Jan. 19, 1943. R. F. MARSCHNER ET AL 2,308,561

ALKYLATION OF HYDROCARBONS

Filed June 18, 1941

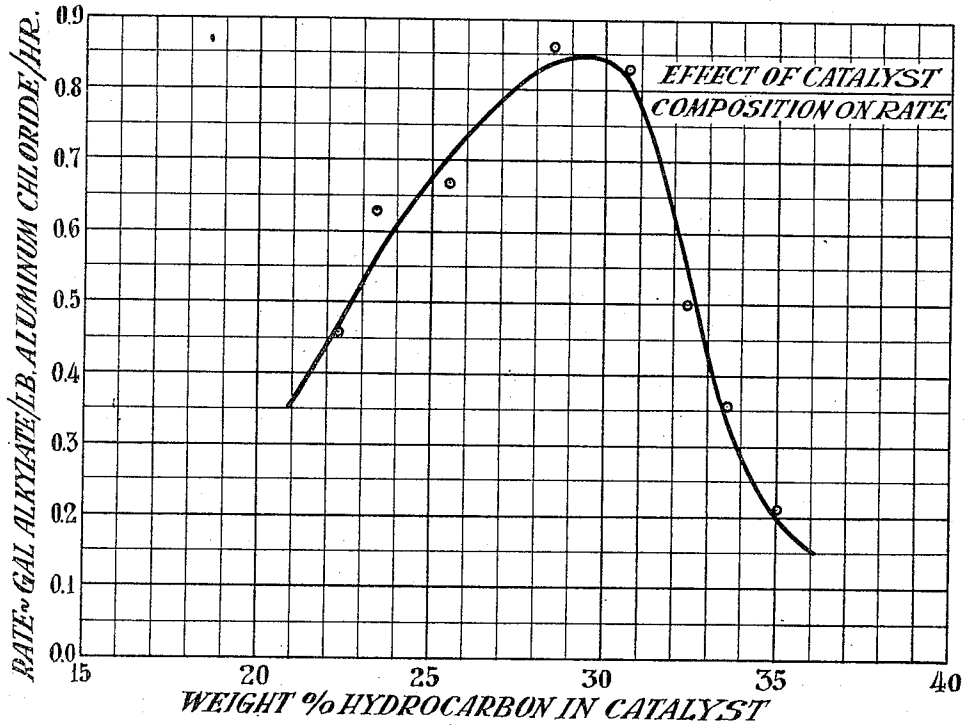


Fig. 1.

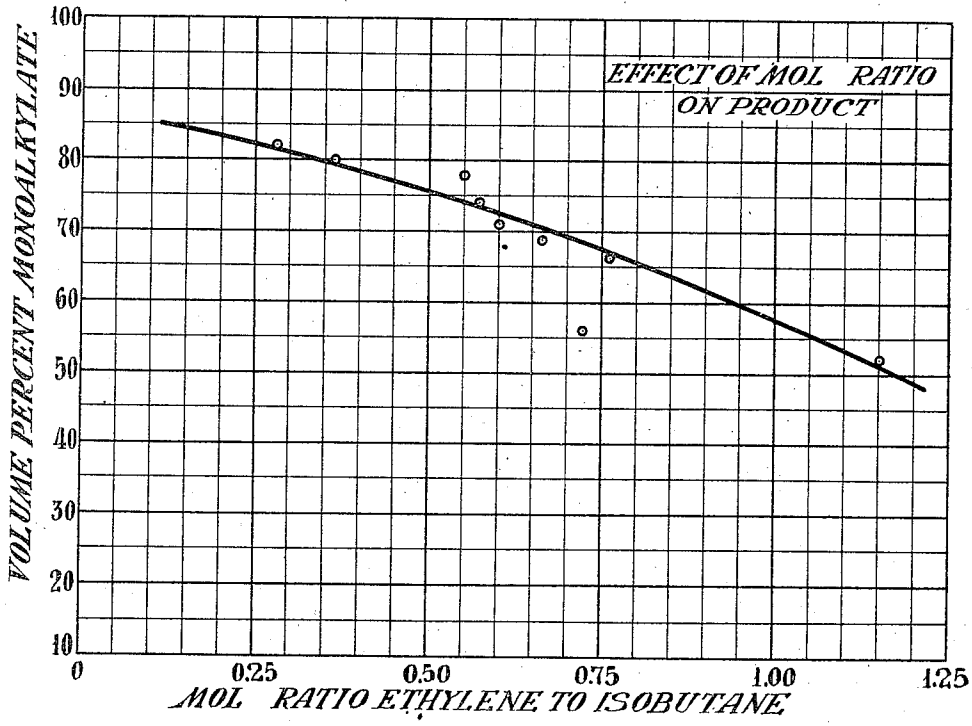


Fig. 2.

Inventors:
Robert F. Marschner
Don R. Carmody
By Donald A. Dickey
Attorney.

Patented Jan. 19, 1943

2,308,561

UNITED STATES PATENT OFFICE

2,308,561

ALKYLATION OF HYDROCARBONS

Robert F. Marschner, Homewood, Ill., and Don R. Carmody, Hammond, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

Application June 18, 1941, Serial No. 398,556

15 Claims. (Cl. 196—10)

This invention relates to the production of normally liquid hydrocarbons from normally gaseous hydrocarbons and relates more particularly to the alkylation of isoparaffinic hydrocarbons with olefinic hydrocarbons in the presence of a catalyst.

For many years, it has been customary to subject petroleum hydrocarbons to cracking operations for the production of gasoline. One of the by-products from this operation is a varying amount of normally gaseous hydrocarbons, usually comprising a mixture of olefinic and paraffinic hydrocarbons in various proportions. These by-product hydrocarbons were considered in the nature of waste gases until recent years when it has been realized that they are a valuable source of initial stock for the production of definite hydrocarbons suitable either as aviation gasoline or as motor fuels of high octane number.

Various commercial operations have been proposed and employed for the conversion of the gaseous hydrocarbons to normally liquid hydrocarbons of gasoline boiling range, including such processes as polymerization plus hydrogenation, alkylation, etc. The products from these processes have proved so valuable that various hydrocarbons from other sources are now being diverted for conversion purposes, including gases from natural gas and from the light ends of products from "distillate well." Cracking, dehydrogenation and isomerization have been employed for the conversion of paraffinic hydrocarbons to feed stocks suitable for these processes. Alkylation is perhaps a more desirable method of obtaining hydrocarbons suitable for gasoline than, for example polymerization, since there is no need for subjecting the alkylation product to hydrogenation in order to obtain saturated hydrocarbons of high octane number. Branched-chain hydrocarbons other than isobutane (the only normally gaseous isoparaffinic hydrocarbon) are also occasionally diverted to alkylation in order to obtain additional amounts of higher boiling hydrocarbons of high octane number.

It is an object of this invention to provide an improved process for the alkylation of isoparaffinic hydrocarbons, and more specifically the alkylation of isobutane with normally gaseous olefins to produce saturated branched-chain hydrocarbons within the gasoline boiling range. Another object of our invention is to provide an improved alkylation process employing a specific type of catalyst under certain conditions of operation. A further object of our invention is to provide a process for the optimum conversion of isoparaffinic hydrocarbons and olefins to branched-chain hydrocarbons suitable for use as aviation fuels. An additional object is to provide a process wherein isobutane is alkylated with ethylene under conditions and with a catalyst whereby the alkylation product is obtained with a minimum of degradation to undesirable by-products. It is also an object of our invention to provide a process for the production primarily of monoalkylate from the reaction of an isoparaffiin and an olefin. Other objects and advantages of our invention will become apparent as the description thereof proceeds.

In the drawing:

Figure 1 is a plot depicting graphically the effect of the ratio of "bound" hydrocarbon to aluminum chloride in the catalyst on the rate of alkylation; and

Figure 2 is a plot depicting graphically the effect of the ratio of olefin reacted to isoparaffin present on the production of monoalkylate.

Briefly stated, our invention contemplates the alkylation of an isoparaffin such as isobutane with an olefin such as ethylene in the presence of a particular catalyst comprising an aluminum halide-hydrocarbon complex under restricted conditions of temperature, pressure, ratio of reactants, and amount of activator.

Aluminum chloride has been employed for the alkylation of isoparaffins by olefins, as well as numerous other hydrocarbon conversion processes, and it has been found by experiment that, generally speaking, pure aluminum chloride is "too active" to be entirely satisfactory as a catalyst; i. e., the activity of the aluminum chloride as such is so great that numerous unwanted side reactions occur, such as polymerization, cracking, isomerization, etc. Various methods have been proposed for modifying the catalytic activity of this compound. For example, very low temperatures can be employed such that cracking and polymerization are substantially avoided and the reaction is primarily one of alkylation. Such temperatures, however, require much longer periods for the reaction to become complete and therefore are neither advisable nor desirable commercially. It has also been found that when reacting aluminum chloride with a normally liquid hydrocarbon, a complex or "red oil" is formed which is still catalytically active but in which the activity is considerably modified. The particular type of hydrocarbon with which the aluminum chloride reacts determines, to a marked degree, the type of complex which is formed, and complexes formed from the various types of hydrocarbons, such as olefins, straight-chain paraffins, branched-chain paraffins, naphthenes or aromatics, differ considerably in their effectiveness in promoting an olefin-paraffin alkylation reaction. Moreover, it has been proposed to form definite complexes between an aluminum halide and a hydrocarbon by employing such methods of synthesis as the Grignard reaction wherein the halogen of the aluminum halide is replaced by one or more hydrocarbon radicals. We have found that an aluminum

halide-hydrocarbon complex prepared by the direct reaction of an aluminum halide with a saturated hydrocarbon is superior to the complexes formed by the reaction of the metal halide with other classes of hydrocarbons, and of the saturated hydrocarbons, the isoparaffinic hydrocarbons yield a complex of especially desirable activity.

The active liquid aluminum halide-hydrocarbon complex employed in our alkylation reaction is prepared by the action of an aluminum halide, such as anhydrous aluminum chloride or aluminum bromide, and an activator comprising a hydrogen halide or a compound affording a hydrogen halide, on a substantially saturated fraction containing predominantly at least one paraffin hydrocarbon preferably having at least two side chains. The reaction is carried out at a temperature in the range of from about 50° F. to about 175° F. This liquid catalyst complex is suitably prepared from aluminum chloride and a substantially saturated fraction containing paraffin hydrocarbons having at least six total carbon atoms, with at least two side chains per molecule. Such saturated fractions include, for example, the hydrogenated polymers and copolymers of olefins having less than six carbon atoms per molecule, namely, ethylene, propylene and the butylenes and amylenes, and the products of alkylation of isobutane and of isopentane with such olefins are particularly suitable. These fractions are very rich in highly branched paraffinic hydrocarbons, for example, isohexanes, isoheptanes or isooctanes. We prefer to prepare our complex from a fraction rich in isooctanes, although fractions more volatile or less volatile but rich in branched-chain hydrocarbons are also effective in producing the desired complex, and fractions containing linear paraffinic hydrocarbons are included.

As an example, an aluminum chloride-hydrocarbon complex was prepared by stirring together at atmospheric pressure a quantity of anhydrous aluminum chloride with an excess of commercial isooctane and a minor amount of hydrogen chloride at 120° F. to 140° F. until a liquid complex resulted. During the complex formation large amounts of isobutane were produced and the remaining hydrocarbon liquid contained a quantity of material of a higher boiling range than that present in the original isooctane. The viscosity of the complex catalyst thus produced was below 1,000 seconds Saybolt viscosity at 100° F. and the complex was easily pumpable. The complex contained approximately 35% by weight of hydrocarbons. No complete and adequate analysis of the hydrocarbons joined to the aluminum chloride in the complex is known but investigations have shown that the hydrocarbons are not present in their original form, i. e., the isooctane is not joined to the aluminum chloride metathetically by the elimination, for example of hydrogen chloride. During the complex formation, the hydrocarbons are apparently converted to complicated ring structures with varying degrees of saturation and unsaturation. Their analysis, of course, is unimportant except in so far as it serves to distinguish the complex from those formed, for example, by means of the Grignard reaction employing alkyl halides and magnesium.

Throughout the specification and claims whenever the term "aluminum chloride-paraffinic hydrocarbon complex" or "paraffinic complex" is employed, it is intended to designate the liquid complex formed by the reaction of an aluminum halide with a paraffinic hydrocarbon in accordance with a procedure of the general type described above. We also refer to our complex as containing "bound" hydrocarbons. This is to designate that the hydrocarbon is joined to the aluminum halide by chemical means, and to distinguish it from such catalysts as those comprising a slurry or solution of an aluminum halide in a liquid hydrocarbon.

In carrying out our alkylation process, isobutane and ethylene for example, are contacted with the catalyst so that there is an intimate mingling of the feed stocks and the catalyst. This can be accomplished by adding the isobutane to the complex with vigorous stirring and introducing the ethylene into the mixture, or the isobutane and ethylene can be intimately contacted and the mixture injected into contact with the complex. Various mechanical expedients can be employed for assuring intimate contact between the reactants and catalyst, such as for example, mechanical stirrers, tubular reactors, packed towers, turbo mixers, jet injectors, etc. The process can be carried out batchwise or continuously, the latter method being the most desirable commercially. In continuous operation, the catalyst and reactants can flow concurrently or countercurrently. Moreover, instead of a single tower, with means for intimate contact, we can use a series of towers, and introduce the olefinic hydrocarbons into each tower in small increments. The catalyst and reactants, as well as the product, can flow from tower to tower concurrently or countercurrently, or we can employ separate catalyst beds in each tower and direct only the hydrocarbons through the entire system.

The catalyst, although it can be used in the form in which it is obtained from the reaction of the isoparaffinic hydrocarbons and aluminum halide, is advantageously "cut back" with anhydrous aluminum chloride so that the composition of the contents is from about 23% to about 32%, and most desirably about 28% by weight of "bound" hydrocarbons. This can be done by adding powdered anhydrous aluminum chloride to the complex previously prepared, to yield a substance of definite over-all aluminum chloride-to-"bound" hydrocarbon ratio, and this complex of limited aluminum chloride-to-"bound" hydrocarbon ratio constitutes our preferred catalyst.

Figure 1 illustrates the effect of employing an aluminum chloride-isoparaffinic hydrocarbon complex having various amounts of "bound" hydrocarbon in the complex as a catalyst in the alkylation of isobutane with ethylene, employing otherwise substantially identical conditions of temperature, pressure, amount of activator and ratio of reactants. The weight percent of "bound" hydrocarbons in the catalyst is plotted along the abscissa, and the rate of alkylation along the ordinate. The rate of alkylation is expressed in terms of gallons of alkylate produced per pound of aluminum chloride per hour. It is obvious from the graph that the rate is much greater when the weight percent of "bound" hydrocarbon in the catalyst lies between about 23% and about 32% than it is for lower or higher percentages of hydrocarbon, peak activity being found at about 28% hydrocarbons by weight. During the course of the alkylation reaction, additional amounts of hydrocarbon are added or "bound" to the complex, and in order to maintain such a catalyst near peak activity, it is only

necessary to add aluminum chloride when the "bound" hydrocarbon content approaches 30%.

In batch processes, the complex is used in quantities of at least 10% by volume, based on the volume of isoparaffinic hydrocarbons employed for alkylation, in order to secure efficient contact. In continuous operation, the process is carried out by adding the olefinic feed stock at a rate of not less than 2 cubic feet of olefin per pound of complex per hour, and preferably at a rate of from about 5 to about 20 cubic feet per pound of complex per hour to obtain the optimum conversion. At rates very much higher than this, and particularly at rates above about 50 cubic feet of olefin per pound of catalyst per hour, not only is there grave danger of the reactants passing through unchanged, but temperature control becomes much more difficult. At rates below that set forth, the contact between olefin and paraffin in the large volume of catalyst becomes more difficult, and polymerization may occur to an undesirable extent. The type of apparatus employed will influence to some extent the rate of olefin addition. If a wide, shallow tower or a tubular reactor of large diameter is employed, then obviously some additional means for mixing must be employed in order to obtain adequate contact between the reactants and the catalyst.

The alkylation is preferably carried out in the presence of an activator, employing for that purpose minor amounts of a hydrogen halide, such as hydrogen chloride or hydrogen bromide, or a substance affording a hydrogen halide under the reaction conditions such as an alkyl halide. Hydrogen chloride and ethyl chloride are particularly desirable activators. The amount of hydrogen halide should be 4% or less by weight, based upon the aluminum chloride or aluminum bromide in the complex, and may be as low as 0.5%.

We have found that the presence of hydrogen during the reaction slows the rate of alkaylation and therefore hydrogen should preferably be excluded from the reaction.

In order to obtain optimum yields of monoalkylate per unit of time it is necessary to use a rather critically controlled ratio of reactants. When using up to about 0.6 mol of ethylene reacted per mol of isobutane present, the product is fairly uniform. When using greater amounts of ethylene, the amount of lower octane number, higher boiling paraffins, especially those above the usual gasoline range, gradually increases. We therefore desire to convert from about 20% to about 40% per pass of the isobutane or other isoparaffins in order to secure the best over-all result. The ethylene stream to the alkylation reaction can be an ethylene-ethane stream containing as little as 7% ethylene. The ethane is not affected during the conversion and should be discarded from the system at the completion of the reaction. Figure 2 illustrates graphically the effect of the mol ratio of ethylene to isobutane on the production of monoalkylate—i. e., hexane. The mol ratio of ethylene to isobutane has been plotted along the abscissa and the percent by volume yield of monoalkylate along the ordinate. The conditions employed for the various points were substantially identical for each run except for the ratio of ethylene to isobutane, and fall well within the preferred range. It will be at once apparent that the yield of monoalkylate falls off appreciably when the mol ratio of ethylene to isobutane is above about 0.6. The yield of dialkylate and higher boiling hydrocarbons increases, however, as will be shown later.

Although alkylation will occur at temperatures within the range of from about 0° to about 212° F., or higher, we have found that it is highly desirable to carry out the alkylation at temperatures within the range of from about 80° to about 150° F. and most desirably at about 125° F. At lower temperatures the rate of alkylation is slower and the amount of heavy alkylate is increased, while at higher temperatures the production of "cracked" or redistributed products which are much less desirable is greatly increased.

The pressure should be superatmospheric and, while it can include a range of from about 30 pounds per square inch up to about 500 pounds per square inch, we prefer that it be maintained below 150 pounds per square inch, although the exact pressure employed does not affect the alkylation reaction to the same extent that certain of the other variables do. In all cases the pressure is sufficiently great to maintain the reactants in the liquid or dissolved phase under the conditions of temperature employed, and usually an ethylene partial pressure of about 50 pounds per square inch is employed.

The following table will illustrate the advantages of carrying out an alkylation process under the conditions herein set forth. Various runs show deviations from the preferred conditions, and the consequent loss of efficiency either as regards yield, product distribution or reaction rate. In all cases the runs were made using isobutane and ethylene as the reactants, and employing an aluminum chloride-isoparaffinic hydrocarbon complex containing at least 23% by weight of "bound" hydrocarbon. Samples of some of the products were analytically fractionated on a laboratory column having an efficiency of about 30 theoretical plates. Overhead cuts having substantially five, six, seven and eight carbon atoms per molecule, and a residual cut containing hydrocarbons having nine or more carbon atoms per molecule were taken.

Run No.	A	B	C	D	E	F	G	H	Preferred range
Temperature °F	130	128	85	48	48	205	112	105	80–150
Reactor pressure, pounds per square inch	130	135	95	100	105	250	150	130	50–150
Weight percent HCl based on $AlCl_3$	3	3	4	4	4	4	8	10	4 or less
Mols ethylene reacted per mol isobutane present	0.56	0.57	0.54	0.47	0.53	0.40	0.48	1.15	Below 0.6
Rate of production of total alkylate—lbs., alkylate/lb., catalyst/hr.	3.8	4.7	2.5	0.4	0.4	4.4	1.7	3.1	
Weight percent total alkylate based on ethylene reacted	255	235	250	191	203	302	262	214	
Weight balance percent	100	98	99	91	101	95	101	97	
Product distribution:									
Pentanes	10	8	1	1	------	45	20	4	
Hexanes	64	67	76	68	------	34	54	46	
Heptanes	6	5	4	3	------	12	8	9	
Octanes	14	15	16	22	------	9	10	20	
Heavier products	6	5	3	6	------	(1)	8	21	

[1] Included in octanes.

Runs A, B and C are illustrative of operation under our preferred conditions, runs A and B differing chiefly in the rate, while run C was carried out at much lower temperature than the other two runs. Runs D and E were carried out at a temperature below our preferred range, and illustrate admirably the effect of such deviation from the preferred conditions, since the amount of dialkylate formed is undesirably increased the yield is smaller and the reaction rate is low. In run F the temperature was above the range desired, and although it will be noted that the yield of alkylate based on ethylene was greatly increased, the product distribution shows that considerable cracking, etc., took place, the volume of pentanes being greatly increased at the expense of the more desired monoalkylate hexanes.

Run G illustrates the effect of too great an amount of activator, the yield of monoalkylate being reduced with the formation of large quantities of pentanes. In run H, the mol ratio of ethylene to isobutane has been increased to 1.15; consequently the yield of dialkylate (octanes) and higher boiling hydrocarbons has greatly increased, with a consequent decrease in monoalkylate. In the final column of the table the preferred conditions are summarized. When more than one of the operating conditions falls outside of these preferred ranges, deviation from the optimum becomes more pronounced and the yield of monoalkylate is correspondingly reduced, or the rate of conversion becomes uneconomically low.

Although we have described our process relative to the alkylation of isobutane with ethylene, it should be understood that this is by way of illustration and not by way of limitation, and that the use of other olefinic hydrocarbons, such as propylene, the butylenes, etc., is contemplated, as well as the use of other low-boiling isoparaffinic hydrocarbons such as isopentane or even isohexane.

We claim:

1. A process for alkylating isoparaffinic hydrocarbons with olefinic hydrocarbons which comprises contacting said isoparaffinic hydrocarbons with said olefinic hydrocarbons in the presence of a catalyst containing an aluminum halide-paraffinic hydrocarbon complex having from about 23% to about 32% by weight of bound hydrocarbons, and a hydrogen halide activator under conditions of temperature, pressure and ratio of reactants adapted to promote the reaction of said isoparaffinic hydrocarbons with said olefinic hydrocarbons.

2. A process for alkylating isoparaffinic hydrocarbons with olefinic hydrocarbons which comprises contacting said isoparaffinic hydrocarbons with said olefinic hydrocarbons in the presence of an aluminum halide-paraffinic hydrocarbon complex containing from about 23% to about 32% by weight of bound hydrocarbons and in the presence of a small amount of a hydrogen halide activator under conditions of temperature, pressure and ratio of reactants adapted to promote the reaction of said isoparaffinic hydrocarbons with said olefinic hydrocarbons.

3. A process for alkylating isoparaffinic hydrocarbons with olefinic hydrocarbons which comprises contacting said isoparaffinic hydrocarbons with said olefinic hydrocarbons in the presence of an aluminum halide-paraffinic hydrocarbon complex containing about 28% by weight of bound hydrocarbons and in the presence of a small amount of a hydrogen halide activator under conditions of temperature, pressure and ratio of reactants adapted to promote the reaction of said isoparaffinic hydrocarbons with said olefinic hydrocarbons.

4. A process according to claim 2 in which said olefinic hydrocarbons are added at a rate of from 5 to 20 cubic feet per pound of said complex per hour.

5. A process according to claim 2 in which said aluminum halide-paraffinic hydrocarbon complex is an aluminum chloride-paraffinic hydrocarbon complex.

6. A process for alkylating isoparaffinic hydrocarbons with olefinic hydrocarbons which comprises contacting said isoparaffinic hydrocarbons with said olefinic hydrocarbons in the presence of a catalyst containing an aluminum halide-paraffinic hydrocarbon complex having from about 23% to about 32% by weight of bound hydrocarbons and a hydrogen halide activator at a temperature within the range of from about 80° F. to about 150° F. under conditions of pressure and ratio of reactants adapted to promote the reaction of said isoparaffinic hydrocarbons with said olefinic hydrocarbons.

7. A process for alkylating isoparaffinic hydrocarbons with olefinic hydrocarbons which comprises contacting said isoparaffinic hydrocarbons with said olefinic hydrocarbons in the presence of a catalyst containing an aluminum halide-paraffinic hydrocarbon complex having from about 23% to about 32% by weight of bound hydrocarbons and in the presence of an effective amount but not more than 4% of a hydrogen halide activator under conditions of temperature, pressure and ratio of reactants adapted to promote the reaction of said isoparaffinic hydrocarbons with said olefinic hydrocarbons.

8. A process for alkylating isoparaffinic hydrocarbons with olefinic hydrocarbons which comprises contacting said isoparaffinic hydrocarbons with said olefinic hydrocarbons in the presence of a catalyst containing an aluminum halide-paraffinic hydrocarbon complex having from about 23% to about 32% by weight of bound hydrocarbons and a hydrogen halide activator, the mol ratio of said olefinic hydrocarbons to said isoparaffinic hydrocarbons being less than 0.6, under conditions of temperature and pressure adapted to promote the reaction of said isoparaffinic hydrocarbons with said olefinic hydrocarbons.

9. A process for alkylating isoparaffinic hydrocarbons and olefinic hydrocarbons which comprises contacting said isoparaffinic hydrocarbons with said olefinic hydrocarbons in the presence of an aluminum halide-paraffinic hydrocarbon complex containing from about 23% to about 32% by weight of bound hydrocarbons and in the presence of an effective amount but not more than 4% by weight, based on the aluminum chloride present, of a hydrogen halide activator at a temperature of from about 80° to about 150° F. in the liquid phase, the mol ratio of said olefinic hydrocarbons to said isoparaffinic hydrocarbons being less than 0.6.

10. A process according to claim 9 in which said isoparaffinic hydrocarbons contain less than six carbon atoms per molecule.

11. A process according to claim 9 in which said olefinic hydrocarbons contain not less than two nor more than five carbon atoms per molecule.

12. A process for alkylating isobutane with ethylene which comprises contacting said iso-

butane with said ethylene in the presence of an aluminum chloride-paraffinic hydrocarbon complex containing from about 23% to about 32% by weight of bound hydrocarbons and in the presence of an effective amount but not more than 4% by weight based on the aluminum chloride present, of hydrogen chloride at a temperature of from about 80° to about 150° F. in the liquid phase, the mol ratio of said ethylene to said isobutane being less than 0.6.

13. A process for continuously alkylating isoparaffinic hydrocarbons with olefinic hydrocarbons which comprises maintaining in a contacting zone an alkylation catalyst consisting essentially of an aluminum halide-paraffinic hydrocarbon complex, maintaining in said complex from about 23% to about 32% by weight of bound hydrocarbons, continuously introducing isoparaffinic hydrocarbons and olefinic hydrocarbons along with a small amount of a hydrogen halide activator into said zone and continuously withdrawing alkylation products therefrom, maintaining the temperature of said contacting zone within the approximate range of about 80° to 150° F., employing a pressure in said contacting zone sufficient for maintaining the reaction mixture in liquid phase at the reaction temperature and maintaining in said contacting zone a mol ratio of olefinic hydrocarbons to isoparaffinic hydrocarbons for effecting the formation of mono-alkylate without producing substantial amounts of dialkylate.

14. The process of alkylating isobutane with ethylene which comprises contacting isobutane and ethylene in a contacting zone with a catalyst consisting essentially of an aluminum halide-paraffinic hydrocarbon complex containing from about 23% to about 32% by weight of bound hydrocarbons in the presence of a small amount of hydrogen halide at a temperature within the approximate range of 80° to 150° F. under sufficient pressure to maintain the reaction mixture substantially in liquid phase, using an amount of catalyst in the reaction zone corresponding to at least 10% based on isobutane in said zone, and maintaining an ethylene to isobutane ratio in said zone for effecting the formation of hexanes without producing substantial amounts of octanes.

15. The process of claim 14 wherein the temperature is in the general vicinity of 125° F. and the mol ratio is in the general vicinity of 0.5 mols of ethylene per mol of isobutane.

ROBERT F. MARSCHNER.
DON R. CARMODY.