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2,726,255

OXIDATION PROCESS

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The present invention relates to methods of oxidizing higher aliphatic hydrocarbons, deals with processes of manufacturing mixtures of oxygen-containing aliphatic compounds and provides a new and improved method of preparing fatty alcohols of from 7 to 12 carbon atoms. The invention deals more particularly with the production of valuable oxygen-containing compounds by the oxidation of alkanes or alkenes of from 7 to 12 carbon atoms or mixtures of the same.

While oxidation of higher alkanes or alkenes or technical mixtures of the same has received considerable attention in the prior art as a possible easy and inexpensive method of producing oxygen-containing aliphatic compounds, prior methods have met with limited, if any, success. Non-catalytic processes, requiring the use of very high temperatures, can be controlled only with difficulty and generally result in very poor conversion to the desired products; and catalytic processes, requiring constant replacement or regeneration of catalyst, generally demand variation of catalyst with each hydrocarbon or with each hydrocarbon mixture.

Now we have found that oxidation of alkanes or alkenes of from 7 to 12 carbon atoms or technical mixtures of the same is effected readily in the liquid state at only moderately elevated temperatures and in the absence of an oxidation catalyst when oxidation is conducted in the presence of an alkali and initiated by including in the hydrocarbon material a small quantity of a hydrocarbon hydroperoxide.

The oxidation of aliphatic hydrocarbons is generally believed to proceed through a general mechanism stemming from the formation of alkyl hydroperoxides (Walsh, Trans. Faraday Soc., 42 269-279 (1946)). The hydroperoxides which are initially formed are believed to participate by decomposing into a ketone, a free hydroxy radical and a free alkyl radical, the free radicals thus formed adding to either another molecule of the original hydrocarbon or to each other. Thus, oxidation of a hydrocarbon generally results in cracking of the hydrocarbon as well as in the formation of oxygen-containing products, oxidation of isooctane, for example, resulting in degradation of the hydrocarbon to acetone, formaldehyde and water. For the preparation of long chain oxygen-containing organic compounds, the direct oxidation procedures have been generally considered undesirable in that the hydroperoxide theory of oxidation presupposed a breakdown of the initial long chained hydrocarbon to yield oxygen-containing compounds having much lower molecular weights than that of the parent hydrocarbon material.

In order to initiate hydrocarbon oxidation the use of peroxidic agents as catalyst has been suggested in prior art, e. g., Armstrong et al. in U. S. Patent No. 2,469,322 employs per compound, generally, as oxidation promoters for the oxidation of sulfuric acid heavy alkylate; and in U. S. Patent No. 2,265,948 Loder mentions organic and inorganic peroxides, among various oxidation initiators. That reactions generally may be ac-

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celerated by including in the initial reaction mixture an intermediate product obtained in a previous reaction is generally known. We have found however, that in the oxidation of higher alkanes or alkenes the choice of intermediate product employed has a definite effect on the nature of the reaction products, and that the addition of hydrocarbon hydroperoxides to this oxidation mixture in alkaline media results in a reaction course which is decidedly different from that which was brought about by employing hydrocarbon peroxides as initiators. While the use of peroxides as initiators apparently results in degradation of the higher alkane or alkenes to yield a preponderance of low molecular weight oxygen-containing compounds such as acetone, acetaldehyde, formaldehyde and acetic acid, the use of hydrocarbon hydroperoxides as initiators, in alkaline media, results in formation of oxygen-containing products with approximately the carbon content of the original hydrocarbon. Also, in the peroxide-initiated prior processes, the chief high-molecular weight products are acids; whereas when operating by the present process, only traces of acids are formed, the chief products being alcohols and ketones. The boiling point range of the products obtained in the present process coincides almost exactly with that of alcohols and ketones having the number of carbon atoms of the parent hydrocarbon stock. The quantity of low-boiling material in the present oxidations is but slightly more than that which would normally come from the degradation of the hydroperoxide initiator.

While we do not know the mechanism which is responsible for producing the high molecular weight alcohols and ketones rather than the low molecular weight mixtures of oxygen-containing compounds, we believe that the presence of an excess of hydroperoxide in the alkaline media is responsible for an oxidation mechanism which differs essentially from that involving degradation.

Oxidation of alkanes or alkenes of from 7 to 12 carbon atoms, or of mixtures of the same, by the present process is effected simply by contacting a mixture of the hydrocarbon, the hydrocarbon hydroperoxide and the alkaline material with an oxygen-containing gas, e. g., air or oxygen, at ordinary or superatmospheric pressures at temperatures of from 50-180° C., and preferably at from 80-150° C. Conveniently, oxidation is effected in a closed vessel and at the pressure developed by the introduced oxygen.

The hydroperoxide employed may be the hydroperoxide of the hydrocarbon which is to be oxidized or another hydrocarbon hydroperoxide, e. g., one of the commercially available hydroperoxides such as tert-butyl hydroperoxide, cumene hydroperoxide, cymene hydroperoxide, etc. Hydroperoxides of hydrocarbons containing a tertiary carbon atom are preferred. The hydroperoxide is present in small quantities i. e., in quantities of from, say, about 1 per cent to about 20 per cent of the total reaction mixture.

Any alkaline agent which is substantially inert during the reaction conditions may be employed; for example, there may be used inorganic alkalis such as the alkali metal or alkaline earth metal hydroxides, oxides or salts such as the sodium, potassium, lithium, magnesium, calcium and barium hydroxides, carbonates, bicarbonates and oxides. The inorganic alkalis are preferred. The quantity of alkaline material employed is generally just sufficient to confer alkalinity to the reaction mixture and ordinarily is from, say, 0.001 per cent to 3.0 per cent of the total reaction mixture.

Hydrocarbons which may be oxidized by the present process are straight-chain or branched chain paraffins or aliphatic mono-olefins of from 7 to 12 carbon atoms or mixtures of the same, for example, heptane, 2,5-dimeth-

ylhexane, isooctane, n-decane, 2-butyloctane, n-dodecane, trimethylnonane, undecane, n-heptene, 2-ethylhexene, n-dodecene, etc. Particularly useful are mixtures of straight chain C₇ to C₁₀ paraffins obtained by the urea adduct process, natural gasoline fractions, alkylation gasolines, etc.

While the oxidation products obtained by the present process predominately comprise compounds having a car-

Example 2

A series of runs was made in which a natural gasoline fraction, B. P. 102° C.-165° C., was oxidized in the presence of tert-butyl hydroperoxide and sodium bicarbonate substantially as described in Example 1. Operating conditions used and the results obtained are summarized in the following table.

Run No.	Wt. Gasoline fraction, g.	Wt. T-BHP, g.	Wt. NaHCO ₃ , g.	Initial gauge pressure, p. s. i.	Temp., ° C.	Time, Hrs.	O ₂ Up-take, moles	Wt. Recovered Hydrocarbons, g.	Wt. Oxygenates, g.
1	246	17.7	1	190	130-136	5	.98	159	40.7
2	421	31.3	2	190	130-145	6	2.15	285	46.1
3	698	39.3	5	180	120-130	5		615	38.3
4	313 ^a	22.8	1	250	132-138	8.5	1.22	155	51.5
5	390 ^b	18	1	250	127-140	8	1.49	367	205.0
6	353	22	1	250	128-140	8	1.79		
7	419	76 ^d	3	180	128-160 ^c	8	0.65	261	42.4
8	364	32.5	2	450	128-140	8	2.56	180	30.0

^aAll recycle.

^bHalf recycle.

^cAccidentally overheated for a short period.

^d20 g. added after the period of overheating.

bon content which corresponds to that of the hydrocarbon employed in the oxidation, it generally consists of a mixture of aldehydes, alcohols, ketones, esters and acids. In order to obtain a higher alcohol concentration in the oxidation product it has been found desirable, for many purposes, to submit it to subsequent hydrogenation, whereby the aldehyde and the ketone content of the product is converted to alcohols. Hydrogenation of the oxidation product is readily effected either by passing hydrogen into the crude reaction product or by first separating the oxygen-containing materials from the reaction product, e. g., by distillation, and introducing hydrogen into the separated material. The hydrogenation may be effected at ordinary or increased temperatures preferably in the presence of a hydrogenating catalyst such as palladium black, platinum, copper, nickel, etc. The hydrogenation product comprises a mixture of alcohols, acids and esters from which the alcohols may be readily separated by refluxing with aqueous alkali to saponify the esters and then distilling off or decanting the resulting aqueous solution of acids. The mixed alcohols thus obtained may be employed for a wide variety of industrial purposes, e. g., for the production of ester-type plasticizers, or if desired, the mixture may be resolved into individual alcohols which are difficultly obtainable by other methods.

The invention is further illustrated, but not limited, by the following examples.

Example 1

A mixture consisting of 208 g. of a natural gasoline fraction B. P. 102-165° C., 21.4 g. of tert-butyl hydroperoxide and 12 g. of magnesium oxide was charged to a pressure vessel, 208 g. of oxygen was introduced into the mixture to a gauge pressure of 188 p. s. i. and the whole was heated with stirring to a temperature of 108-126° C. for 11 hours. During this time additional oxygen was introduced to give a total consumption of 1.33 moles of oxygen. The reaction mixture was then filtered, washed with water and 5 per cent aqueous sodium bicarbonate, and the resulting organic phase was distilled to yield 34.2 g. of a fraction B. P. 72-130° C. at 80 mm., comprising oxygenated products having approximately the carbon content of the gasoline fraction employed. This fraction was found to be 60% soluble in concentrated sulfuric acid, which indicates a very high concentration of oxygenated materials. By determining the neutralization equivalent of the fraction, it was found to contain 4.8% acids (computed as caprylic acid), and 12.3% (computed as octyl formate) esters were determined by saponification.

25 In each of the above runs the aqueous phase which separated upon treatment of the reaction product with 5 per cent aqueous sodium bicarbonate was separated and discarded.

30 The oxygenate from run No. 1 above was found by assay to contain 8.1% carboxylic acids (as caprylic acid) and 9.8% esters (as octyl formate).

Example 3

35 163.5 g. of 2,4-dimethylpentane, 9.1 g. of tert-butyl hydroperoxide and 1 g. of sodium bicarbonate was charged to a pressure vessel and oxygen was introduced during a time of 4 hours at 130° C. to maintain a gauge pressure of oxygen of 190 p. s. i. Fractionation of the resulting reaction product gave a fraction B. P. 73-105° C./700 mm. (16.1 g.), comprising a mixture of oxygenated products.

Example 4

45 A mixture consisting of 222.7 g. of n-heptane, 108 g. of tert-butyl hydroperoxide and 1.0 g. of sodium bicarbonate was charged to a pressure vessel and 0.84 moles of oxygen was introduced into the mixture at 132° C. during a time of 12 hours while maintaining a gauge pressure of 190 p. s. i. Distillation of the resulting reaction mixture gave 17.7 g. of a fraction B. P. 74-120° C./80 mm., comprising a mixture of oxygenated products.

Example 5

55 A mixture consisting of 140.4 g. of octene-1, 7.9 g. of tert-butyl hydroperoxide and 1.0 g. of sodium bicarbonate was charged to a bomb. Oxygen was introduced to a gauge pressure of 145 p. s. i. and the mixture was heated for 3 hours at 131° C. with continuous shaking. Distillation of the product yielded 27.9 g. of a mixture of oxygen-containing compounds B. P. 76.5-130° C. at 80 mm. In two subsequent runs, conducted on a larger scale, there was obtained an additional 98.2 g. of the oxygenated material.

Example 6

65 This example shows further treatment of the oxygenated products of some of the previous examples to yield alcohols. The oxygenated products from Example 1 and runs 1 and 2 of Example 2 were combined (total weight 68.7 g.) and charged to a hydrogenation bomb together with 0.6 g. of Raney nickel catalyst. Hydrogen at a gauge pressure of 500 p. s. i. was admitted to the bomb and the mixture was shaken and heated to 130-150° C. for 7 hours. The drop in pressure indicated that 0.43 mole of hydrogen had been consumed. The reaction product was then filtered and distilled to yield a fraction

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B. P. 88.5–131° C./80 mm., assaying 26.2 per cent alcohol (as octanol).

In order to remove acids and esters from the reduced product obtained above it was refluxed with ethanol-potassium hydroxide. The ethanol was removed by distillation and the potassium hydroxide by washing the residue with water. The residue was distilled to yield a fraction B. P. 85–130° C. at 80 mm., which assayed 32.5 per cent alcohol (as octanol).

Example 7

The combined oxygenated material from the runs of Example 5 were charged to a hydrogenation bomb together with 2 g. of Raney nickel. Hydrogen at a gauge pressure of 500 p. s. i. was admitted to the bomb and the mixture was heated at 100–130° C. for 3 hours. The uptake of hydrogen amounted to 0.9 mole. Filtration and distillation of the reduced material yielded a fraction assaying 39.3 per cent alcohol (as octanol). Refluxing of this fraction with alcoholic potassium hydroxide, washing of the refluxing material with water, drying and distillation gave a fraction B. P. 85–130° C./80 mm., which assayed 53.8 per cent alcohol (as octanol).

What we claim is:

1. The method which comprises contacting a mixture of a feed consisting of hydrocarbon selected from the class consisting of acyclic alkanes and acyclic alkenes containing from 7 to 12 carbon atoms, and a hydrocarbon hydroperoxide in the presence of an alkaline agent with an oxygen-containing gas at a temperature of from 80° C. to 150° C. and recovering from the resulting reaction product a mixture of oxygenated products containing pre-

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dominantly alcohols and ketones having a carbon content corresponding to that of the hydrocarbon which is oxidized.

2. The method which comprises contacting a mixture of a natural gasoline fraction consisting of hydrocarbons selected from the class consisting of acyclic alkanes and acyclic alkenes containing from 7 to 12 carbon atoms, and a hydrocarbon hydroperoxide in the presence of an alkaline agent with an oxygen-containing gas at a temperature of from 80° C. to 150° C. and recovering from the resulting reaction product a mixture of oxygenated products containing predominantly alcohols and ketones having a carbon content corresponding to that of the hydrocarbon which is oxidized.

3. The method as described in claim 2 wherein the hydrocarbon hydroperoxide is tert.-butyl hydroperoxide and the alkaline agent is sodium bicarbonate.

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