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ALKYLATION OF HYDROCARBONS

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This invention relates to the alkylation of hydrocarbons and especially to the alkylation of aliphatic and aromatic hydrocarbons with olefinic compounds. More particularly, it relates to an alkylation process carried out in the presence of an alkylation catalyst and an agent effective in promoting the alkylation reaction.

The process of alkylating aliphatic and aromatic hydrocarbons with olefinic hydrocarbons has been widely utilized by refiners to provide high octane components for gasoline blending, to provide compounds useful as intermediates in organic processes, to produce solvents, etc. One of the major problems encountered in carrying out the alkylation process has been the difficulty in controlling the alkylation reaction to provide a maximum of desired product with a minimum of catalyst fouling and catalyst consumption. Because of the high degree of reactivity of olefinic materials in the presence of an alkylation catalyst, there is a tendency for these compounds to react with each other as well as with alkylatable hydrocarbons. This not only increases the consumption of olefinic reactants but also produces undesirable polymer byproducts. According to one theory, the principal reactions which take place initially in the alkylation process result in the union of olefinic material with the alkylation catalyst to produce intermediate catalyst-hydrocarbon compounds such as esters. The formation of these compounds is not undesirable since they may be considered an intermediate step in the production of the desired product, namely by the further reaction of the compounds with the aliphatic or aromatic hydrocarbon reactant to produce the desired product and release the catalyst for further use. Unfortunately, the alkylation reaction is not always carried to completion and quantities of these intermediate compounds are present in the reaction product. Since, in their formation, the catalyst serves as an intermediate reactant, failure of the reaction to go to completion increases both the consumption of olefin and the consumption of catalyst. These compounds exert a further detrimental effect because of their solubility in the catalyst which causes them to accumulate in this material thereby decreasing the effectiveness of the catalyst. The olefin polymers previously mentioned are also undesirable since they are separated from the catalyst with difficulty, and those which remain in the catalyst act as contaminants and decrease catalyst effectiveness.

It is an object of this invention to provide an improved process for the alkylation of aliphatic and aromatic hydrocarbons with olefinic hydrocarbons.

It is another object of this invention to decrease catalyst contamination in the catalytic alkylation of aliphatic and aromatic hydrocarbons with olefinic hydrocarbons.

It is still another object of this invention to decrease catalyst consumption in the catalytic alkylation of aliphatic and aromatic hydrocarbons with olefinic hydrocarbons.

Yet another object of this invention is to improve alkylation product yield in the reaction of aliphatic and aromatic hydrocarbons with olefinic hydrocarbons.

Another object of this invention is to improve alkylate

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yield and quality in the catalytic alkylation of isoparaffins with olefins in the presence of a catalyst.

These and other objects of the invention will become more apparent from the following detailed discussion and description.

Broadly the invention is concerned with the alkylation of an alkylatable compound with an olefin in the presence of a promoting agent and an alkylation catalyst. More specifically the invention is concerned with the use of a mercaptan promoting agent.

It has been found that the addition of a mercaptan to an alkylation reaction provides a process in which increased yields and higher quality products are obtained with a lower consumption of alkylation catalyst.

The mechanism by which these unusual and desirable results are obtained is not clearly understood. Studies of alkylation reactions indicate that where such reactions are heterogeneous, that is the reactions take place in more than one phase, for example, the reaction of isoparaffins with olefins in the presence of a liquid acid catalyst, the extent of the common surface presented by the two phases is of extreme importance in determining both the alkylation reaction rate and the products formed in the reaction. A common method of increasing contiguous phase surface is to agitate mechanically the catalyst-reactant mixture thereby creating an emulsion. This method is very useful; however, it is limited to the effects producible by mechanical means which apparently are not great enough to prevent some undesirable side reactions. The extent of phase contact is also favorably affected by heat, that is by increasing the temperature; however, operation at low temperatures is desirable in carrying out alkylation reactions in order to minimize polymerization of the olefinic reactant.

According to one theory, introducing a mercaptan into the reaction mixture has a similar effect on the reactant phases as agitation and increased temperature. The increase in contact phase surface which results from the presence of this material apparently comes about because of the attraction of the —SH or mercapto or sulfhydryl group for the catalyst phase and the attraction of the organic group for the hydrocarbon phase. This attraction is sufficiently strong to overcome partially the surface tension of the separate phases, thereby increasing the common phase surface area. There is a good possibility that this attraction is simply a matter of solubility of the organic and mercapto radicals in the respective phases. On the other hand, the attraction of the mercapto and organic radicals for the different phases may not be limited to a solubility effect alone; it may be instead a true chemical affinity resulting in a chemical bonding or reaction between the radicals and the respective affined phases. The latter is a definite possibility in the case of the mercapto radical because of the presence in this group of the low valence sulfur atom with electron pairs available for bonding. Still another theory is that the beneficial effects realized by the use of a mercaptan are due, not to a phase surface effect, but rather to the fact that the mercapto radical acts as a catalytic material per se or more likely that it in some manner promotes the activity and/or selectively of the alkylation catalyst. Whatever the reasons for the marked effects resulting from the use of a mercaptan, it is not intended that the invention be limited by the above discussion but that the theories are merely offered as possible explanations.

Mercaptans useful as promoters of the alkylation reaction are selected from a variety of classes of compounds such as for example the aliphatic mercaptans, aryl mercaptans, alkyl aryl mercaptans, arylalkyl mercaptans, cycloaliphatic mercaptans, etc. The organic moiety can be a hydrocarbon radical or it can contain elements other than carbon and hydrogen such as for example,

oxygen, halogen, nitrogen, etc. Among the various classes of mercaptans which are useful in carrying out this invention, it is preferred to employ the acyclic type or more preferably an alkyl mercaptan. The alkyl mercaptans which show a greater effect in promoting the alkylation reaction are those containing about 10 to 20 carbon atoms per molecule and at least 8 carbon atoms per molecule. Specific examples of mercaptans which may be used as promoters are decyl mercaptan, undecyl mercaptan, dodecyl mercaptan, tridecyl mercaptan, tetradecyl mercaptan, pentadecyl mercaptan, hexadecyl mercaptan, alkyl naphthyl mercaptan with at least two carbon atoms in the alkyl substituent or substituents, alkylphenyl mercaptans with at least two carbon atoms in the alkyl substituent or substituents, alkylbenzyl mercaptans with at least two carbon atoms in the alkyl substituent or substituents etc. Effectiveness of the mercaptan is attributed primarily to the presence of the mercapto group, therefore, the general class of compounds are considered suitable for promoting alkylation reactions. However, while the various mercaptans can be used for this invention, it should be understood that they are not all equivalent, but that some are more effective than others. The beneficial effect derived from the use of mercaptans in general will vary in degree with the additive used, the hydrocarbon reactants and the alkylation catalyst. The only limitations on the use of mercaptans as promoters is their solubility. They may be either liquids or solids at the alkylation conditions of temperature and pressure; however, they must be soluble in at least one of the two phases, that is either the hydrocarbon or the catalyst phase. The amount of mercaptan additive which can be used will vary widely. Although very high and low concentrations can be usually the concentration of mercaptan is between about 0.2 and about 0.001 mol of mercaptan per mol of catalyst or more preferably between about 0.04 and about 0.002 mol per mol.

In addition to mercaptans, other organic compounds are useful as promoters of the alkylation reaction. These include aliphatic amines containing at least one normal alkyl chain having 8 to 20 carbon atoms, for example normal dodecyl amine, normal dodecyl trimethyl ammonium chloride, normal tetradecyl amine, etc., and aliphatic sulfonic acids in which the aliphatic substituent is an alkyl group containing from 8 to 20 carbon atoms or an alkaryl group in which the alkyl group contains from 4 to 20 carbon atoms, for example dodecylbenzene sulfonic acid, normal dodecyl sulfonic acid, etc.

The present invention is applicable to alkylation reactions generally, such as the reaction of an olefin with an alkylatable compound for example an aliphatic hydrocarbon, an aromatic compound, a cycloaliphatic compound, etc. A well known process for which this invention is applicable and one which is applied widely on a commercial scale involves the reaction of an isoparaffin with an olefin to form a high octane mixture boiling in the gasoline range. In carrying out this reaction, it is customary to utilize feed stocks of varying compositions containing a variety of saturated and unsaturated compounds. A primary source of feed materials for this reaction exists in refinery process gases which may contain paraffins having from 1 to 6 carbon atoms, isoparaffins including isobutane, isopentane, isohexane and higher molecular weight compounds and numerous low boiling olefins and their isomers, for example propylene, butylene, isobutylene, etc. It is within the scope of this invention to use feed stocks containing these and higher boiling compounds in widely varying proportions.

A wide variety of catalysts are available for use in the alkylation of an alkylatable compound with an olefin or more specifically an isoparaffin with an olefin. Those frequently employed include acids such as sulfuric, hydrofluoric, phosphoric, chlorosulfonic, fluorosulfonic etc., which may be used either singly or in mixtures. Non-solid Friedel-Crafts catalysts which form a liquid phase sub-

stantially immiscible with the hydrocarbon phase may be used. They include the conventional Friedel-Crafts metallic halides in acids such as those just enumerated and metallic halide-hydrocarbon complexes. Other liquid catalysts which provide a heterogeneous reaction mixture with hydrocarbons may also be used within the scope of this invention.

While the various kinds of catalysts can be used, the invention is especially adapted to the sulfuric acid alkylation. The alkylation of isoparaffins with olefins in the presence of sulfuric acid is preferably conducted at temperatures between about 0° F. and about 150° F. The pressure in the reaction zone is maintained at a level sufficient to keep the reactants in a liquid state usually between about atmospheric and about 100 p.s.i.g. In order to obtain a high quality product, it is desirable to maintain a high isoparaffin to olefin ratio in the feed to the reaction zone, preferably between about 2 and about 20 mols per mol and it is necessary to keep the acid catalyst strength above about 80% and preferably above 90%. The time required to carry out the alkylation reaction varies with the operating conditions; however, in general a reaction time between about 2 minutes and about 200 minutes suffices.

The alkylation of an isoparaffin with an olefin is preferably conducted in the liquid phase and under conditions of agitation whereby good contact is obtained between the hydrocarbon reactants and the alkylation catalyst. It is not necessary, however, that all of the reactants be present as liquids. The olefin, for example, may be added to the isoparaffin acid mixture as a gas, such as by bubbling the olefin through the liquid, by spraying the liquid into the olefin or by some other suitable method. To minimize the formation of undesirable side products which contaminate both the product and the alkylation catalyst, it is customary to carry out the reaction in the presence of an excess of isoparaffins and at low temperatures. A preferred method of providing the desired reactant ratio is to conduct the process in several reaction stages with series flow of the isoparaffin and catalyst through each stage and parallel flow of olefin to each stage.

The alkylation of an aromatic or a cycloaliphatic compound with an olefinic compound results in the production of compounds which may be useful in themselves, but which generally are more useful as intermediates in the manufacture of other chemical compounds. Examples of aromatic and cycloaliphatic alkylation reactions include the reaction of benzenes, naphthalenes, phenols, etc., and their homologues with olefins in the presence of mixed catalysts, for example hydrofluoric acid-boron trifluoride or liquid complexes of aluminum chloride with acids and/or hydrocarbons. In general, these reactions are carried out between about 30 and about 120° F. under atmospheric or super atmospheric pressures, as required to maintain the reactants in a liquid state. Other typical reactions are benzene with propylene in the presence of liquid phosphoric acid, benzenes with isoparaffins in the presence of olefins and an acid such as sulfuric or hydrofluoric, isoparaffins with alkyl substituted cyclopentanes in the presence of an acid such as sulfuric or hydrofluoric etc.

The reaction conditions used in these and similar reactions involve temperatures and pressures comparable to those illustrated. Normally the alkylatable compound is present in greater quantity than the olefinic reactant, and the relative concentrations of catalyst and hydrocarbon reactants in general conform to those required for the alkylation of isoparaffins. The pressures may vary from sub-atmospheric to several atmospheres depending on the particular reactants, and the reaction time required varies from as low as a few minutes to several hours.

The olefinic reactants used in alkylating acyclic, cycloaliphatic and aromatic compounds are usually the low boiling olefins previously mentioned, however, other more

complex olefinic compounds well known to those in the art which are capable of entering into alkylation reactions are also included within the scope of this invention.

The following specific examples disclose a procedure which is utilized in carrying out one embodiment of this invention and illustrate the effectiveness of mercaptans in promoting specific alkylation reactions. This data is not presented in any limiting sense and is not intended to restrict the scope of the invention.

EXAMPLE

Alkylation tests

To determine the effectiveness of certain additives in the alkylation of isoparaffins with olefins, a laboratory scale batch type glass alkylation apparatus was designed and a series of tests were run utilizing isopentane, pentene-1 and sulfuric acid. Isopentane and pentene-1 were used rather than butane and butylene in order to eliminate the requirement of super atmospheric pressure. The reaction vessel consisted of a creased three necked flask fitted with a high speed stirrer, thermometer and addition funnel. During the reaction the flask was surrounded by a thermostated alcohol bath maintained at a pre-set temperature below that of the reaction mixture by means of the intermittent introduction of a coolant through a copper coil in the bath. In each case, pentene-1 (21 parts) was added to a stirred mixture of 98% sulfuric acid (39.5 parts), isopentane (39.5 parts) and the additive (0.01 part where present). The additives employed were normal dodecyl mercaptan, sodium lauryl sulfate and normal dodecene-1. The data from these tests is given in Table I. Four runs were made with olefin addition times of from 21 to 27 minutes. When the olefin addition was completed the mixture was stirred several minutes longer after which time the reaction was considered complete. The determinations of acidity were made by direct titration with a base at zero degrees centigrade and free sulfuric acid was determined by precipitation with aniline, filtration and titration with a base. The hydrocarbon layer was rectified into two fractions. The quantity boiling below 50° centigrade was analyzed for isopentane and pentene-1; the material boiling above 50° centigrade was considered as alkylate.

TABLE I

Run No.	Additive (parts) ¹	Time for Adding Olefin (min.)	Sulfuric Acid Layer						
			Temp. (° C.)	Initial		Final			
				Parts	Total Acid, Percent	Parts	Total Acid, Percent	Free Acid, Percent	Increase in Free Acid, Percent
1-----	None-----	21	4.5-7	181.8	98.0	193.7	90.6	90.6	-----
2-----	n-Dodecyl Mercaptan (0.05)-----	27	3-7.5	179.8	98.0	186.1	94.0	94.1	3.87
3-----	n-Dodecene-1 (0.042)-----	27	2-13	181.7	98.3	195.2	87.8	88.1	-2.76
4-----	Sodium lauryl sulfate (0.0715)-----	23	3-7	182.1	98.1	193.9	91.2	91.8	1.33

Run No.	Hydrocarbon Layer						Octane No. (Research)	Bromine No. (gm./100 gm.)
	Initial, Parts	Final						
		Parts	Isopentane, Percent	Pentene-1, Percent	Alkylate, Percent	Increase in Alkylate, Percent		
1-----	279.6	254.8	44.7	0.0	55.3	-----	67.0	11.6
2-----	277.9	258.7	37.9	0.0	62.1	12.3	68.1	7.2
3-----	277.9	250.7	42.9	0.0	57.1	3.3	66.8	11.6
4-----	279.5	255.2	41.3	0.0	58.7	6.1	66.8	9.8

¹ Equimolar quantities of the additives were employed.

The data from the table clearly shows the beneficial effects which result from the use of normal dodecyl mercaptan as an additive. Through the use of this compound as compared to the run with no additive the amount of free acid in the catalyst increased 3.87 percent and the alkylate yield increased 12.3 percent. To check the effect of this additive on alkylate quality, research octane numbers were determined for the alkylate produced in this run and the run with no additive. Here also the mercaptan showed a very significant effect, increasing the alkylate quality by 1.1 octane numbers. Similar determinations and tests were made on the catalyst used and alkylate produced in the runs using sodium lauryl sulfate and normal dodecene-1. These compounds failed entirely to improve alkylate quality and produced very little improvement in alkylate yield and acid consumption.

Effect of additive concentration

The preceding runs were made with the use of equimolar amount of the various additives. To determine the effect, if any, of varying the amount of additive, additional runs with normal dodecyl mercaptan were carried out with an olefin addition time of 48-53 minutes. The results of these runs are compared with the initial run in Table II.

TABLE II

Additive	Amount, parts	Free Acid, percent	Increase in Free Acid, percent
n-Dodecyl Mercaptan.....	0.05	94.1	3.87
Do.....	0.25	93.2	2.90
Do.....	0.011	93.9	3.64

Having thus described the invention by reference to a specific application thereof, it is understood that no undue limitations are to be imposed by reason thereof but that the scope of the invention is defined by the appended claims.

We claim:

1. A heterogeneous liquid phase alkylation process which comprises contacting an alkylatable hydrocarbon with an olefin in the presence of an added mercaptan having an alkyl group containing at least 8 carbon atoms

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and a liquid alkylation catalyst under alkylation conditions suitable to produce a conversion product.

2. An improved alkylation process which comprises contacting an isoparaffin with an olefin in the presence of a liquid alkylation catalyst in a heterogeneous liquid phase system with an added mercaptan containing at least 8 carbon atoms under suitable reaction conditions to effect alkylation of the isoparaffin with the olefin.

3. The process of claim 2 in which the mercaptan is an acyclic mercaptan.

4. The process of claim 2 in which the mercaptan is an aryl mercaptan.

5. The process of claim 2 in which the mercaptan contains a cyclo aliphatic group.

6. A heterogeneous liquid phase alkylation process which comprises contacting an isoparaffin with an olefin in the presence of sulfuric acid and an added acyclic mercaptan having a normal alkyl group containing at least 8 carbon atoms under suitable reaction conditions to effect alkylation of the isoparaffins with said olefins.

7. The process of claim 1 in which the mercaptan has a normal alkyl group containing between about 10 and about 20 carbon atoms.

8. The process of claim 6 in which the mercaptan has a normal alkyl group containing between about 10 and about 20 carbon atoms.

9. A heterogeneous liquid phase alkylation process which comprises contacting a low-boiling isoparaffin with a low-boiling olefin in the presence of an added high-boiling mercaptan having at least 8 carbon atoms and a liquid alkylation catalyst under suitable reaction conditions to effect alkylation of the isoparaffin with the olefin.

10. The process of claim 9 in which the mercaptan is an acyclic mercaptan having a normal alkyl group containing at least 8 carbon atoms.

11. The process of claim 1 in which the mercaptan is an acyclic mercaptan having a normal alkyl group containing between about 10 and about 20 carbon atoms.

12. An improved alkylation process which comprises forming a slurry of isopentane and sulfuric acid to which has been added a small amount of normal dodecyl mercaptan and contacting the slurry under alkylation conditions with an olefin stream containing pentenes to obtain an improved alkylation product.

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13. A heterogeneous liquid phase alkylation process which comprises contacting a low-boiling isoparaffin with a low-boiling olefin in the presence of a liquid alkylation catalyst to which has been added a high-boiling mercaptan containing at least 8 carbon atoms, said mercaptan being added in an amount of between about 0.2 and about 0.001 mol of mercaptan per mol of catalyst under suitable reaction conditions to effect alkylation of the isoparaffin with the olefin.

14. A heterogeneous liquid phase alkylation process which comprises contacting a low-boiling isoparaffin with a low-boiling olefin in the presence of a liquid alkylation catalyst to which has been added a high-boiling mercaptan containing at least 8 carbon atoms, said mercaptan being added in an amount of between about 0.04 and about 0.002 mol of mercaptan per mol of catalyst under suitable reaction conditions to effect alkylation of the isoparaffin with the olefin.

15. An alkylation catalyst comprising essentially a liquid acid alkylating agent and a mercaptan having at least 8 carbons atoms per molecule.

16. The catalyst of claim 15 wherein the alkylating agent is sulfuric acid.

17. The catalyst of claim 15 wherein the mercaptan is dodecyl mercaptan.

18. The catalyst of claim 15 wherein the mercaptan is decyl mercaptan.

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