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ALKYLATION OF HYDROCARBONS

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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.

In the modern operation of a petroleum refinery, it is customary to subject the heavier fractions of crude oil to a cracking operation in order to produce additional amounts of gasoline. In the course of such a process, varying amounts of normally gaseous hydrocarbons are produced, these hydrocarbons including those having two, three and four carbon atoms per molecule, both saturated and unsaturated, as well as methane and hydrogen. Until comparatively recent years, these gases were considered in the nature of waste gases, and were to a large extent used as fuel gases or discarded, although portions of the least volatile gases, such as the butanes and butenes, might be incorporated in the gasoline itself in limited amounts. It has since been realized that these normally gaseous hydrocarbons are a valuable source material for the synthesis of gasoline range hydrocarbons, and under proper conditions, will yield motor fuels or motor fuel blending stocks of high antiknock value characterized by the presence of large amounts of branched chain or aromatic hydrocarbons. The processes employed include polymerization (with hydrogenation, if desired), alkylation, etc. both thermal and catalytic of which catalytic alkylation is perhaps the most desirable due to the comparative ease of formation of valuable saturated branched chain hydrocarbons without further treatment.

It is an object of this invention to provide an improved process for the alkylation of isoparaffinic hydrocarbons and, more specifically, 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 catalyst for effecting such an alkylation reaction. A still further object is to provide a catalytic process for the production of high antiknock motor fuel from normally gaseous hydrocarbons of two, three and four carbon atoms per molecule. A further object is to provide an alkylation process utilizing ethylene as the olefinic stock. Another object of this invention is to provide an alkylation process wherein the activity of the catalyst is maintained within a definite range throughout the process. Further objects and advantages will become apparent as the description of the invention proceeds.

Briefly stated, our invention contemplates the alkylation of an isoparaffin, particularly isobutane, with one or more mono-olefins having two, three or four carbon atoms per molecule in the presence of an aluminum halide-hydrocarbon complex, particularly an aluminum chloride-hydrocarbon complex. The isoparaffin and olefins can come from any source, as for instance refinery gases or partially dehydrogenated constituents of natural gas. Moreover, they need not be (and usually are not) pure hydrocarbons but may be mixtures of hydrocarbons falling within this general class. The isobutane, for example, can be an ordinary "plant butane" cut from the absorption of gases or the debutanization of gasoline and may contain various amounts of normal butane and isobutane, as well as the corresponding olefins, and may also contain minor amounts of three and five carbon atom hydrocarbons, due to imperfect separation. The isobutane may also be obtained as the off gas from the selective polymerization of the butylene present in a "plant butane" fraction, or from the decomposition of hydrocarbons of higher molecular weight during an isomerization, catalytic cracking or catalytic reforming operation. The source and purity of the feed stock is immaterial within reasonable limits, and dilution with unreactive gases, such as normal butane can be tolerated although it is desirable to use as feed stock a gaseous hydrocarbon containing as large an amount of the reactive constituent as is practical. The feed stock should be free of water, ammoniacal substances and the like.

Our process can be carried out either batchwise or in a continuous operation and the conditions employed will vary to some extent depending upon the reacting ingredients. Generally speaking, it is desirable to use temperatures of from about 0° F. to about 212° F. and preferably from about 50° F. to about 175° F., and to employ pressures of from about atmospheric to about 1000 pounds per square inch gauge, preferably from about 50 to about 500 pounds per square inch gauge; the pressure in any case being sufficient to maintain the reactants in the liquid phase at the temperature employed.

The catalyst used forms an important part of this invention. The use of aluminum chloride or aluminum bromide for the promotion of catalytic reactions, such as condensation, polymerization, cracking, alkylation, isomerization, etc. is well known. However, the alkylation reaction

ordinarily proceeds with too great violence in the presence of pure aluminum chloride or aluminum bromide to permit the controlled production of desired products. We have found that if anhydrous aluminum chloride or aluminum bromide is reacted with a liquid hydrocarbon to form a complex having certain critically defined characteristics, a modified catalyst is produced which is effective for promoting the alkylation of isoparaffinic hydrocarbons with olefines without too great violence.

This catalyst is especially suitable for use when ethylene is employed as the alkylating hydrocarbon, although it gives equally good results with other normally gaseous olefinic hydrocarbons. Moreover, the ethylene may form only a small part of the alkylating gas used, being diluted with ethane, hydrogen and methane, and still alkylate isoparaffins in the presence of this catalyst. Although propylene and the butylenes may be reacted with isoparaffins in the presence of a catalyst such as sulfuric acid with comparative ease, it has been found extremely difficult to promote the similar reaction with ethylene under like conditions. Therefore, a catalyst which will permit the utilization of ethylene, and particularly dilute ethylene in the production of saturated hydrocarbons of branched-chain configuration is especially valuable. The isohexane produced by our process is primarily 2,3,dimethyl butane of extraordinarily high octane number which is obtained only in limited amounts by thermal alkylation and not at all by sulfuric acid alkylation. It should be understood, however, that the use of propylene or the butylenes for this process is included within the scope of this invention.

The catalyst is prepared by refluxing an excess of normally liquid hydrocarbon with anhydrous aluminum chloride until the aluminum chloride has been converted to the liquid complex, stirring the reactants meanwhile. Gaseous hydrogen chloride is added at a rate sufficient to keep the hydrocarbon saturated to promote the reaction. Although the normally liquid hydrocarbons may contain minor amounts of aromatics and olefins, they are preferably aromatic and olefin-free. Paraffinic or cycloparaffinic hydrocarbons having six or more carbon atoms per molecule have been found to be preferable, and the feed stock may be a mixture of hydrocarbons of this general description, any of the pure hydrocarbons falling within this classification, or a mixture of any of the saturated hydrocarbons of this nature. At the end of the refluxing and stirring period, the aluminum chloride has formed a "complex" with the hydrocarbon, a heavy oily liquid, usually yellow to red in color. The hydrocarbons remaining as an upper layer are separated from the complex. In place of aluminum chloride, aluminum bromide can be used for the formation of the catalytic complex or a mixture of aluminum chloride and aluminum bromide can be employed to yield a mixed aluminum chloride complex-aluminum bromide complex suitable for promoting catalytic alkylation.

The exact nature of the formation of the complex by the reaction of anhydrous aluminum chloride or aluminum bromide with a liquid hydrocarbon in the presence of a promoter such as gaseous hydrogen chloride or hydrogen bromide, is not completely understood. There appears to be, however, a considerable variation in the effectiveness of the complexes formed by this reaction when various types of hydrocarbons are employed as feed stock. While a large variety of hydrocarbons and hydrocarbon stocks can be used, paraffinic hydrocarbons and oils rich in paraffinic hydrocarbons are in general distinctly preferable. Naphthenes or naphthene-containing hydrocarbons are also advantageous. Attempts have been made to analyze the organic compounds present in the complex by breaking down the complex into its component parts but the products are of such complex nature that they defy exact analysis. All of the complexes, however, have a measurable heat of reaction when the complex is added to water. We have discovered that the most effective aluminum halide-hydrocarbon complex catalysts for the promotion of the alkylation of isoparaffinic hydrocarbons with olefinic hydrocarbons are those which, in the case of aluminum chloride complexes, have heats of hydrolysis between the limits of 60 large calories per gram atom of active aluminum and 75 large calories per gram atom of active aluminum, and in the case of aluminum bromide complexes between 67 and 82 large calories per gram atom of active aluminum. By maintaining the activity of the catalyst within these limits an alkylation process can be carried out continuously with increased yield of product having the desired gasoline characteristics. By the expression "active aluminum" as used above, in the tables below, in other places in this specification, and in the claims of this application is meant the aluminum content of the hydrolyzable aluminum compounds in the liquid phase aluminum halide-hydrocarbon complex. Inactive aluminum compounds, such as, for example, the hydroxide that is present in a partially hydrolyzed complex, is not included in the term "gram atom of active aluminum."

The heat of hydrolysis can be determined by any well known calorimetric method wherein the temperature rise occasioned by the addition of one mol of the complex to approximately 100 mols of water can be measured.

Table I shows a series of typical experiments made with aluminum chloride-hydrocarbon complexes of different activities as indicated by their heats of hydrolysis. It can be readily seen that complexes having heats of hydrolysis within the above range, preferably in the upper part of that range, are particularly advantageous for the alkylation reaction.

Table I

	Catalyst-$AlCl_3$-hydrocarbon complex		
	Heat of hydrolysis 67 Cal./gr. atom of active aluminum	Heat of hydrolysis 59.5 Cal./gr. atom of active aluminum	Heat of hydrolysis 54 Cal./gr. atom of active aluminum
Isoparaffin, parts by wt. (i-C_4H_{10})	290	290	290
Olefin, parts by wt. (C_3H_6)	84	82	84
Temperature, ° F	14–24	18	14–24
Wt. percent yield (on olefin)	161.0	144.0	117.8
Distillation of product vol. percent—			
C_5		2.1	
C_6	4.4	1.2	3.5
C_7	27.2	14.6	3.7
C_8	1.6	3.1	1.3
C_9	11.1	3.3	1.6
C_{10}	7.6	5.3	
C_{11} and $_{12}$	8.9	4.1	1.6
C_{12}+	39.2	64.3	88.3
	100.0	100.0	100.0

Table II compares two typical experiments, one using pure aluminum chloride as the catalyst and the other an active aluminum chloride-hydrocarbon complex. The pure aluminum chloride catalyst yields a relatively high percentage of products, i. e., C_5, C_7, C_9 and heavier products, resulting from secondary reactions, such as cracking, polymerization, etc. The product from the aluminum chloride-hydrocarbon complex catalyst is essentially only primary alkylate.

Table II

	Catalyst	
	Pure $AlCl_3$	$AlCl_3$-hydrocarbon complex-heat of hydrolysis 67 Cal./gr. atom of active aluminum
Isobutane, parts by wt.	467	390
Ethylene, parts by wt.	92	94
Temperature, °F.	105	105
Pressure, lbs./sq. in.	155–180	70–150
Duration (hrs.)	6.5	5
Stabilized product, parts by wt.	200	235
Wt. percent yield (on olefin)	218	250
Distillation of product vol. percent—		
C_5	15.3	7.4
C_6	45.4	69.0
C_7	6.1	2.1
C_8	16.6	13.8
C_9	5.1	2.1
C_{10}+	11.5	5.6

Table III compares the hexanes produced from pure aluminum chloride catalyst and the hexanes from an aluminum chloride-hydrocarbon complex having a heat of hydrolysis of 67 large calories per gram atom of active aluminum. In the second case, the modified activity of the catalyst has yielded a purer product with a higher octane number than that from the aluminum chloride.

Table III

	Catalyst	
	Pure $AlCl_3$	$AlCl_3$-hydrocarbon complex-heat of hydrolysis 67 Cal./gr. atom of active aluminum
Hexanes from isobutane and ethylene—		
2,2-dimethylbutane	15 vol. percent.	Trace.
2,3-dimethylbutane	45 vol. percent.	88 vol. percent.
2-methylpentane	40 vol. percent.	12 vol. percent.
Octane number CFR-M	85.2	92.9.

In carrying out the alkylation process olefins, for example ethylene, propylene and/or butylenes, together with an iso-paraffin, for example isobutane, are added to the complex at a temperature of from about 50° to about 175° F., for example 105° F., and at pressures of from about 50 pounds per square inch gauge to about 500 pounds per square inch gauge, for example 145 pounds per square inch gauge. The mixture is stirred to insure intimate contact between the reactants and the catalyst and the time of reaction can vary of course with temperature, intimacy of contact, composition of gases, etc. over a wide range, from a few seconds to several hours.

By carrying out the alkylation reaction under a superimposed hydrogen partial pressure of 50 to 1000 pounds per square inch, preferably about 200 to 800 pounds per square inch, and under temperature conditions ranging from —35° F. to 400° F. the life or activity of the catalyst may be greatly extended by thus maintaining the heat of hydrolysis in the optimum range.

It is preferable that there be maintained an excess of iso-paraffin over the amount of olefins present, and in any case the iso-paraffin should be present in at least equimolecular proportions as compared with the olefins since an excess of olefins leads to the formation of high boiling products of unsaturated nature. The mol ratio of iso-paraffins to olefins should preferably be within the range from about 3:1 to about 6:1.

During the alkylation reaction the activity of the complex catalyst is reduced through involved and little understood side reactions which initially reduce the heat of hydrolysis of the complex below the heat of hydrolysis found effective for the optimum promotion of alkylation. In order to prevent this the activity of the catalyst can be maintained by the addition thereto of regulated amounts of fresh aluminum chloride or aluminum bromide. By the judicious employment of activating material a continuous process may be set up wherein the alkylation is carried out under conditions yielding an optimum amount of gasoline of high octane number. We have found the most effective aluminum chloride complex to have a heat of hydrolysis of about 65 to about 75 large calories per gram atom of active aluminum while an aluminum bromide complex having a heat of hydrolysis of about 72 to about 82 large calories per gram atom of active aluminum will yield optimum conversion.

In the event that a mixture of aluminum chloride and aluminum bromide complexes are employed, the heat of hydrolysis should be that determined by multiplying the optimum heat of hydrolysis for the aluminum chloride complex by the mol fraction of aluminum chloride and that for the aluminum bromide complex by the mol fraction of aluminum bromide and adding the two. Similarly, the desirable range of heat of hydrolysis may be obtained by substituting the maximum and minimum heats of hydrolysis for the optimum heats of hydrolysis in the above.

Other isoparaffins, for example, isopentane or isohexane, may be used in place of isobutane. The use of these isoparaffins is determined not by their reactivity or availability, since they are equally suitable with isobutane for this purpose and may be found in substantial quantities in petroleum refinery naphthas and gasolines, but upon the economic factors of the process. They form one of the valuable consituents of motor fuels, since they boil in the lower range of the gasoline hydrocarbons and have the desirable characteristic of high octane number. Therefore, as a practical matter, isopentane or isohexane will not ordinarily be used for the synthesis of high antiknock fuels unless there is a surplus above that readily utilizable, or unless the isoheptanes, isooctanes or isononanes which would result from the alkylation are considered more desirable than the isopentane or isohexane itself. The use of isopentane and higher molecular weight isoparaffins as a paraffinic feed stock for this alkylation process is therefore contemplated within the scope of this invention.

This application is a continuation-in-part of our copending application, Serial No. 287,088, filed July 28, 1939.

We claim:

1. A method of converting an isoparaffinic hydrocarbon into hydrocarbons of higher molecular

weight which comprises alkylating said hydrocarbon with at least one normally gaseous olefinic hydrocarbon in the presence of a catalyst comprising a complex formed by the reaction of a hydrocarbon with an aluminum halide of the class consisting of aluminum chloride and aluminum bromide in the presence of a hydrogen halide of the class consisting of hydrogen chloride and hydrogen bromide, said complex having a heat of hydrolysis of from about 60 to about 75 large calories per gram atom of active aluminum in the case of aluminum chloride and from about 67 to about 82 large calories per gram atom of active aluminum in the case of aluminum bromide.

2. A method of converting an isoparaffin into hydrocarbons of higher molecular weight which comprises alkylating said isoparaffin with at least one normally gaseous olefin in the presence of a catalyst comprising a liquid complex formed by the reaction of a paraffinic hydrocarbon oil and aluminum chloride in the presence of hydrogen chloride, said complex having a heat of hydrolysis of from 60 to 75 large calories per gram atom of active aluminum.

3. A method of converting an isoparaffinic hydrocarbon into hydrocarbons of higher molecular weight which comprises alkylating said isoparaffinic hydrocarbon with a normally gaseous olefin in the presence of a catalyst comprising a complex formed by the reaction of at least one hydrocarbon and aluminum bromide in the presence of a hydrogen halide of the class consisting of hydrogen bromide and hydrogen chloride, said complex having a heat of hydrolysis of from about 72 to about 82 large calories per gram atom of active aluminum.

4. A method of converting isobutane into hydrocarbons of higher molecular weight which comprises alkylating said isobutane with at least one normally gaseous olefin in the presence of a catalyst comprising a complex formed by the reaction of a hydrocarbon liquid with an aluminum halide of the class consisting of aluminum chloride and aluminum bromide in the presence of a hydrogen halide of the class consisting of hydrogen chloride and hydrogen bromide, said complex having a heat of hydrolysis of from about 60 to about 75 large calories per gram atom of active aluminum in the case of aluminum chloride and from about 67 to 82 large calories per gram atom of active aluminum in the case of aluminum bromide.

5. A method of converting an isoparaffinic hydrocarbon into a hydrocarbon of higher molecular weight which comprises alkylating said isoparaffinic hydrocarbon with an ethylene-containing gas in the presence of a catalyst comprising a complex formed by the reaction of a hydrocarbon and aluminum chloride in the presence of a hydrogen halide of the class consisting of hydrogen bromide and hydrogen chloride, said complex having a heat of hydrolysis of from about 60 to about 75 large calories per gram atom of active aluminum.

6. A method of converting isobutane into a hydrocarbon of higher molecular weight which comprises alkylating said isobutane with an ethylene-containing gas in the presence of a catalyst comprising a complex formed by the reaction of a hydrocarbon and aluminum chloride in the presence of a hydrogen halide of the class consisting of hydrogen bromide and hydrogen chloride, said complex having a heat of hydrolysis of from about 60 to about 75 large calories per gram atom of active aluminum.

7. A method according to claim 4 in which said hydrocarbon liquid is predominantly paraffinic.

8. A method according to claim 4 in which said hydrocarbon liquid is predominantly cycloparaffinic.

9. A method of alkylating an isoparaffinic hydrocarbon with at least one olefinic hydrocarbon which comprises reacting said isoparaffinic hydrocarbon and said at least one olefinic hydrocarbon in the presence of a catalyst comprising a complex formed by the reaction of a hydrocarbon material with an aluminum halide of the class consisting of aluminum chloride and aluminum bromide in the presence of a hydrogen halide of the class consisting of hydrogen chloride and hydrogen bromide and maintaining the activity of said catalyst by the addition of a sufficient amount of an aluminum halide-containing material of high heat of hydrolysis to maintain the heat of hydrolysis of said catalyst within the range of from about 60 to about 75 large calories per gram atom of active aluminum in the case of aluminum chloride and from about 67 to about 82 large calories per gram atom of active aluminum in the case of aluminum bromide.

10. A method of converting an isoparaffinic hydrocarbon into hydrocarbons of higher molecular weight which comprises contacting said isoparaffinic hydrocarbon with at least one normally gaseous olefinic hydrocarbon in the presence of a catalyst comprising a complex formed by the reaction of a hydrocarbon with an aluminum halide of the group consisting of aluminum chloride and aluminum bromide in the presence of a hydrogen halide of the group consisting of hydrogen chloride and hydrogen bromide, said complex having a heat of hydrolysis of from about 60 to about 75 large calories per gram atom of active aluminum in the case of aluminum chloride and from about 67 to about 82 large calories per gram atom of active aluminum in the case of aluminum bromide under a hydrogen partial pressure of from about 50 pounds to 1000 pounds per square inch, at a temperature adapted to promote the alkylation of said isoparaffinic hydrocarbon with said at least one normally gaseous olefinic hydrocarbon.

11. A method of converting an isoparaffinic hydrocarbon into hydrocarbons of higher molecular weight which comprises contacting said isoparaffinic hydrocarbon with at least one normally gaseous olefinic hydrocarbon in the presence of a catalyst comprising a complex formed by the reaction of a hydrocarbon with an aluminum halide of the group consisting of aluminum chloride and aluminum bromide in the presence of a hydrogen halide of the group consisting of hydrogen chloride and hydrogen bromide, said complex having a heat of hydrolysis of from about 60 to about 75 large calories per gram atom of active aluminum in the case of aluminum chloride and from about 67 to about 82 large calories per gram atom of active aluminum in the case of aluminum bromide under a hydrogen partial pressure of from about 200 pounds to 800 pounds per square inch, at a temperature adapted to promote the alkylation of said isoparaffinic hydrocarbon with said at least one normally gaseous olefinic hydrocarbon.

12. A method of converting isobutane into hydrocarbons of higher molecular weight which

comprises contacting said isobutane with at least one normally gaseous olefin in the presence of a catalyst comprising a complex formed by the reaction of a hydrocarbon liquid with an aluminum halide of the group consisting of aluminum chloride and aluminum bromide in the presence of a hydrogen halide of the group consisting of hydrogen chloride and hydrogen bromide, said complex having a heat of hydrolysis of from about 60 to about 75 large calories per gram atom of active aluminum in the case of aluminum chloride and from about 67 to 82 large calories per gram atom of active aluminum in the case of aluminum bromide under a hydrogen partial pressure of from about 50 to 1000 pounds per square inch at a temperature adapted to promote the alkylation of said isobutane with said at least one normally gaseous olefin.

13. The method of making 2,3,dimethyl butane which method comprises alkylating isobutane with ethylene in the presence of a catalyst comprising a liquid complex formed by the reaction of a hydrocarbon liquid with an aluminum halide of the class consisting of aluminum chloride and aluminum bromide in the presence of a hydrogen halide of the class consisting of hydrogen chloride and hydrogen bromide, said complex having a heat of hydrolysis of from about 60 to about 75 large calories per gram atom of active aluminum in the case of aluminum chloride and from about 67 to 82 large calories per gram atom of aluminum in the case of aluminum bromide.

14. The method of claim 13 which includes the steps of effecting said alkylation at a temperature within the approximate range of 50° to 175° F. and under a pressure sufficient to maintain the reactants in the liquid phase at the temperature employed.

15. The method of claim 13 which includes the step of charging a mol ratio of isobutane to ethylene within the approximate range of 3:1 to 6:1 to the alkylation step.

16. The method of claim 13 wherein the alkylation is effected at a temperature within the approximate range of 50° to 175° F. at a pressure within the approximate range of 50 to 500 pounds per square inch sufficient to maintain the reactants in the liquid phase at the temperature employed and wherein an excess of isobutane is maintained as compared with ethylene in the alkylation step.

17. The method of obtaining 2,3,dimethylbutane by alkylating isobutane with ethylene which method comprises alkylating isobutane with ethylene in the presence of a catalyst comprising a liquid complex formed by the reaction of a hydrocarbon liquid with an aluminum halide of the class consisting of aluminum chloride and aluminum bromide in the presence of a hydrogen halide of the class consisting of hydrogen chloride and hydrogen bromide, said complex having a heat of hydrolysis of from about 60 to about 75 large calories per gram atom of active aluminum in the case of aluminum chloride and from about 67 to 82 large calories per gram atom of active aluminum in the case of aluminum bromide, maintaining at least an approximately equimolecular proportion of isobutane to ethylene in the alkylating step, effecting the alkylation at a temperature within the approximate range of 50 to 175° F. under a pressure sufficient to maintain the reactants in liquid phase at the temperature employed and separating products of the alkylation reaction to obtain a stabilized product.

18. The method of claim 17 wherein the predominating component of the stabilized product is a C_8 component and wherein the C_8 component consists chiefly of 2,3,dimethylbutane.

19. The method of claim 17 wherein the reaction temperature is in the general vicinity of 105° F., the reaction pressure is within the general vicinity of 150 pounds per square inch and the stabilized product consists chiefly of 2,3,dimethylbutane.

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