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DEGRADABLE DETERGENT ALKYLBENZENE PROCESS

Joseph Z. Pasky, Oakland, Calif., assignor to Chevron Research Company, a corporation of Delaware

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This invention relates to an improved aromatic hydrocarbon alkylation process. More particularly, it relates to improved hydrogen fluoride catalyzed aromatic hydrocarbon alkyl halide alkylations accelerated and modified by added hydrogen chloride.

It is now well established that biologically degradable alkylbenzene sulfonate detergents are highly desirable for household uses in order to minimize contamination of natural water resources. Such detergents can be synthesized from alpha-olefins obtained by thermal cracking of substantially straight-chain paraffins. However, only a minor fraction of the paraffinic hydrocarbon cracking feed is converted to useful detergent range olefins. The balance of the product is mainly light olefins and saturated light hydrocarbon ends.

A very much more efficient use of straight-chain paraffinic hydrocarbons for detergent production could be via the monochlorination or monobromination of detergent range normal paraffins provided that these alkyl halides could be used to alkylate benzene and particularly to do so by the use of mild hydrogen fluoride catalysis. It is well known to alkylate benzene in the presence of olefinic agents but to date no practical and satisfactory means to dehydrohalogenate monoalkyl halides to alkenes is known. The experience has been that in every instance, the dehydrohalogenation is accompanied by a substantial amount of carbon-carbon skeletal rearrangement of the alkyl group. Briefly, a correlation between nonbiodegradable alkylbenzene sulfonate and the degree of carbon-carbon isomerization experienced in dehydrohalogenations to produce alkene is apparent when such alkene is used to produce detergent sulfonate.

On the other hand, conventional hydrogen fluoride alkylation catalyst normally employed with olefins in the alkylation of benzene appears to be ineffective for the satisfactory catalysis of secondary alkyl chloride and bromide alkylations of benzene and the like aromatic hydrocarbons (cf. J. H. Simons and G. C. Bassler, JACS 63, 880 (1941)). Roughly 90% of the monohalogenation product in the halogenation of paraffin is secondary product.

It has now been found that although low temperature hydrogen fluoride catalyzed alkylations of aromatic hydrocarbons with secondary alkyl chlorides and bromides are impracticably slow and that although corresponding appreciably higher temperature alkylations produce mainly undesirable olefin hydrocarbon polymer, that, when alkylation temperatures in the range from about 40° C. to 130° C. are employed, effective alkylations result provided that at least about a 0.1 atmosphere partial pressure of hydrogen chloride is maintained in the alkylation reaction zone.

This novel process may be illustrated by an example in which an alkylatable aromatic hydrocarbon is charged to a suitable corrosion-resistant pressure autoclave together with at least catalytic amounts of substantially anhydrous hydrogen fluoride and a secondary alkyl chloride of the desired molecular weight range. Specifically, in a usual alkylation for detergent range alkylbenzene production, a charge of 1 mol of dodecyl chloride, 10 mols of benzene, and 60 mols of anhydrous hydrogen fluoride is a representative charge. The autoclave is then

sealed and hydrogen chloride gas is charged into the autoclave to yield a hydrogen chloride partial pressure of about 10 atmospheres. In the preferred mode of operation the autoclave is fitted with a pressure relief valve set to vent at about 10 atmospheres pressure. The autoclave and charge is then heated to about 100° C., and, as the alkylation reaction proceeds, the by-product hydrogen chloride is vented from the reaction zone via the relief valve. After about a 30 minute reaction time, the secondary dodecyl chloride is essentially completely converted to the desired alkylbenzene. The reaction autoclave and contents is then cooled, the catalyst phase is separated from the hydrocarbon phase and may be returned to the reactor for reuse. The hydrocarbon phase is further processed as desired.

While a primary objective is a process for the production of detergent range alkylbenzene characterized in particular by substantially complete susceptibility in its sulfonate form to biological degradation, the present process is effective for the alkylation of aromatic hydrocarbons in general where secondary alkyl chlorides are to be used in conjunction with hydrogen fluoride catalyst. As in the case of benzene, other alkylatable aromatic hydrocarbons are also alkylated by secondary alkyl chlorides under the subject inventive conditions.

Thus, the aromatic hydrocarbons contemplated for use in the present process includes benzene as well as all alkylatable aromatic hydrocarbons. More particularly, aromatic hydrocarbons known in the art to be alkylatable by an alkene in the presence of anhydrous hydrogen fluoride are useful feeds for the instant process. Still more particularly, all aromatic hydrocarbons alkylatable by dodecene-1 in the presence of anhydrous hydrogen fluoride at about 15° C. are contemplated.

Representative examples of aromatic hydrocarbons intended are benzene, naphthalene, biphenyl, anthracene, toluene, ethylbenzene, the xylenes, α-methyl naphthalene, and the like, including the higher polynuclear alkylatable aromatic hydrocarbons as defined above. The more practicable aromatic hydrocarbons are, of course, found in the class having less than about 15 aromatic carbocyclic carbon atoms per molecule.

In general, secondary alkyl chlorides and bromides are contemplated for use in the process. Consequently, the subject secondary halides must contain at least 3 carbon atoms. Very high molecular weight secondary alkyl halides are also useful, for example, secondary eicosanyl chloride, s-$C_{25}H_{51}Cl$, s-$C_{30}H_{61}Br$, and the like. Because the alkylation reaction is a liquid phase reaction, the alkyl halide-aromatic hydrocarbon reaction pair must be capable of existence in the solution phase within the temperature range of the present process. Thus, any secondary alkyl chloride or bromide having at least about a 1 weight percent solubility in the desired alkylatable aromatic hydrocarbon within the reaction temperature range of the present process may be used as the alkylation agent.

Preferred alkylation agents are the secondary n-alkyl chlorides and bromides having from 3 to 35 carbon atoms per molecule.

Representative secondary alkyl chlorides and bromides useful in the subject process are 2-chloro-dodecane, 3-bromo-undecane, 3 - chloro-octane, 2 - chloro-butane, 5-chloro-hexadecane, 2-methyl - 8 - chloro-octadecane, 3-bromo-pentadecane, 7-chloro-3-ethyl-dodecane, 2-chloro-6 - ethyl-decane, 3 - chloro-pentane, 3 - bromo-hexane, 2-chloro-heptane, 3-bromo-heptane, 5-chloro-tridecane, 4-chloro-tetra-decane, cyclohexyl chloride, cyclooctyl chloride, cyclododecyl chloride, and the like.

The present alkylations are preferably accomplished in an anhydrous system. However, commercial hydrogen fluoride usually has a small amount of water present,

sometimes as much as 1 weight percent, and such can be used. As the amount of water impurity exceeds trace amounts, however, the quality of the catalysis suffers as shown, for example, by slower alkylation rates. Consequently, care must be taken to minimize and exclude water from the reaction system.

Temperature is a critical variable in the subject process. At conventional hydrogen fluoride alkylation temperatures from about −14 to 26° C., no appreciable alkylation results in the use of the subject secondary halide agents. At substantially higher temperatures, for example. 130° C. and higher, where satisfactory rates can be expected in view of kinetic considerations, a competitive reaction, olefin formation and polymerization essentially preempts the desired alkylation reaction. Only a minor amount of alkylate is formed which often is in large part of the undesirable side-chain isomerized variety.

In surprising contrast, within a limited temperature range, and under an appreciable partial pressure of hydrogen chloride, the subject hydrogen fluoride alkylations are efficiently accomplished. The presence of added hydrogen chloride notwithstanding, little or no advantage results until an alkylation temperature of at least 40° C. is used. At about 60° C. and at least a partial pressure of 0.1 atmosphere of gaseous hydrogen chloride significant rates for secondary halide alkylation of aromatic hydrocarbons result. In the range from about 80 to 110° C. and at least about a 5 atmosphere partial pressure of hydrogen chloride, very satisfactory results are achieved. With increasing reaction temperatures above about 130° C., concurrent by-product polymer formation becomes increasingly significant until at about 150° C. the desired alkylate is an insignificant fraction of the product.

The relative amounts of hydrogen fluoride, secondary alkyl halide, and aromatic hydrocarbon which may be used vary widely, depend upon the degree of alkylation desired, i.e., whether mono- or polyalkyl aromatic hydrocarbon products are desired, and, in general, these amounts will be comparable to those used in the somewhat analogous HF-olefin alkylation art.

The following examples are illustrative of various aspects of the subject invention. Variations can be made, of course, and should be understood to be within the scope of the invention in view of the above disclosure and succeeding comments and claims.

The examples listed in Table I following were carried out in a corrosion-resistant copper pressure autoclave. The reactor was fitted with a stirring means, a reflux condenser, a Grove loader relief valve, a temperature probe, and an auxiliary feed line for pressurizing the reaction system with hydrogen chloride gas as required. During the course of the runs as indicated, temperature was maintained by immersion of the reactor in a suitable temperature bath. In the runs, benzene, hydrogen fluoride, and the alkyl halide were charged to the reactor in the mol ratio 10:60:1, respectively, and hydrogen chloride, hydrogen bromide, or nitrogen charged as indicated:

TABLE I.—HF CATALYZED ALKYLATION OF BENZENE WITH ALKYL HALIDES

Run No.	Halide [1]	Temperature, °C.	Time, min.	HCl Pressure, p.s.i.g.	Grove Loader, p.s.i.g.	Percent Secondary Reacted [5]
1	Dodecyl Chloride	100	30	150	150	100
2	do	90	20	150	150	94–99
3	do	90	20	150 N [3]	150	75–80
4	do	60	50	150 [2]	155	50–60
5	do	60	50	150 N [3]	150	20–25
6	Dodecyl Bromide	60	50	145 [2]	150	45–55
7	do	60	50	150 HBr [4]	150	20–25
8	Dodecyl Chloride	40	75	150	150	6–7
9	do	50	65	150	150	25–38
10	do	70	50	150	150	66–73
11	do	80	45	150	150	93–96
12	do	85	40	150	150	91–98
13	2-chlorododecane [2]	90	30	150	150	>95

[1] Halide was prepared by chlorinating or brominating dodecane to the extent of approximately 20%.
[2] Prepared by adding HCl to 1-dodecene.
[3] Nitrogen used in place of HCl.
[4] HBr used in place of HCl.
[5] The first number refers to the percent of the 2- and 3-isomers reacted; the second number refers to the percent of the 4-, 5-, and 6-isomers reacted.

In addition to the above-listed data, it was found that the resulting alkylate had an unexpectedly low 2-phenyldodecane content. Conventionally produced dodecyl benzenes using dodecyl chloride and aluminum chloride catalyst are found to have a 32% 2-phenyl-dodecane content. The present hydrogen chloride promoted runs yielded a product having only a 20% content of the 2-phenyl product. Low 2-phenyl contents are highly desirable in view of the fact that this isomer has now been found to inhibit foam production maxima.

Surprisingly, primary alkyl chlorides and bromides are essentially inert under the subject process conditions. Thus at 100° C., in Run No. 1, all of the primary chloride appeared to be recoverable from the reaction product mixture. Similarly, in Runs Nos. 6 and 7, no primary bromide, appeared to be utilized. As a corollary, the present process is therefor an effective means for the efficient removal of secondary alkyl chlorides and bromides from primary alkyl chlorides and bromides.

Within the limits of accuracy of the chromatographic techniques employed, i.e., estimated ±2%, no evidence of carbon-carbon side-chain skeletal rearrangement could be found in the above runs.

In view of Runs Nos. 1–13 above, the following is notable:

(1) Both secondary alkyl chlorides and bromides are effective alkylation agents for the subject process for the production of biodegradable detergent alkylbenzenes.

(2) Hydrogen chloride is unique in its effect. Thus, hydrogen bromide is ineffective (compare Runs 6 and 7); and mere pressure, inert nitrogen, as shown by Runs 5 and 4, is ineffective.

(3) Below about 40° C., little or no secondary chloride alkylation results over a reasonable reaction period, i.e., one hour or less.

(4) The addition of hydrogen chloride gas to HF catalyst alkylations at temperatures above about 40° C. using secondary alkyl chlorides increases the reaction rate at least by a factor of 2.

Run No. 14.—Into a monel bomb were charged monochlorinated dodecane, dodecane, benzene, and hydrogen fluoride in the mol ratio respectively of 1:8:20:100. The bomb was sealed and heated to a temperature in the range 143–162° C. for a period of 2.8 hours. The conversion of the chloride was 95–97% but the yield of alklybenzene was only 3%. The balance of the chloride was found as polymeric by-product.

Run No. 15.—As in Run No. 14, a run was made except that one mol of dodecylbenzene alkylate was charged in place of the mol of secondary chloride. The sealed reactor

and contents were heated in the range 149–171° C. for a period of 2.5 hours. Most of the dodecylbenzene was destroyed with the concurrent production of by-product polymer as in Run No. 14.

The data of Runs Nos. 14 and 15 demonstrate that at elevated temperatures of the order of 150° C. and higher hydrogen fluoride is unsatisfactory as an alkylation catalyst.

In view of the foregoing, it is clear that alkylatable aromatic hydrocarbons in general can now be alkylated using secondary alkyl chlorides and bromides by the process of the subject invention.

I claim:

1. In the liquid phase hydrogen fluoride catalyzed alkylation of alkylatable aromatic hydrocarbons, the improvement which comprises alkylating said hydrocarbons with secondary alkyl halides selected from the group consisting of chlorides and bromides, wherein said alkylation is effected in the presence of hydrogen chloride at a partial pressure of at least 0.1 atmosphere but less than 100 atmospheres and at a total pressure sufficient to maintain said liquid phase at a temperature in the range from about 40° C. to 130° C.

2. In the liquid phase hydrogen fluoride catalyzed alkylation of benzene, the improvement which comprises alkylating with secondary normal alkyl halides selected from the group consisting of chlorides and bromides, wherein said alkylation is effected in the presence of

hydrogen chloride at a partial pressure of at least 0.1 atmosphere but less than 100 atmospheres and at a total pressure sufficient to maintain said liquid phase at a temperature in the range from about 40° C. to 130° C.

3. In the liquid phase alkylation process wherein alkylatable aromatic hydrocarbons are reacted in the presence of hydrogen fluoride with secondary alkyl halide alkylation agents selected from the group consisting of chlorides and bromides at a temperature in the range 40° C. to 130° C., the step which consists of charging hydrogen chloride to said alkylation to a partial pressure in the range from 0.1 to 100 atmospheres.

4. Process of claim 2 wherein of said alkyl halides, said secondary halide is a minor fraction of the corresponding primary-secondary halide mixture and said secondary halide alkylation is the means of reducing secondary halide content in said mixture.

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DELBERT E. GANTZ, *Primary Examiner.*

C. R. DAVIS, *Assistant Examiner.*