normal butane entering the system through inlet 1 is separated into its components by fractionator 2. The isobutane is passed through conduits 3 and 4 to alkylators 5 and 6, which preferably are so designed that the incoming isobutane sweeps any corrosive mixture away from any bearing box or packing gland. The normal butane is passed through conduit 7 to dehydrogenator 8, in which it is catalytically dehydrogenated in known manner to normal butylenes. The resulting dehydrogenation effluent is passed through conduit 9 to fractionator 10, which comprises a system of fractional-distillation columns. From this system, butene-1 is passed through conduit 11 to the isobutane stream in conduit 3; undehydrogenated normal butane is recycled through conduit 12 to dehydrogenator 8; butene-2 is passed through conduit 13 to the isobutane stream in conduit 4; and by-products of the dehydrogenation are removed, mostly as a low-boiling fraction, in a manner obvious to those skilled in the art, as through conduit 10A.

In each of alkylators 5 and 6, the incoming mixture of isobutane and normal butylene is intimately mixed under alkylation conditions with an alkylation catalyst, which enters the alkylator from conduit 14 or 15, respectively. For alkylator 5, in which the alkylating butylene is butene-1, the catalyst is hydrofluoric acid containing approximately 5.0 per cent by weight of water; for alkylator 6, in which the alkylating butylene is butene-2, the catalyst is hydrofluoric acid containing about 3.0 per cent by weight of water. Except for the difference in water content of the hydrofluoric acid, the alkylation conditions in the two alkylators may be substantially alike. The pressure should be sufficient to maintain the reaction mixture in liquid phase, but above this point it may be as high as may be desired for such purposes as effecting proper movement of the various streams in the system or the like. The temperature and the contact time, or average time of residence or mixing in the alkylator, may vary widely; for a temperature in the range of 90 to 120° F., which is preferred as being readily obtainable by water-cooling, the contact time is preferably approximately 10 minutes. The volume ratio of hydrocarbons to hydrofluoric acid in the alkylator is preferably approximately 1:1. The mol ratio of isobutane to butylene in the incoming hydrocarbon stream is preferably as high as is economically feasible; usually it is from 4:1 to 10:1.

The reaction mixture effluent from alkylator 5 is passed through conduit 16 to separator 17, in which it is separated by gravity into two liquid phases. The hydrocarbon phase may be passed through conduits 18 and 34 to fractionator 19 for separation into various fractions, but it is preferably passed through conduit 20 to extractor 21 for removal of organic fluorine compounds by extraction with substantially anhydrous hydrofluoric acid, which is introduced through conduit 22, in a manner indicated in the aforementioned Patent 2,320,629. The hydrofluoric acid phase from separator 17 in part is recycled through conduit 14 to alkylator 5 and in part is passed through conduit 24 to fractionator 25. From fractionator 25, anhydrous hydrofluoric acid, accompanied by some light hydrocarbons, is passed overhead through conduit 22 to extractor 21; a constant-boiling aqueous hydrofluoric acid, containing approximately 40 per cent of hydrogen fluoride, is passed in part through conduit 26 to alkylator 5 and in part through conduit 27 to alkylator 6, but part or all of it may be withdrawn, if desired, through outlet 28; and a relatively small fraction of so-called "acid-soluble oil" is withdrawn through outlet 29. Make-up hydrofluoric acid, which is obtained commercially in substantially anhydrous form, may be added as required through inlet 30, and make-up water is added as required through inlet 31.

The reaction mixture effluent from alkylator 6 is passed through conduit 32 to separator 33, in which it is separated by gravity into two liquid phases. The hydrocarbon phase may be passed through conduit 34 to fractionator 19, for separation into various fractions, but it is preferably passed through conduit 35 to extractor 21 for removal of organic fluorine compounds by extraction with hydrofluoric acid; inasmuch as this hydrocarbon phase at times contains slightly less organic fluorine than the hydrocarbon phase from separator 17, it is preferably introduced into extractor 21 at a point correspondingly relatively upstream with respect to the stream of extracting acid. The hydrofluoric acid phase from separator 33 in part is recycled through conduit 15 to alkylator 6 and in part is withdrawn through outlet 37 or, preferably, is passed through conduit 38 to fractionator 25 for purification. Make-up hydrofluoric acid may be added through inlet 39, but it is preferably added entirely through inlet 40 to extractor 21; make-up water, when required, may be added through inlet 41, but ordinarily sufficient water is brought in in the acid flowing in conduit 27.

From extractor 21 the hydrofluoric acid extract is passed through conduit 42 to alkylator 6, carrying with it the extracted organic fluorine compounds, which thus become available for the alkylation in alkylator 6 with advantageous recovery of the organic fluorine as hydrogen fluoride.

From extractor 21 the organic fluorine-depleted hydrocarbon mixture is passed through conduit 43 to fractionator 19, which generally is a system of fractional-distillation columns. From this system hydrofluoric acid dissolved in the hydrocarbon mixture is distilled overhead in company with some isobutane and is passed through conduit 44 to alkylator 6. Isobutane is recycled to alkylators 5 and 6 through conduits 45 and 46. Normal butane is withdrawn through outlet 47, or is passed to dehydrogenator 8 by means not shown. A motor fuel of high octane rating is withdrawn as the principal product of the process through outlet 48. A small fraction of heavy hydrocarbons may be withdrawn through outlet 49.

It will be understood that the flow-diagram is schematic and that auxiliary equipment, not

shown or described, such as pumps, valves, controllers, and the like, may be desirable or even necessary at various points in the process. As such auxiliary equipment are well known, they can be readily supplied by those skilled in the art.

The following data are illustrative of some of many aspects of the invention, without being necessarily limitative.

Two continuous pilot-plant runs were made for the alkylation of isobutane with butene-1 under similar alkylation conditions except that in one run the hydrofluoric acid contained 5.0 per cent by weight of water (based on anhydrous HF), whereas in the other run the acid was anhydrous. The data obtained may be summarized as follows:

Run	With 5% water	Without water
Temperature, ° F	92	88
Contact time, min	10.1	11.1
Isobutane/butene-1 (mol)	4.7:1	4.7:1
Hydrocarbons/HF (vol.)	1:1	1:1
Organic F in hydrocarbon effluent, wt. per cent	0.0165	0.0159
Total debutanized alkylate:		
Gravity, ° API	68.1	67.8
Reid vapor pressure, lb	2.30	2.75
ASTM distillation, ° F.—		
First drop	178	162
5% evap	202	196
10	210	203
20	214	213
30	218	218
40	221	223
50	223	227
60	227	233
70	231	239
80	238	253
90	262	293
95	325	380
Dry point	392	463
ASTM octane number	91.0	85.3
Light Alkylate:		
Cut Point, ° F	365	365
Yield, vol. per cent of total	97.2	92.5
Gravity, ° API	68.4	69.0
Reid vapor pressure, lb	1.75	2.80
ASTM distillation, ° F.—		
First drop	190	151
5% evap	206	194
10	211	204
20	215	212
30	218	216
40	220	220
50	222	224
60	224	227
70	227	229
80	232	234
90	242	250
95	270	302
Dry point	358	368
ASTM octane number	92.0	87.4

It will be noted that the octane number of the total alkylate was increased by 5.7 units because of the presence of the water in the hydrofluoric acid and that the octane number of the light or aviation-range alkylate was increased by 4.6 units. Furthermore, it will be noted that the light alkylate constituted 97.2 per cent of the total alkylate when water was present, whereas it was only 92.5 per cent when water was absent, indicating that the formation of exceedingly heavy hydrocarbons was advantageously decreased; inasmuch as the yield of total alkylate was approximately the same in both runs, being approximately 200 per cent by weight of the original butene-1, this fact indicates that an advantageously somewhat higher yield of light alkylate is obtained from butene-1 when the present invention is practiced.

It may be pointed out that in both these runs the mol ratio of isobutane to butene-1 in the feed was fairly low, 4.7:1. There are a number of factors that at present make it desirable to conduct commercial alkylation at such a fairly low value for this ratio, even though it causes the yield and the quality of the alkylate to be somewhat adversely affected. When as at present, the need for high-quality alkylate is great, the available alkylation equipment is quite limited, and the amount of isobutane is insufficient for all needs, it is desirable to conduct the alkylation at a fairly low mol ratio of isobutane to olefin, in the interest of obtaining as much alkylate as possible from the available isobutane with the available equipment. Also, for a given output of alkylate, the concomitant undesirable isomerization of isobutane to normal butane that occurs during alkylation is decreased by decrease in the ratio of isobutane to olefin, so that the over-all consumption of isobutane is decreased. In line with these considerations, it may be observed that the yield and the quality of the alkylate obtained in the run made without water reflect the influence of the ratio of isobutane to butene-1, for at a mol ratio twice as large the yield of light alkylate is approximately 98 per cent by volume of the total alkylate and the octane number is approximately 89. But in the run made with water, the yield and the octane number of the alkylate approach closely those that are obtained in hydrofluoric acid alkylation of isobutane with butene-2 without water at a mol ratio of isobutane to olefin approximately twice that used in the present run. In other words, the practice of this invention appears to contribute the unexpected but important advantage of overcoming to a large degree the unfavorable influence attending a low value for the ratio of isobutane to olefin in the feed.

Although the advantages of some aspects of the present invention are obtained when the alkylating olefin is substantially solely butene-1, other advantages are obtained in addition when the detailed procedure indicated by the drawing is followed. This procedure provides a unitary, integrated process for alkylating with both butene-1 and butent-2, each under conditions peculiarly adapted to obtaining an alkylate of optimum yield and quality. This result is obtained with the use of a minimum of equipment and with less expenditure of time, effort, and materials than is required by a process calling for separate isomerization of butene-1 to butene-2, followed by conventional hydrofluoric acid alkylation of isobutane, such as that disclosed in the aforementioned copending application, Serial Number 467,873.

Inasmuch as this invention may be practiced other wise than as specifically described or illustrated, and inasmuch as many variations and modifications of it will be obvious to those skilled in the art, this invention should not be restricted otherwise than as specified in the appended claims.

I claim:

1. In a process for the alkylation of isobutane with butenes comprising normal butenes in the presence of a concentrated hydrofluoric acid catalyst, the improvement which comprises maintaining in said hydrofluoric acid catalyst a content of a water in weight per cent of hydrogen fluoride present within a range, the approximate lower limit of which range is determined by 4 times the mol fraction of butene-1 of the total of the butenes plus 2 times the mol fraction of butene-2 of the total of the butenes and the approximate upper limit of which range is determined by 6 times the mol fraction of butene-1 of the total of the butenes plus 4 times the mol fraction of butene-2 of the total of the butenes.

2. In a process for the alkylation of isobutane with a mixture of normal butenes in the presence of a concentrated hydrofluoric acid catalyst, the improvement which comprises maintaining in said hydrofluoric acid catalyst a content of water in weight per cent of hydrogen fluoride present which is 5 times the mol fraction of butene-1 of the total of the butenes plus 3 times the mol fraction of butene-2 of the total of the butenes.

MARYAN P. MATUSZAK.

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