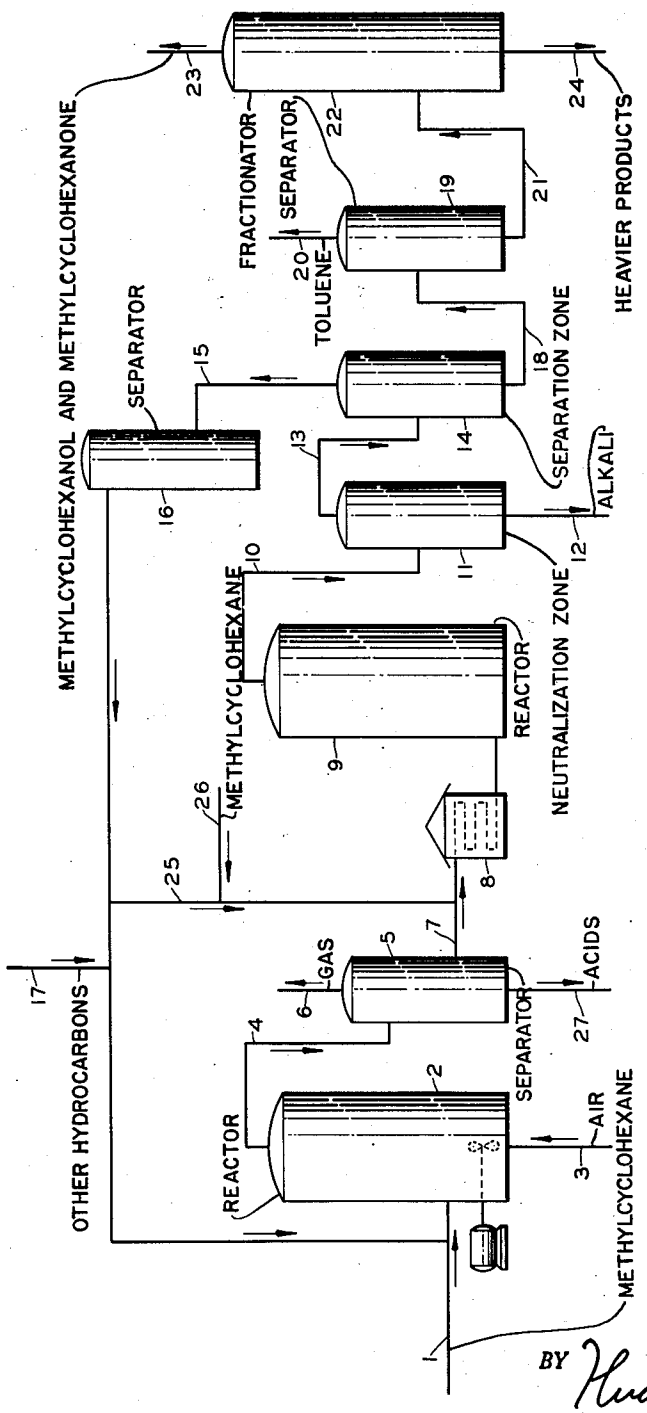
Sept. 2, 1952 C. F. DOUGHERTY, JR., ET AL 2,609,395

OXIDATION OF HYDROCARBONS

Filed Dec. 16, 1949



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Patented Sept. 2, 1952

2,609,395

UNITED STATES PATENT OFFICE

2,609,395

OXIDATION OF HYDROCARBONS

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Application December 16, 1949, Serial No. 133,282

17 Claims. (Cl. 260—586)

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This invention relates to a process for partially oxidizing alicyclic hydrocarbons to produce corresponding alcohols and ketones. In one of its aspects it relates to a two-step process for oxidizing a cycloalkane with limited portions of an oxygen-containing medium and then treating the resulting oxidation effluent under controlled conditions of time, temperature, and pressure to selectively produce the corresponding cycloalkanol and cycloalkanone. In still another of its aspects this invention relates to a process for preferentially producing a secondary alkyl cyclohexanol to the substantial exclusion of the tertiary alkyl cyclohexanol by oxidizing a corresponding alkyl cycloalkane under closely controlled reaction conditions in an oxidation zone and then treating the resulting oxidation product in a deperoxidization zone with an alkyl cycloalkane to produce the desired secondary alkyl cycloalkanol without concomitantly producing substantial quantities of the tertiary alkyl cycloalkanol. In yet another of its aspects this invention relates to a process for reacting a cycloalkane hydroperoxide with a cycloalkane to produce cycloalkanols as well as cycloalkanones. In yet still another of its aspects, this invention relates to a process for oxidizing a cycloalkane with limited quantities of an oxygen-containing medium and under closely controlled reaction conditions to produce principally a cycloalkane hydroperoxide. In still yet another of its aspects, this invention relates to a process for separating an aromatic hydrocarbon from admixture with an alicyclic hydrocarbon by oxidizing said alicyclic hydrocarbon with limited quantities of an oxygen containing medium and then separating said aromatic hydrocarbon from the resulting effluent.

The oxidation of various hydrocarbons to alcohols, ketones and the like has long been known and practiced in the prior art. It is also known in the prior art to oxidize unsubstituted cycloalkanes. In such processes it is known that in addition to the alcohols and ketones thereby produced, considerable quantities of tars and polymers are likewise produced as undesirable by-products. It is known that these tars and polymers are decomposition and degradation products of cycloalkane hydroperoxides which are formed while oxidizing the cycloalkane. It is further known that cycloalkane hydroperoxides are unstable in nature and if concentrated to any large extent that they are highly explosive and therefore dangerous to handle. Hence it has been an object of the prior art to minimize the production of these hydroperoxides and to

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rapidly decompose those which are formed in order to avoid the damage of explosions.

In the prior art processes, alkyl cycloalkanes have been oxidized to produce principally tertiary alkyl cycloalkanols and acyclic ketones. As is obvious to one skilled in the art, a tertiary alcohol, such as tertiary alkyl cycloalkanol, is a less desirable compound than the corresponding secondary alkyl cycloalkanols because the tertiary alcohols in general, and the tertiary alkyl cycloalkanols in particular, are difficult to convert to esters which is one of the principal applications of the alkyl cycloalkanol compounds. It is also well known in the prior art to oxidize the various alkyl cycloalkanes to produce acyclic ketones but in such processes the production of the alkyl cycloalkanones is not accomplished. The alkyl cycloalkanones are widely used as specialty solvents in many industrial processes where the acyclic ketones are not applicable. As stated, the oxidation of cycloalkanes results in the production of considerable amounts of cycloalkane hydroperoxides and it would be highly advantageous to provide a process for not only avoiding dangerously explosive concentrations of these hydroperoxides but to also convert these hydroperoxides into a desired and useful product instead of to tars and polymers. Also, as stated, secondary alkyl cycloalkanols are widely used and therefore it would be advantageous to provide an oxidation process for producing predominantly secondary alkyl cyclohexanols and alkyl cyclohexanones from a readily available starting material without substantial production of the tertiary alkyl cycloalkanols and without incurring the disadvantages of the prior art processes such as the formation of excessive amounts of undesirable tars and the danger of exploding the concomitantly formed hydroperoxides. Such a process was not known to the present inventors prior to the making of the instant invention.

Still further in the prior art, it is known that admixtures of certain alicyclic hydrocarbons, such as methylcyclohexanes, and certain aromatic hydrocarbons, such as toluene, are very difficult to separate by a fractional distillation process. It is the usual practice to employ several fractional distillation steps involving "heart" cutting operations with the resultant disadvantage that only a small percentage of the original alicyclic hydrocarbon is recovered in a pure state.

It has now been found that a cycloalkane can be oxidized to produce a corresponding cycloalkanol and cycloalkanone without concomitantly producing any substantial quantities of polymers

or tars and without incurring the danger of explosive concentrations of an intermediately produced cycloalkane hydroperoxide and that a cycloalkane hydroperoxide produced during the oxidation of a cycloalkane can be further converted to a desirable cycloalkanol and cycloalkanone by oxidizing the cycloalkane in a first zone with limited quantities of an oxygen-containing medium and then in the substantial absence of any free oxygen, reacting said hydroperoxide with a cycloalkane in a second zone maintained under carefully controlled reaction conditions. It has also been found that a cycloalkane can be oxidized with limited quantities of oxygen from an oxygen-containing medium under controlled reaction conditions to produce a cycloalkane hydroperoxide as the principal product. Furthermore, it has been found that an alkyl cycloalkane can be oxidized to secondary alkyl cycloalkanol to the substantial exclusion of the tertiary alkyl cycloalkanol in a two-step process comprising an oxidation step wherein an alkyl cycloalkane is reacted with limited quantities of oxygen to produce predominately an alkyl cycloalkane hydroperoxide and a deperoxidization step wherein the alkyl cycloalkane hydroperoxide thus produced is deperoxidized by reaction with an alkyl cycloalkane to produce the desired product without concomitantly producing undesirable tars and without incurring the risk of dangerous explosions of the hydroperoxide. Still further, it has been found that an aromatic hydrocarbon can be readily separated from an admixture with a cycloalkane by first oxidizing the mixture with limited quantities of an oxygen-containing medium and separating the unreacted cycloalkane and the aromatic hydrocarbon from the oxidation effluent. The aromatic hydrocarbon, under the oxidation conditions employed, is not oxidized and therefore passes through the oxidation process unchanged. The oxidation effluent has been found to be readily fractionatable into a substantially pure cycloalkane stream and an oxidate stream which contains the unoxidized aromatic hydrocarbon. The latter stream can then be easily separated into an aromatic hydrocarbon fraction and an oxygenated hydrocarbon fraction. Thus, the presence of the small amount of oxygenated cycloalkane permits an easy separation of the ordinarily difficultly separable cycloalkane-aromatic hydrocarbon admixture into cycloalkane and aromatic hydrocarbon fractions.

Thus, a cycloalkane is oxidized to a limited extent in an oxidation zone by limited amounts of oxygen to form principally a cycloalkane hydroperoxide. A mixture of such hydroperoxide and cycloalkane is then passed to a deperoxidization zone wherein the cycloalkane hydroperoxide is deperoxidized in the substantial absence of any free oxygen and under carefully controlled reaction conditions by reaction with a cycloalkane to produce a cycloalkanol and a cycloalkanone. Thus the following equations can be used to demonstrate the process of this invention:

Step I:

$$R + O_2 \longrightarrow \underset{|}{R'OOH}$$

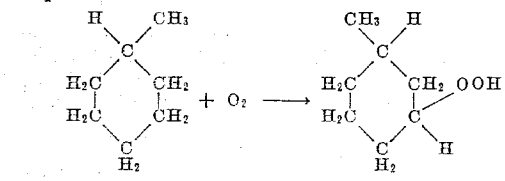
Step II:

$$\underset{|}{R'OOH} + R \longrightarrow 2\underset{|}{R'OH}$$

wherein R is a cycloalkane hydrocarbon and R' is a cycloalkane radical.

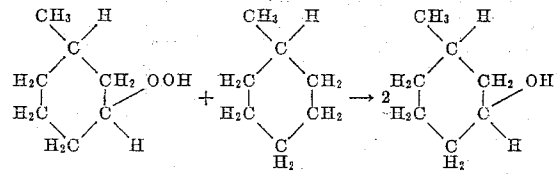
When operating in accordance to this invention, an alkyl cycloalkane can be oxidized in a first step and the resulting alkyl cycloalkane hydroperoxide deperoxidized in a second step. The principal product is a secondary alkyl cycloalkanol. Smaller amounts of a 2-, 3- and 4-alkylcycloalkanone and a 2-alkanone are also produced but substantially no 1-alkyl-cycloalkanol is formed. Furthermore, substantially no tars or polymers are produced. Thus, for example, when the alkylcycloalkane is methylcyclohexane, the reactions occurring in the process of this invention can be demonstrated by the following equations:

Step I:



Methylcyclohexane — Methylcyclohexane hydroperoxide

Step II:



Methylcyclohexane hydroperoxide — Methylcyclohexane — 3-methylcyclohexanol

Hence it is apparent that the process of this invention provides a means for producing a cycloalkanol and cycloalkanone without producing undesirable tars and polymers inherently produced in the prior art processes. It is also apparent that when an alkyl cycloalkane is oxidized the principal product is a desirable secondary alkyl cycloalkanol and alkyl cycloalkanone and not the less desirable tertiary alkyl cycloalkanol. It is further apparent that the process of this invention does not seek to avoid the production of hydroperoxides but, on the contrary, is specifically directed to their production in order that they can be converted into the desired cycloalkanol and cycloalkanone using additional quantities of cycloalkane, as described herein. It is also apparent that when a cycloalkane-aromatic hydrocarbon admixture is desired to be separated into its components, the process of this invention provides an easy method for so doing without resorting to extended fractionation procedures and without incurring the disadvantage of recovering only a small percentage of the original cycloalkane component in the cycloalkane-aromatic hydrocarbon admixture.

In order to more fully set forth and to describe this invention, it will be described with particular reference to the attached drawing which illustrates one of the embodiments of the process of this invention and with reference to a specific reaction, namely the oxidation of methylcyclohexane to produce predominantly 3-methylcyclohexanol and lesser quantities of methylcyclohexanone to the substantial exclusion of 1-methylcyclohexanol. However, it is to be understood that cycloalkanes other than methylcyclohexane can be readily employed in the process of this invention to realize the advantages thereof. Thus this invention contemplates oxidizing not only methylcyclohexane but also other cycloalkanes containing from 5 to 8 carbon atoms in the cyclic ring as well as the alkylated derivatives thereof. Thus cyclopentane, cyclohexane, cycloheptane, cyclo-octane, etc., as

well as the various mono- and dialkyl cycloalkanes such as the methyl, dimethyl, ethyl, propyl, butyl, etc., substituted products of the above-mentioned cycloalkanes.

In the drawing, a methylcyclohexane feed is passed through line 1 to reactor 2. The methylcyclohexane feed preferably contains minor portions of other hydrocarbon constituents such as cycloalkanes other than methylcyclohexane. Some straight-chain paraffins having a boiling point near that of methylcyclohexane can also be used as a feedstock component. It has been found that when methylcyclohexane contains minor portions of these hydrocarbon impurities, it is oxidized at a faster rate than pure methylcyclohexane. These impurities may be partially oxidized in reactor 2 but their oxidized products are readily separated by fractional distillation from the principal products, methylcyclohexanols and methylcyclohexanones. Under some circumstances, where the methylcyclohexane feed is very pure, it is advantageous to add sufficient amounts of the above-mentioned impurities to the pure feed in order to maintain a high oxidation rate of the methylcyclohexane feed. An oxygen-containing medium such as air, is passed through line 3 into reactor 2 wherein it is intimately admixed with the methylcyclohexane feed by means of mechanical stirrers, jet mixers, or the like. It is important to produce a very intimate admixture of the oxygen and hydrocarbons in reactor 2 in order to ensure complete reaction of the oxygen with the hydrocarbons without excessive oxidation of the hydrocarbons to undesirable products, such as organic acids. The oxygen-containing medium is fed into the oxidation reactor at a rate sufficient to supply the oxygen necessary to effect the desired conversion of the methylcyclohexane to a corresponding hydroperoxide. The amount of oxygen employed per volume of methylcyclohexane feed should be limited to an amount such that the oxygenated products comprise principally a methylcyclohexane hydroperoxide. The exact amount of oxygen used depends on a number of factors such as the desired degree of conversion of the methylcyclohexane feed, the temperature and residence time of the reactants in reactor 2, etc. In any event, the exact amount of oxygen can be determined by mere routine test and is preferably within the range of about 0.05 to about 0.2 mol, more preferably about 0.10 to about 0.15 mol of oxygen per mol of methylcyclohexane feed. The temperature in oxidation reactor 2 is maintained at such a level that the formation of a methylcyclohexane hydroperoxide is effected without substantial decomposition thereof into undesirable products such as tars, polymers, and organic acids. Temperatures in a range of about 150° to about 210° C., preferably from about 155° to about 180° C. are employed. The pressure in the reactor 2 is sufficient to maintain the reactants in a liquid state and is from about 50 to about 1000 pounds per square inch gage, preferably from about 100 to about 500 pounds per square inch gage. The residence time of the reactants in reactor 2 is adjusted to permit substantially complete consumption of the oxygen added to the hydrocarbon reactants. Generally, the residence time in reactor 2 is correlated with the reaction temperature and with the amount of oxygen originally added to the hydrocarbon reactants so that the oxidized effluent from reactor 2 contains substantially no free oxygen. That is, longer reaction times are required for low reaction temperatures than for high reaction temperatures. And, at any given temperature, longer reaction times are required for large amounts of added oxygen than for small amounts. When the above-specified ranges of oxygen concentrations and reaction temperatures are employed, the residence time is from about 50 minutes to about 3 minutes, preferably from about 15 to about 5 minutes. Generally, 3 minutes is about the shortest time which will effect the required oxygen consumption to produce the desired hydroperoxide products and the likewise desired oxygen-free effluents from reactor 2.

The reaction products leave oxidation reactor 2 via line 4 and are passed to gas separator 5 wherein any gases such as those accompanying the oxygen introduced through line 3 as well as small amounts of unreacted oxygen are removed via line 6 from the liquid oxidation reactor effluent. A hydrocarbon insoluble phase containing organic acids can be withdrawn from separator 5 via line 27 and discarded. The oxidation reactor hydrocarbon soluble effluent is then passed through line 7 and heat exchanger 8 to deperoxidization reactor 9. As will be explained hereafter, the temperature of the deperoxidization reactor 9 can be maintained higher or lower than that of oxidation reactor 2 and hence, heat exchanger 8 is employed to add heat or to cool the feed to the reactor. The oxidation reactor effluent passing through line 7 will ordinarily contain substantially no free oxygen since the conditions in reactor 2 have been regulated to effect its substantial consumption. However, if a minor amount of oxygen is contained in the effluent from reactor 2, it is removed therefrom in gas separator 5 to thereby furnish an oxygen-free charge to deperoxidization reactor 9 whereby any ketones formed in deperoxidization reactor 9 will not be further oxidized to the less desirable acids. The charge to reactor 9 then comprises principally a major portion of unreacted methylcyclohexane and a lesser quantity of the intermediate methylcyclohexane hydroperoxide and also varying quantities of 2-heptanone.

It has been found that when a methylcyclohexane hydroperoxide containing oxidation reaction effluent is fractionated at low temperatures, say at about 125° C., to recover oxidized products, then the hydroperoxides decompose substantially completely to polymers, tars, etc., which are not only of no commercial value but also tend to coat and cokify any equipment in which they are handled. It is also noteworthy that when these hydroperoxide-containing oxidation effluents are fractionated to recover other oxidized products, the hydroperoxides will concentrate in one fraction and, since they are chemically unstable in nature, there is a definite risk of an explosion occurring. As stated, according to this invention, it has been found that it is possible to convert a hydroperoxide formed in the oxidation reactor to the desired secondary methylcyclohexanols and methylcyclohexanones without substantial decomposition of the hydroperoxide into undesirable products such as polymers, tars, etc. and without danger of violent reactions or explosions by the unstable hydroperoxide. Thus it has been found that when a methylcyclohexane hydroperoxide is treated under comparatively severe reaction conditions with an excess of methylcyclohexane, the hydroperoxide will be converted substantially quantitatively to the desired secondary alcohols and ketones by reaction with a portion of the

methylcyclohexane. The mode of accomplishing this desirable conversion is by utilizing a long reaction time and/or high reaction temperatures in the deperoxidization reactor 9 and by maintaining methylcyclohexane in a substantial excess over that required to react with the hydroperoxide in order to maintain the latter in a dilute state thereby preventing any violent reactions or explosions. It is readily apparent that the reaction conditions in deperoxidization reactor 9 must be closely controlled to prevent the hydroperoxide decomposing to form tars, etc. and since any high concentrations of hydroperoxide in reactor 9 are apt to result in an explosion. As a general rule, we have found that the reaction temperature in deperoxidization reactor 9 tends to be from about 5° to about 50° C. higher than the temperature in oxidation reactor 2. The increase in temperature is due at least in part to the exothermicity of the reaction in the deperoxidization reactor 9. However, it is not essential to this invention that the deperoxidization zone operate at a higher temperature than the oxidization zone and hence, the temperatures in the deperoxidization reactor 9 can range from about 160° to about 260° C., preferably from about 175° to about 205° C. The choice of the exact operating temperature will depend upon the residence time of the liquid in reactor 9 as will be more fully explained hereafter. The pressure in reactor 9 should be maintained at a level high enough to permit liquid phase conditions to obtain therein. Generally the pressure can range from about 50 to about 1000 pounds per square inch gage, preferably from about 100 to about 500 pounds per square inch gage. As stated, the reaction temperature maintained in reactor 9 will depend upon the liquid residence time of the reactants in reactor 9. When employing the ranges of temperature specified above, it has been found that the liquid residence time can range from about 200 to about 10 minutes, preferably from about 60 to about 20 minutes. The residence time should be so adjusted and so correlated with the reaction temperature that the methylcyclohexane hydroperoxide is all substantially converted to the desired methylcyclohexanols and methylcyclohexanones. Thus, longer reaction times are required for low reaction temperatures than for high reaction temperatures. At any given temperature the optimum residence time can be determined by mere routine test.

The ratio of methylcyclohexane to methylcyclohexane hydroperoxide is regulated to maintain a dilute solution of the latter in the former in order to prevent explosive concentrations of the hydroperoxides from accumulating and to ensure substantially complete conversion of the hydroperoxides to secondary alcohols and ketones instead of to tars, polymers, etc. Generally the mol ratio of methylcyclohexane to methylcyclohexane hydroperoxide can range from about 30 to 1 to about 5 to 1 and preferably it is about 10 to 1. Within these ranges, there is substantially no likelihood of an explosion and the conversion of the hydroperoxides is substantially quantitative. In the ordinary operation of the process of this invention, the unreacted methylcyclohexane accompanying the oxidized products from oxidation reactor 2 will be sufficient to maintain the above diluent ratios. However, in those cases wherein the methylcyclohexane in reactor 2 is converted to such a large extent that the unreacted methylcyclohexane in the effluent products from said zone is insufficient to maintain the desired diluent ratios, additional methylcyclohexane can be added from an outside source through line 26 or some recycle methylcyclohexane from line 15 can be diverted through line 25 to line 7. Upon completion of the deperoxidization reaction in reactor 9, the deperoxidization reactor effluent is passed through line 10 to an acid neutralization zone 11 wherein minor quantities of acid are neutralized by reaction with an alkaline medium such as sodium or potassium hydroxide and then can be withdrawn via line 12. In separation zone 14, unreacted methylcyclohexane is removed through line 15 and returned to line 1 for further reaction in oxidation reactor 2. In some instances the returning methylcyclohexane in line 15 contains considerable water formed in previous processing steps, especially in the neutralization step. In such cases it is desirable to separate the water from the returning methylcyclohexane by passing it through separator 16. Separator 16 can be of any suitable type such as filter, bauxite dryer, etc. In addition, as above noted, it is advantageous in our process to employ methylcyclohexane feed which contains minor portions of other cycloalkanes and/or straight chain paraffins to promote the oxidation reaction. Hence if the returning methylcyclohexane in line 15 contains insufficient amounts of these impurities, additional amounts are added through line 17.

The residual product from fractionator 14 passes through line 18 to toluene separator 19. The inclusion of toluene separator 19 in this process is highly desirable when the original methylcyclohexane feedstock contains appreciable quantities of toluene which is very difficult to separate prior to the oxidation of the feedstock but is unexpectedly easy to separate after the oxidation and deperoxidization steps. Thus it is possible to remove a toluene concentrate from fractional distillation column 19 through line 20. Toluene is substantially unreactive in the oxidation process and therefore there is no advantage in recycling this material to the process. The toluene-free product comprising substantially oxygenated hydrocarbons is passed through line 21 to fractionator 22. In fractionator 22 the desired secondary methylcyclohexanols and methylcyclohexanones are removed overhead through line 23, and other heavier oxygenated hydrocarbon byproducts can be removed through line 24. If desired, further separation between the methylcyclohexanols and methylcyclohexanones and/or the respective isomers thereof can be accomplished through processes not forming a part of this invention.

The following examples will serve to illustrate the process of this invention:

Example I

Methylcyclohexane of 85 per cent purity was pumped into a turbine-stirred oxidation reactor at a rate sufficient to maintain a total residence time of the liquid phase in the reactor at 7 minutes. Compressed air was fed into the reactor at a rate sufficient to supply 0.11 mol oxygen per mol methylcyclohexane. The oxidation reactor was maintained at 171–174° C. and at 500 p. s. i. g. and after 50 minutes the oxygen content of the spent gases was found to be between 0.0–0.2 per cent and a steady state had been reached with respect to reactant and product concentrations. The concentration of methylcyclohexane hydro-

peroxides in the oxidation reactor effluent was then 2.5 mol per cent. After separation of off-gases and a hydrocarbon insoluble liquid phase, hot effluent stream was carried to a deperoxidization reactor, the exothermic heat generated in said reactor being sufficient to maintain the temperature therein at 177° C. The residence time of the liquid within this reactor was 60 minutes and the pressure employed was 200 pounds per square inch gage. The deperoxidized effluent contained less than 0.005 mol per cent peroxides calculated as methylcyclohexane hydroperoxide in methylcyclohexane. The effluent was cooled and all liquid phases thereof were combined and treated with sufficient potassium carbonate to neutralize the acids present. The solution of neutral products in unreacted hydrocarbon was fractionally distilled, first at 200 mm. of Hg pressure to remove the unreacted hydrocarbon and then at 90 mm. of Hg pressure to recover the volatile alcohols and ketones as overhead fractions.

The ultimate yield of volatile alcohol and ketone products based on the methylcyclohexane consumed in the process was 74 mol per cent. The products were comprised of 31 per cent 3-methylcyclohexanol, 29 per cent methylcyclohexanones, 25 per cent 2-heptanone, 13 per cent 2- and 4-methylcyclohexanols and 2 per cent 1-methylcyclohexanol.

Example II

The above conversion was repeated under identical conditions except that the deperoxidization reaction was omitted. The distillation was carefully carried out at a pressure such that the maximum kettle temperature did not exceed that in Example I above. The ultimate yield of volatile alcohols and ketone products was only 75 per cent of that obtained in Example I and the ketone content of the product was somewhat less. An almost two-fold increase in tars over that of Example I was observed.

Example III

Methylcyclohexane of 85 per cent purity was oxidized at 120° C. and at 500 pounds per square inch gage pressure. The residence time of the liquid phase in the oxidation reactor was maintained at 180 minutes. The oxygen consumed during the oxidation reaction was 0.11 mol per mol methylcyclohexane. The oxidized effluent stream contained 3.8 mol per cent methylcyclohexane hydroperoxides. The deperoxidization reaction was not employed and the oxidation effluent was neutralized and distilled very carefully to avoid an explosion.

The ultimate yield of volatile alcohols and ketones based on the methylcyclohexane consumed in the process was 64 mol per cent. The products were comprised of 65 per cent 1-methylcyclohexanol, 25 per cent 2-heptanone, and only 10 per cent methylcyclohexanones and secondary methylcyclohexanols. The productivity of the oxidation reactor, based on gallons of volatile alcohols and ketones produced per gallon of oxidation reactor space in one day was 3.3 per cent of that obtained in Example I.

Example IV

Methylcyclohexane of 85 per cent purity was oxidized as in Example I except that the deperoxidization reactor was maintained at 205° C. instead of 177° C. and the total residence time of the liquid phase in said reactor was 20 instead of 60 minutes. The yield of volatile alcohols and ketones based on the methylcyclohexane consumed in the process was substantially the same as in Example I. The effect of higher deperoxidization temperature was to increase the ketone content of the volatile, neutral products. In the instant example the ketone content of the products was 65 per cent. In Example I, the ketone content of the products was 54 per cent. Despite the short residence time employed in this example in the deperoxidization reactor, the crude product was free of peroxides.

Example V

Methylcylohexane of 85 per cent purity was pumped into a turbine-stirred oxidation reactor at a rate sufficient to maintain the residence time of the liquid phase in the reactor at 50 minutes. Compressed air was fed into the reactor at such a rate as to supply 0.11 mol of oxygen per mol methylcyclohexane. The oxidation reactor was maintained at 155° C. and at 500 pounds per square inch gage. The oxidation effluent which contained 3.5 mol per cent methylcyclohexane hydroperoxides, was passed through a preheater where heat from the deperoxidization reactor effluent was utilized to bring the oxidation reactor effluent stream to 175° C. The stream was then passed through an auxiliary heat exchanger where its temperature was raised to 195° C. The exothermic heat generated in the deperoxidization reactor was sufficient to bring the temperature of the reactants in this reactor to 205° C. The residence time in the deperoxidizing reactor was 20 minutes which was sufficiently long to permit reduction of the peroxides in the effluent products to below 0.005 mol per cent based on methylcyclohexane hydroperoxide in methylcyclohexane. The crude deperoxidized product was purified as in Example I. The ultimate yield of volatile alcohols and ketones was 80 mol per cent based on the methylcyclohexane consumed in the process and the distribution of oxidation products was similar to that obtained in Example I. However, the productivity based on the volume of oxidation reactor space was only 15 per cent of that obtained in Example I.

In accordance with this invention a cycloalkane can be oxidized to produce cycloalkanols and cycloalkanones in a two-step process comprising an oxidation step wherein a cycloalkane is reacted with limited quantities of oxygen and a deperoxidization step wherein the cycloalkane hydroperoxides produced in said first mentioned step are deperoxidized by reaction with a cycloalkane to produce the desired product without concomitantly producing undesirable tars and without incurring the risk of dangerous explosions of the said hydroperoxides, said second step of the deperoxidization of the said hydroperoxides being considered an important and highly advantageous step forward in art and further, that any aromatic hydrocarbons present in the cycloalkane feedstock can be readily separated therefrom by a simple fractional distillation of the oxidized effluent from said oxidation reaction steps.

While the invention has been described in connection with a present, preferred embodiment thereof, it is to be understood that this description is illustrative only and is not intended to limit the invention, the scope of which is defined by the appended claims.

We claim:

1. A process for producing 3-methylcyclohexa-

nol to the substantial exclusion of 1-methylcyclohexanol which comprises passing methylcyclohexane hydroperoxide to a deperoxidization zone, maintaining an excess of methylcyclohexane in said zone whereby the said hydroperoxide is reacted with a portion of said excess methylcyclohexane, maintaining said zone at a temperature of about 160° to about 260° C. and under a pressure of about 50 to about 1000 pounds per square inch, adjusting the rate of flow of total feed to said zone to be such that the residence time of said feed in said zone is about 200 to about 10 minutes whereby the methylcyclohexane hydroperoxide is substantially converted to the desired product without any substantial production of tars and without incurring the risk of explosive concentrations of said hydroperoxide.

2. A process for producing 3-methylcyclohexanol to the substantial exclusion of 1-methylcyclohexanol which comprises passing methylcyclohexane hydroperoxide to a deperoxidization zone, maintaining a substantial excess of methylcyclohexane in said zone whereby the said hydroperoxide is reacted with a portion of said excess methylcyclohexane, maintaining said zone at a temperature of about 175° to about 205° C. and under a pressure of about 100 to about 500 pounds per square inch, adjusting the rate of flow of total feed to said zone to be such that the residence time of said feed in said zone is about 60 to about 20 minutes whereby the methylcyclohexane hydroperoxide is substantially converted to the desired product without any substantial production of tars and without incurring the risk of explosive concentrations of said hydroperoxide.

3. A process for producing a cycloalkanol and a cycloalkanone which comprises reacting a cycloalkane hydroperoxide with a stoichiometric excess of a cycloalkane at a temperature in the range 160 to 260° C., a pressure in the range 50 to 1000 p. s. i., and a reaction time in the range 10 to 200 minutes, and recovering a cycloalkanol and a cycloalkanone as products of the process

4. The process of claim 3 wherein the cycloalkane hydroperoxide is an alkyl cycloalkane hydroperoxide and the cycloalkane is an alkyl cycloalkane whereby a secondary alkyl cycloalkanol is preferentially produced with respect to tertiary alkyl cycloalkanol.

5. The process of claim 3 wherein the cycloalkane hydroperoxide is cyclohexane hydroperoxide and the cycloalkane is cyclohexane.

6. The process of claim 3 wherein the cycloalkane hydroperoxide is methylcyclohexane hydroperoxide and the cycloalkane is methylcyclohexane whereby 3-methylcyclohexanol is preferentially produced with respect to 1-methylcyclohexanol.

7. A two-step process for producing principally 3-methylcyclohexanol and lesser amounts of 2- and 4-methylcyclohexanol and 2-, 3- and 4-methylcyclohexanone to the substantial exclusion of 1-methylcyclohexanol which comprises oxidizing methylcyclohexane feed in the presence of minor portions of cycloalkanes other than methylcyclohexane in an oxidation zone with air added to said zone at a rate equivalent to about one-tenth mol of oxygen per mol of methylcyclohexane feed, maintaining said oxidation zone at a temperature of 171° to 174° C. and under a pressure of about 500 pounds per square inch gage, adjusting the rate of flow of hydrocarbon feed to said oxidation zone to be such that the residence time of said feed in said oxidation zone is about 7 minutes whereby the effluent products from said zone are substantially free of unreacted oxygen; passing said effluent products from said oxidation zone to a deperoxidization zone, maintaining a substantial excess of unreacted methylcyclohexane in said deperoxidization zone whereby a methylcyclohexane hydroperoxide produced in said oxidation zone is reacted with a portion of said excess methylcyclohexane, maintaining said deperoxidization zone at a temperature of 177° C. and under a pressure of 200 pounds per square inch, adjusting the rate of flow of feed to said deperoxidization zone to be such that the residence time of said feed in said zone is about 60 minutes whereby the methylcyclohexane hydroperoxide is substantially converted to the desired products without any substantial concomitant production of tars and without incurring any risk of explosive concentrations of said hydroperoxide.

8. A two-step process for producing principally 3-methylcyclohexanol and lesser amounts of 2- and 4-methylcyclohexanols and 2-, 3- and 4-methylcyclohexanones to the substantial exclusion of 1-methylcyclohexanol which comprises oxidizing methylcyclohexane feed in the presence of minor portions cycloalkanes other than methylcyclohexane in an oxidation zone with air added to said zone at a rate equivalent to about 0.1 to about 0.15 mol oxygen per mol of methylcyclohexane feed, maintaining said oxidation zone at a temperature of about 155° to about 180° C. and under a pressure of about 50 to about 1000 pounds per square inch gage, adjusting the rate of flow of hydrocarbon feed to said oxidation zone to be such that the residence time of said feed in said oxidation zone is about 15 to about 5 minutes whereby the effluent products from said zone are substantially free of unreacted oxygen; passing said effluent products from said oxidation zone to a deperoxidization zone, maintaining a substantial excess of unreacted methylcyclohexane in said deperoxidization zone whereby a methylcyclohexane hydroperoxide produced in said oxidation zone is reacted with a portion of said excess methylcyclohexane, maintaining said deperoxidization zone at a temperature of about 175° to about 205° C. and under a pressure of about 100 to about 500 pounds per square inch, adjusting the rate of flow of feed to said deperoxidization zone to be such that the residence time of said feed in said zone is about 60 to about 20 minutes whereby the methylcyclohexane hydroperoxide is substantially converted to the desired product without any substantial concomitant production of tars and without incurring any risk of explosive concentrations of said hydroperoxide.

9. A two-step process for producing principally 3-methylcyclohexanol to the substantial exclusion of 1-methylcyclohexanol which comprises oxidizing methylcyclohexane feed in an oxidation zone with an oxygen-containing medium added to said zone at a rate equivalent to about 0.05 to about 0.2 mol oxygen per mol of methylcyclohexane feed, maintaining said oxidation zone at a temperature of about 150° to about 210° C. and under a pressure sufficient to maintain liquid phase conditions in said oxidation reactor, adjusting the rate of flow of hydrocarbon feed to said oxidation zone to be such that the residence time of said feed in said oxidation zone is about 50 to about 3 minutes whereby the liquid effluent products from said zone are substantially free of unreacted oxygen; passing all of said effluent liquid products from said oxidation zone to a deperoxidization zone whereby a methylcyclohexane hydroperoxide produced in said oxidation zone is reacted with a portion of the unreacted

methylcyclohexane from said oxidation zone, maintaining said deperoxidization zone at a temperature of about 160° to about 260° C. and under a pressure sufficient to maintain liquid phase conditions in said deperoxidization zone, adjusting the rate of flow of feed to said deperoxidization zone to be such that the residence time of said feed in said zone is about 200 to about 10 minutes whereby the methylcyclohexane hydroperoxide is substantially converted to the desired product without any substantial production of tars and without incurring the risk of explosive concentrations of said hydroperoxide.

10. A process for producing a cycloalkanol which comprises partially oxidizing a cycloalkane in an oxidation zone with an oxygen-containing gas added to said oxidation zone at a rate in the range 0.05 to 0.2 mole of oxygen per mole of cycloalkane, maintaining said oxidation zone at a temperature in the range 150 to 210° C. and a pressure sufficient to maintain said cycloalkane substantially in the liquid phase, maintaining a residence time of cycloalkane in said oxidation zone in the range 3 to 50 minutes; passing effluent products containing a cycloalkane hydroperoxide and a stoichiometric excess of unreacted cycloalkane from said oxidation zone to a deperoxidization zone, maintaining said deperoxidization zone at a temperature in the range 160 to 260° C. and a pressure in the range 50 to 1000 p. s. i., maintaining a residence time of said effluent products in said deperoxidization zone in the range 10 to 200 minutes, and recovering a cycloalkanol as a product of the process.

11. The process of claim 10 wherein the cycloalkane is an alkyl cycloalkane whereby a secondary alkyl cycloalkanol is preferentially produced with respect to tertiary alkyl cycloalkanol.

12. The process of claim 10 wherein the cycloalkane is methylcyclohexane whereby 3-methylcyclohexanol is preferentially produced with respect to 1-methylcyclohexanol.

13. The process of claim 10 wherein the cycloalkane is cyclohexane.

14. A process for producing methylcyclohexane hydroperoxide which comprises oxidizing a methylcyclohexane feed in the presence of minor portions of cycloalkanes other than methylcyclohexane in an oxidation zone with air added to said zone at a rate equivalent to about one-tenth mol oxygen per mol of methylcyclohexane feed, maintaining said oxidation zone at a temperature of 170° to 174° C. and under a pressure of about 500 pounds per square inch gage, adjusting the rate of flow of hydrocarbon feed to said oxidation zone to be such that the residence time of said feed in said zone is about 7 minutes whereby the desired hydroperoxide is produced.

15. A process for producing methylcyclohexane hydroperoxide which comprises oxidizing a methylcyclohexane feed in an oxidation zone with an oxygen-containing medium added to said zone at a rate equivalent to about 0.05 to about 0.2 mol oxygen per mol of methylcyclohexane feed, maintaining said oxidation zone at a temperature of 150° to about 210° C. and under a pressure sufficient to maintain liquid phase conditions in said zone adjusting the rate of flow of hydrocarbon feed to said oxidation zone to be such that the residence time of said feed in said zone is about 50 to about 3 minutes whereby the desired hydroperoxide is produced.

16. A process for concomitantly producing a secondary cycloalkanol and cycloalkanone and separating an aromatic hydrocarbon from a cycloalkane hydrocarbon which comprises passing a feedstock comprising a mixture of said aromatic and said cycloalkane hydrocarbons to an oxidation zone, oxidizing said feedstock with air added to said zone at a rate equivalent to 0.05 to 0.2 mol oxygen per mol of cycloalkane in said feedstock, maintaining said oxidation zone at a temperature between 150° and 210° C. and under a pressure sufficient to maintain liquid phase conditions in said oxidation reactor, adjusting the rate of flow of hydrocarbon feedstock to said oxidation zone to be such that the residence time of said feedstock in said oxidation zone is from 50 to 3 minutes whereby the liquid effluent products from said zone are free of unreacted oxygen; passing said effluent liquid products from said oxidation zone to a deperoxidization zone wherein a cycloalkane hydroperoxide produced in said oxidation zone is reacted with a stoichiometric excess of unreacted cycloalkane from said oxidation zone, maintaining said deperoxidization zone at a temperature between 160° and 260° C. and under a pressure sufficient to maintain liquid phase conditions in said deperoxidization zone, adjusting the rate of flow of feed to said deperoxidization zone to be such that the residence time of said feed in said zone is 200 to 10 minutes; passing the resulting oxidized and deperoxidized effluent from said deperoxidization zone to a fractional distillation zone, removing substantially pure cycloalkane, said aromatic hydrocarbon and the oxygenated products as separate products of the process.

17. The process of claim 16 wherein the said cycloalkane is methylcyclohexane and the said aromatic hydrocarbon is toluene.

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