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**CATALYTIC DEHYDROHALOGENATION OF
ALKYL HALIDES IN PRESENCE OF NITRO-
GEN-CONTAINING COMPOUNDS**

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This invention relates to a process for the dehydrohalo-
genation of alkyl halides. In another aspect, this inven-
tion relates to a process for the dehydrohalogenation of
alkyl halides to form olefins.

Currently considerable interest and much research ef-
fort have been devoted to the production of biodegrad-
able detergents. A proposed method comprises halogenat-
ing normal paraffins, dehydrohalogenating the resulting
alkyl halides to produce olefins, alkylating benzene or
other aromatics with these olefins in the presence of HF,
and subsequently sulfonating the product alkylate to pro-
duce a biodegradable detergent. These produced alkyl-
benzene sulfonates are rapidly degraded by bacteria be-
cause of a lack of branching of the substituent alkyl
group.

It has been observed that in the production of olefins
by the dehydrohalogenation of the alkyl halides employ-
ing conventional dehydrohalogenation process conditions,
considerable isomerization of the carbon skeleton of the
produced olefins results. While for some uses this is not
damaging, branched olefins are of little value when it is
desired to form biodegradable detergents via alkylation
for reasons previously stated.

Accordingly, an object of our invention is to provide
an improved process for the dehydrohalogenation of alkyl
halides.

Another object of our invention is to provide a process
for the dehydrohalogenation of straight chain alkyl halides
to produce straight chain olefins.

Another object of our invention is to provide a process
for the dehydrohalogenation of straight chain alkyl halides
wherein carbon skeleton isomerization is minimized.

Other objects, advantages and features of our inven-
tion will be readily apparent to those skilled in the art
from the following description and the appended claims.

We have discovered that in the dehydrohalogenation
of alkyl halides to olefins, the formation of branched
chain olefins through isomerization is minimized by the
introduction of a nitrogen-containing compound selected
from the group consisting of ammonia, amines, and nitro-
substituted hydrocarbons into the dehydrohalogenation
zone.

The quantity of nitrogen-containing compound intro-
duced into the dehydrohalogenation zone will preferably
range from 0.1 to 2.5 weight percent based on the alkyl
halide feed to the dehydrohalogenation zone, although
concentrations outside this range can be employed. The
nitrogen-containing compound will normally contain from
1 to 20 carbon atoms and will be selected from the group
consisting of ammonia, primary amines, secondary amines,
tertiary amines, and nitro-substituted hydrocarbons, in-
cluding nitro-substituted aromatics, paraffins, cycloparaf-
fins, cycloolefins, and olefins, preferably nitro-substituted
hydrocarbons containing one substituent nitro group.

Some specific examples of nitrogen-containing com-
pounds which can be introduced into the dehydrohalo-
genation zone are: ammonia, methylamine, diethylamine,
tri-n-butylamine, n-octylamine, isopropylamine, tertiary-
butylamine, n-decylamine, eicosylamine, aniline, cyclo-
hexylamine, bendylamine, p-tolylamine, methylcyclohex-
ylamine, pyridine, 2-ethyl-5-ethylpyridine, N-methylpiperi-

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dine, ethylenediamine, 1,4-diaminobutane, 1,2,3-triamino-
propane, diethylenetriamine, nitromethane, nitroethane,
nitrooctane, nitrodecane, nitroeicosane, nitrobenzene,
nitrocyclohexane, nitrocyclopentane, 4-nitrobutene-1, and
the like. The particular nitrogen-containing compound
selected should preferably have a boiling point sufficient-
ly higher or lower than the reaction products to permit
ready separation from the reaction products.

Alkyl halides which are dehydrohalogenated accord-
ing to the process of this invention normally contain
from 3 to 18 carbon atoms. The invention is applicable
to the dehydrohalogenation of halogenated alkanes, in-
cluding mono- and polyhalosubstituted alkanes of the
straight chain and branched chain type. The invention is
particularly applicable to the dehydrohalogenation of
straight chain alkyl halides. The alkyl halides which are
dehydrohalogenated can be chlorides, iodides, bromides
and fluorides. However, the invention is particularly ap-
plicable to the dehydrohalogenation of alkyl chlorides.
Some specific examples of alkyl halides which can be
dehydrohalogenated by the process of this invention are:
n-butyl chloride, n-hexyl bromide, n-octyl iodide, n-meth-
yl iodide, n-dodecyl chloride, 4-chlorododecane, 6-chloro-
tetradecane, n-octadecyl bromide, and the like, including
mixtures of two or more of such alkyl halides as occur
from the halogenation of n-paraffin mixtures such as
1,4-dichlorobutane, 1,3-dibromohexane, 2,4-dichlorooct-
ane, 1,3,5-trichlorododecane, and 2,4,6,8-tetrachloro-
octadecane.

The dehydrohalogenation is conducted as a catalytic
dehydrohalogenation process, employing such dehydro-
halogenation catalysts as alumina, silica-alumina, oxidi-
zed charcoal, bauxite, leaching earth, and the like.
A preferred dehydrohalogenation catalyst which is em-
ployed in the process of this invention is an oxidized
activated charcoal. The charcoal portion of the oxidized
activated charcoal catalyst is a conventionally activated
charcoal such as is prepared from such sources as ba-
gasse, bones, coconut shells, corn cobs, cottonseed hulls,
fruit pits, lignin, lignite, nut shells, peat, petroleum coke,
sawdust, and the like. After initial carbonization, such
as by heating in the absence of air at about 600° C.,
the charred material is activated by such means as con-
tinued heat treating, treatment at elevated temperatures
with CO₂, steam, chlorine, SO₂, etc. By activation, the
charcoal is given an extended surface area.

The preferred oxidized charcoal dehydrohalogenation
catalysts which are employed in our inventive process
are prepared by subjecting an activated charcoal to oxidi-
zing treatment, said oxidizing treatment being carried
out by heating the activated charcoal and air to a tem-
perature above about 300° C., preferably to a tempera-
ture in the range of from 500 to 700° C. At these tem-
peratures, the time of treatment will vary between about
1 second to about 1 hour, but will generally range from
about 1 to 15 minutes. Some minor loss of carbon usually
occurs during the oxidation step. If desired, the air em-
ployed for the oxidizing treatment may be diluted with
gases to better control the treatment and to minimize
combustion losses. When oxidized, activated charcoal, the
preferred catalyst, is employed, the particle size will nor-
mally vary from smaller than 325 mesh (U.S. series)
to granules of 6 mesh or larger. Granular material is
favored for continuous fixed bed type reactions.

The dehydrohalogenation process can be conducted
as a batch or continuous process, utilizing either liquid
phase or vapor phase operation. Preferably, the process
is conducted in the vapor phase and it is further pre-
ferred to operate continuously by passing a mixture of
the volatilized alkyl halide and volatilized nitrogen-con-
taining compound through a bed of the dehydrohalogena-

tion catalyst at a rate selected to provide the desired degree of conversion. Although preferably the nitrogen-containing compound is mixed with the alkyl halide feed and the mixture passed to the dehydrohalogenation zone, the invention is not limited thereto. The nitrogen-containing compound can be introduced directly into the dehydrohalogenation zone. Various methods of adding the nitrogen-containing compound to the alkyl halide feed can be employed. For example, the nitrogen-containing compound can be added to the alkyl halide prior to vaporization, or the materials can be separately vaporized and mixed as vapors prior to entering the catalyst bed.

The dehydrohalogenation of the alkyl halides is effected at temperatures of from about 225 to about 500° C. When conducting a batch process, the catalyst concentration will range from about 0.01 to about 25 weight percent of the straight chain alkyl halide feed. When conducting a continuous process, the liquid hourly space velocity will range from about 0.01 to about 10 volumes of alkyl halide feed per volume of catalyst per hour.

It is within the scope of this invention to employ a carrier gas, inert to the reaction process, to assist the flow of products and by-products within the reaction system. It is also within the scope of this invention that as the activity of the catalyst decreases, operation at excessively higher temperatures can be employed until regeneration of the catalyst as required.

The product olefins are separated from the effluent mixture withdrawn from the reaction zone. The separated unreacted alkyl halides and nitrogen-containing compound can be recycled to the dehydrohalogenation zone. A suitable separation process comprises passing a liquid effluent from the dehydrohalogenation zone to a first distillation zone wherein dissolved hydrogen halide is separated from the effluent and the remainder of the effluent passed to a second distillation zone wherein the olefin product is separated from the unconverted alkyl halides and nitrogen-containing compound.

A vaporous effluent withdrawn from the dehydrohalogenation zone can be partially condensed and the hydro-

glowing charcoal. After about 5 minutes of such treatment, the tray was set out to cool and reweighed. The prepared charcoal was then employed for the dehydrochlorination of a mixture of primary and secondary dodecyl chlorides, principally secondary chlorides formed by the chlorination of n-dodecane.

Both runs were conducted in a 12 ml. quartz catalyst tube to which the charcoal was charged. The quartz tube was mounted inside a refractory tube which contained electric heating elements with the entire arrangement surrounded by one-half inch asbestos insulation. In each run, nitrogen was metered into the reactor under 5 pounds pressure and at a flow rate of 2.4. liters/hour. The reactor was heated by means of the electric heaters to 300° C., and after the reactor stabilized at 300° C., the dodecyl chlorides were charged at a space velocity of 0.6 (LHSV) through a 6-inch hypodermic needle. These conditions were maintained for 30 minutes to establish equilibrium and were maintained until dehydrohalogenation, as determined by analysis of effluent dropped to 95 percent. When this occurred, the temperature was raised to 350° C., and when dehydrohalogenation had again dropped to 95 percent, the temperature was raised to 400° C.

Both dehydrohalogenation runs were conducted by the above described procedure. In Run 1, the feed comprises dodecyl chlorides, while the feed in Run 2 comprised the dodecyl chlorides containing 0.5 weight percent of 2-methyl-5-ethylpyridine.

Conversions in each of the runs were determined by chromatographic analysis on a 10-foot by ¼-inch diameter column packed with glass beads coated with di(n-dodecyl) phthalate. The liquid effluent was weighed, and the dissolved HCl was removed by placing the collected effluent in an oven at 80° C. and 20 mm. Hg absolute pressure for 30 minutes. The stripped liquid was then analyzed for chlorine content and for straight-chain olefin content. The amount of branched hydrocarbons formed by isomerization during dehydrochlorination was determined by gas-liquid chromatography. The results of these tests are expressed below in Table I.

TABLE I

Feed	300° C.		350° C.		400° C.	
	Percent Dehydrohalogenation	Wt. Percent Branched Chain	Percent Dehydrohalogenation	Wt. Percent Branched Chain	Percent Dehydrohalogenation	Wt. Percent Branched Chain
Run 1.....	99.1	10.1	98.9	10.2	99.1	11.8
Run 2.....	99.5	2.8	99.5	4.8	99.7	7.3

gen halide separated from the condensed fraction containing the olefin product. The condensed fraction can then be subjected to a distillation step as previously described.

The following specific example is presented to illustrate the advantages of the process of this invention and to clearly demonstrate the minimization of the isomerization by the addition of a nitrogen-containing compound to the alkyl halide feed. However, it is not intended that the invention should be limited to the features shown therein.

Example

Two runs were conducted in which oxidized charcoal was employed for the dehydrohalogenation of straight chain alkyl halides. In Run No. 1, no nitrogen compound was added to the alkyl halide feed, while in Run No. 2, a small amount of an amine was added.

The oxidized charcoal catalyst employed in these runs was prepared by placing a weighed sample of petroleum base coke in a quartz tray which had been preheated to 650 to 700° C. in a muffle furnace. The tray was then placed in the muffle furnace operating at 650 to 700° C. and the tray rapidly shaken while blowing air over the

The results obtained in the dehydrochlorination of straight chain dodecyl chlorides when employing a nitrogen-containing compound clearly demonstrates the effectiveness of the nitrogen-containing compound to minimize isomerization of the hydrocarbons recovered from the dehydrogenation zone when compared with the results obtained by dehydrohalogenation of the dodecyl chlorides in the absence of the amine.

Various modifications of this invention can be made, or followed, in view of the foregoing disclosure, without departing from the spirit or scope thereof.

We claim:

1. A process which comprises introducing a straight chain alkyl halide feed into a dehydrohalogenation zone containing a dehydrohalogenation catalyst, introducing into said dehydrohalogenation zone a nitrogen-containing compound in an amount sufficient to minimize carbon skeleton isomerization, and withdrawing an olefin product from said dehydrohalogenation zone.

2. The process of claim 1 wherein the quantity of said nitrogen-containing compound introduced into said dehydrohalogenation zone is in the range from 0.1 to 2.5

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weight percent based on the alkyl halide feed and the nitrogen-containing compound is selected from the group consisting of ammonia, amines, and nitro-substituted hydrocarbons.

3. The process of claim 2 wherein said dehydrohalogenation catalyst comprises an oxidized activated charcoal.

4. The process of claim 2 wherein the temperature of said dehydrohalogenation zone is maintained in the range from about 225 to about 500° C.

5. The process of claim 4 wherein the dehydrohalogenation process is a batch process and the catalyst concentration is in the range from about 0.01 to about 25 weight percent of the straight chain alkyl halide feed.

6. The process of claim 4 wherein the dehydrohalogenation process is continuous and the liquid hourly space velocity through said dehydrohalogenation zone is maintained in the range from about 0.01 to about 10 volumes of alkyl halides per volume of catalyst per hour.

7. The process of claim 4 wherein said alkyl halide and said nitrogen-containing compound introduced into said dehydrohalogenation zone are in the vapor phase.

8. The process of claim 7 wherein said alkyl halide feed and said nitrogen-containing compound are mixed prior to the introduction of the mixture into said dehydrohalogenation zone.

9. A process which comprises admixing a straight chain alkyl halide with a nitrogen-containing compound in an amount sufficient to minimize carbon skeleton isomerization, passing the resulting mixture into a dehydrohalogenation zone containing a dehydrohalogenation catalyst, and withdraw an olefin product from said dehydrohalogenation zone.

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10. A process which comprises introducing a straight chain alkyl halide into a dehydrohalogenation zone containing a dehydrohalogenation catalyst, introducing into said dehydrohalogenation zone a nitrogen-containing compound in an amount sufficient to minimize carbon skeleton isomerization, withdrawing an effluent mixture from said dehydrohalogenation zone, separating an olefin product from said dehydrohalogenation zone effluent mixture in a separation zone, and recycling an alkyl halide stream and a nitrogen-containing compound from said separation zone to said dehydrohalogenation zone.

11. The process of claim 1 wherein the straight chain alkyl halide comprises a mixture of primary and secondary dodecyl chlorides.

12. The process of claim 1 wherein the nitrogen-containing compound comprises 2-methyl-5-ethylpyridine.

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