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PRODUCTION OF TRIALKOXYBOROXINE

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This invention relates to the production of alcohols by the controlled oxidation of paraffins. More particularly, this invention is concerned with the production of secondary alcohols by the controlled reaction of paraffins with an oxygen-containing gas in the presence of certain oxyboron compounds.

Oxidation of organic compounds with the aid of a variety of oxyboron compounds has been accomplished. The oxidation of aliphatic hydrocarbons to secondary alkyl borate esters with oxygen in the presence of boric oxide or boric acid is known (see, for example, T. Hellthaler et al., German Patent 552,886, Apr. 19, 1934). The borate esters can be hydrolyzed to yield corresponding secondary alcohols. Saturated hydrocarbons can also be converted to alcohols by reaction with oxygen and borate esters or esters of boronic and borinic acids (see, for example, Netherlands application 64—9,181, Feb. 22, 1965). Similarly oxidation in the presence of metaboric acid is known (see, for example, S. N. Fox et al., U.S. 3,109,864, Nov. 5, 1963). These processes suffer from disadvantages which make the oxidation process inefficient and economically undesirable. Certain of the aforementioned oxyboron compounds are solids, thereby creating handling and solubility problems, particularly in multistage continuous processing; some yield "glassing" at high temperatures. In the prior art processes the protective reaction of the oxyboron compound for achieving alcohol production is slow. Therefore, the oxidation reaction rate must be kept low in order to attain highest selectivity to the production of alcohol over other oxidation products, thereby diminishing the commercial feasibility and utility of the prior art processes.

It is, therefore, a principal object of the present invention to provide a rapid, efficient, and improved process for the controlled and continuous oxidation of paraffins. A further object of the invention is to provide an improvide process for the production of predominantly secondary alcohols by carrying out the controlled oxidation of paraffins in the presence of certain boron compounds.

These objects will be better understood and others will be apparent from the description of the invention as given hereinafter.

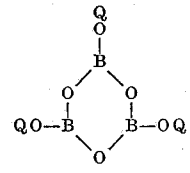
Now, in accordance with this invention, it has been found that aliphatic secondary alcohols are prepared, preferentially over ketones, by contacting a paraffin in liquid phase at a temperature within the range of about 100° to about 300° C. with an oxygen-containing gas and carrying out the controlled oxidation of said paraffin in the presence of trialkoxyboroxine containing alkoxy of 4 or more carbon atoms to form from said paraffin secondary alcohols and their boron esters, followed by recovery of the secondary alcohols with means which provide for hydrolysis of the corresponding secondary alkyl borate ester.

The paraffins useful in the process of this invention are saturated aliphatic hydrocarbons of from 6 to 40 carbon atoms which can be normal or branched but preferably acyclic and essentially free of aromatics. Satisfactory results are obtained especially with paraffin designated R–H where R is an aliphatic hydrocarbyl of 8 to 30 carbons and preferably of 10 to 20 carbons, especially alkyl of 10 to 20 carbons. Representative examples of suitable hydrocarbons include n-hexane, n-octane, 2-ethylhexane, n-nonane, n-dodecane, n-tetradecane, eicosane, hexacosane, triacontane, and the like, including their mixtures.

The paraffin is oxidized in liquid phase with molecular oxygen, the controlled oxidation being carried out in the presence of trialkoxyboroxine and in the optional presence of a polyvalent heavy metal catalyst.

The source of molecular oxygen is any oxygen-containing gas as, for example, air or oxygen diluted to any desired extent with an inert gas such as nitrogen, methane, carbon dioxide, and the like.

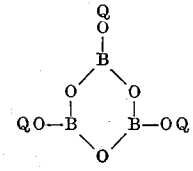
The trialkoxyboroxines useful in the process are those containing alkoxy of 4 or more carbon atoms. Especially preferred are those containing from 4 to 10 carbon atoms in each alkoxy, wherein the alkoxy contains at least 2 less carbons than the paraffin to be oxidized, with the proviso that the alkoxy contains at least 4 less carbons than the paraffin to be oxidized when the paraffin is of at least 10 carbon atoms. They may be represented as



or $(QOBO)_3$ where Q is appropriate alkyl.

The trialkoxyboroxines are particularly advantageous in that their selectivity to the production of desired secondary alcohol is high, accompanied by a low selectivity to production of ketone, as compared to the poorer selectivity to alcohol, accompanied by high selectivity to ketone, obtained with the aforementioned prior art oxyboron compounds. In continuous operation, for example, the alkyl ortho borates of the prior art yield higher ketone and lower alcohol selectivity for the same reaction rate. A further advantage of trialkoxyboroxines is that only one Q radical per boron atom is exposed to oxidative attack during the process as compared to three Q radicals per boron atom for the alkyl ortho borates. The net result is that oxidative losses of Q are much lower in the process of the invention. Another advantage in the use of trialkoxyboroxines is their wide range of solubility in paraffin. Representative useful trialkoxyboroxines include tri(n-butoxy)boroxine, tri(isobutoxy)-boroxine, tri(sec-butoxy)boroxine, tri(n-heptoxy)-boroxine, tri(2-ethylhexoxy)boroxine, tri(n-nonoxy)-boroxine, tri(decoxy)boroxine, and the like. The preparation of trialkoxyboroxines are well summarized in H. Steinberg, "Organoboron Chemistry," vol. 1, 445–454, Interscience Publishers (Wiley), New York, 1964.

For each molecule of secondary alcohol (ROH) produced by the oxidation reaction, a molecule of the lower boiling alkanol (QOH) is liberated from the trialkoxyboroxine.



By selecting a trialkoxyboroxine of alkoxy at least 2 to 4 less carbons than the paraffin to be oxidized as described hereinabove, it is comparatively easy to conduct the oxidation under conditions of temperature and pressure at which the liberated lower alkanol (QOH) is rapidly stripped into the reactor off-gas. This rapid removal of the lower boiling alkanol assures that it will not

remain in solution in the reactor and be subjected to degradation by oxidation. Conversely, the trialkoxyboroxine must have alkoxy of long enough carbon chain, i.e., at least 4, so that the trialkoxyboroxine is sufficiently high boiling to remain in the reaction system and not be stripped therefrom during reaction. Hence, a lower limit of 4 carbons for the alkoxy of the trialkoxyboroxine is essential. The alkoxy carbon content will preferably be as low as possible consistent with the aforesaid requirements so that there will be the fewest carbon atoms per boron atom exposed to oxidative attack, thereby lowering the oxidative losses of Q.

In general, it is desirable to provide at least one gram atom of boron in the form of trialkoxyboroxine for each mol of paraffin being oxidized. However, greater or lesser amounts may be utilized if desired. A suitable range may include, for example, the use of about 0.1 to about 1.5 mols of trialkoxyboroxine per mol of paraffin being oxidized. A preferred range includes the use of about 0.2 to about 0.7 mol of trialkoxyboroxine per mol of paraffin being oxidized.

A polyvalent heavy metal compound catalyst which is soluble in the reaction mixture may optionally be employed in a catalytically effective amount. Thus, for example, soluble salts of cobalt, manganese, lead, iron, and the like, may be used in the form of acetate, octoate, stearate, and the like. Preferred compounds include those such as cobalt octoate, cobalt stearate, and the like. The amount of such additional reagent may be such that the reaction mixture contains from about 0.001 to 0.2% by weight (based on total weight of paraffin to be oxidized) of solubilized polyvalent heavy metal.

The controlled oxidation and concomitant esterification are conducted at a temperature within the range of about 100° to about 300° C. at a pressure sufficient to prevent excessive loss of paraffin with the exit gas. Pressures within the range of about 15 to about 1000 p.s.i.g. can be employed. A preferred temperature range is from about 150° to about 190° C.

At the completion of the controlled oxidation, unconverted paraffin and ketone by-product are removed from the mixture by any suitable means, for example, by vacuum flashing. The remaining product is a boron ester complex of the alkoxyboroxine and a secondary alcohol, from which the desired secondary alcohol is recovered by subsequent hydrolysis. Although any suitable hydrolyzing agent well known to the art may be used, the preferred agent is water. The hydrolysis is accomplished conveniently by adding water to the ester complex at a temperature sufficient to maintain a liquid medium. The complex is substantially hydrolyzed thereby to produce secondary alcohol, lower alkanol derived from the alkoxy of trialkoxyboroxine, and aqueous boric acid. These products may then be resolved by any suitable method, for example, distillation, phase separation, fractional crystallization, or a combination thereof, in order to recover the desired secondary alcohol. A preferred mode of operation encompasses separating the boric acid in aqueous phase and vacuum distilling the nonaqueous phase to obtain secondary alcohol free of lower alkanols, i.e. the light ends, and diol impurities arising in the oxidation, i.e. the heavy ends. The secondary alcohol may be hydrogenated to reduce any carbonyl and unsaturation content.

In order to improve the over-all efficiency of the process, the separated mixture of unconverted paraffin and ketone by-product may be hydrogenated to convert the ketone to paraffin or alcohol and the resulting material recycled to the oxidation reactor. Alternatively, the ketone may be removed by adsorption, for example, on alumina.

The aqueous boric acid from the hydrolysis of the boron ester complex is reconverted to trialkoxyboroxine for reuse in the process. Continuous operation can be achieved therein by a novel regeneration method. In this method, hot aqueous boric acid from the hydrolysis is mixed with normally liquid, water-insoluble alkanol of at least 4 carbon atoms such that the alkanol to boron mole ratio is about 4 and the resulting mixture is fed to a continuous esterification column which yields trialkyl ortho borate plus a slight excess of alkanol as bottoms and an alkanol-water azeotrope as overhead. From an overhead phase-splitter, alkanol is returned to the column while water, saturated with alkanol, goes back to the hydrolyzer of the initial system—possibly after alkanol recovery. Trialkyl ortho borate from the column is partially hydrolyzed to trialkoxyboroxine:

$$3B(OQ)_3+3H_2O\rightarrow(OBOQ)_3+6QOH$$

where Q is alkyl or 4 or more carbon atoms. This partial hydrolysis is smoothly achieved, contrary to the teachings in the prior art (see, for example, M. F. Lappert, J. Chem. Soc. 1958, 2790), at elevated temperatures, at about 130 to about 225° C. and preferably at about 150–160° C., under a partial pressure of water vapor no higher than 250 mm. Hg. These conditions are conveniently achieved, for example, by passing either water-containing nitrogen or steam under reduced pressure through the liquid trialkyl ortho borate. Overheaded alkanol is recycled to the esterification column. Too low a temperature or too high a partial pressure of water at this step in the method leads to the highly undesirable precipitation of boric acid. There is no real lower limit for the partial pressure of water. From a practical standpoint though, the lower the partial pressure the slower the regeneration of trialkoxyboroxine. Hence, a preferred range of partial pressure of water vapor is from about 150 to about 200 mm. Hg. It is possible to use the oxidation reactor off-gas, if necessary admixed with steam, to carry out this partial hydrolysis step.

The partial hydrolysis to the alkoxyboroxine may be carried out after addition of paraffin to the trialkyl ortho borate in continuous production. The paraffin is preferably that which is to be oxidized, thereby providing a paraffin solution of the alkoxyboroxine which can be fed directly to the oxidation zone. The partial hydrolysis is preferably carried to about 90% conversion rather than to completion because overshooting may result in formation of excessively viscous, gel-like, highly condensed polyborates, which are undesirable for the process of this invention. Preferred trialkoxyboroxines to be used in such a continuous regeneration cycle are tri(n-butoxy) boroxine, tri(iso-butoxy)boroxine, or tri(sec-butoxy) boroxine because of the relative volatilities of the various components of the system. Additionally, these butyl oxyboron compounds yield a more favorable alkanol/water azeotrope, i.e. butanol/water.

As an alternative to the production of trialkoxyboroxine for recycle by the partial hydrolysis of trialkyl ortho borate, trialkoxyboroxine can be prepared in one step by feeding alkanol and boric acid in a ratio of from 1:1 to 1.2:1 to the esterification column and operating with alkanol reflux high enough to prevent crystallization of boric acid in the column.

The following specific examples of the invention will serve to illustrate more clearly the application of the invention, but the details thereof are not to be construed as limiting the invention.

Example I

n-Dodecane is contacted with 20% oleum at ambient temperature to remove aromatic components. Following the acid treatment, the n-dodecane is charged to a stainless-steel oxidation reactor vessel containing the trialkoxyboroxine indicated in Table 1 below. To the well-agitated reactor vessel, equipped with a reflux condenser, is passed a N_2/O_2 mixture containing 10% by vol. of oxygen. The mixture is heated to temperature indicated below for 4 hours. The heat of reaction is removed by boiling water in internal coils. Unreacted n-dodecane and by-product ketone are removed from the resulting

boron esters of secondary C_{12} alcohol by flashing at about 171° C., in two stages, one at 25 mm. Hg and the other at 8 mm. Hg. The boron esters of secondary alcohol are then hydrolyzed with water at 121° C. A rotating disk contactor (see G. T. Reman, U.S. 2,601,674, June 24, 1952) is used to provide the necessary staging for essentially complete hydrolysis. Hydrolyzer products are crude secondary alcohols, lower alkanols corresponding to the alkoxy of trialkoxyboroxine, and approximately 20% by wt. aqueous boric acid. The aqueous and nonaqueous phases are separated. The nonaqueous phase containing the secondary alcohol and lower alkanols is treated with KOH for ester removal and then distilled to remove the lower alkanols and heavy ends. The heavy ends are mainly diols. The results are shown in Table 1.

TABLE 1

Dodecane Charge, g	120	560
Temperature, ° C	182	182
Trialkoxyboroxine	(a)	(b)
Amount of Trialkoxyboroxine, g	12	56
Dodecane Conversion, percent	16.1	14.2
Selectivity, percent:		
C_{12} Alcohol	91	84
C_{12} Ketone	6	4

[a] $(n\text{-}C_4H_9OBO)_3$ [b] $(i\text{-}C_4H_9OBO)_3$

Example II

In a manner similar to Example I, n-dodecane was oxidized in the presence of tributoxyboroxine and cobalt octoate. The results are summarized in Table 2.

TABLE 2

Conditions: 10.5% O_2 in N_2 at 4200 cc./min., 180° C.	
Tributoxyboroxine, atoms B/mole $C_{12}H_{26}$	0.26
Cobalt octoate, percent wt. as Co	0.006
Dodecane conversion rate, percent/hr.	11
Dodecane conversion, percent	16
Selectivity, percent:	
Alcohol	80
Ketone	9.5

Example III

In a manner similar to Example I, n-dodecane was oxidized in a glass oxidation reactor vessel in the presence of tri(isobutyl) ortho borate and tri(isobutoxy)boroxine, respectively, to approximately the same dodecane conversion level. The comparative results are summarized in Table 3.

TABLE 3

Dodecane Conversion, percent	11	13
Temperature, ° C	165	165
Oxyboron Compound (B)	(a)	(b)
Amount B, percent wt. of boron (based on wt. of dodecane)	1.1	1.1
Wt. Ratio of C_{12} Alcohol/C_{12} Ketone	3.7	12.0

[a] Tri(isobutyl) ortho borate. [b] Tri(isobutoxy)boroxine.

These results demonstrate that the trialkoxyboroxine of the invention yields the desired high selectivity to alcohol and low selectivity to ketone compared to the alkyl ortho borate of the prior art, which yields poorer selectivity to alcohol and higher selectivity to ketone.

Example IV

n-Dodecane is passed through a continuous reaction cycle and oxidized in the presence of tri(n-butoxy) boroxine to yield dodecyl alcohols in the following manner:

n-Dodecane containing 10% by weight of tri(n-butoxy) boroxine is pumped at a rate of 500 ml. per hour through a continuous oxidation reactor consisting of four well-stirred stages, each of 500 ml. of volume, arranged in series with respect to liquid flow and in parallel with respect to gas flow. As oxidizing gas, nitrogen containing 10% by volume of oxygen, is sparged into each stage at a rate of 220 ml. per minute (STP). The reactor temperature is maintained at 170° C. and the pressure, atmospheric. Of the n-dodecane passed through the reactor, 19.5% is oxidized, and 74.5% of the oxidation products

are dodecyl alcohols, in the form of their borate esters. The exit gas from the reactor is cooled to condense water and n-butanol, which are charged to the esterification column described below. n-Butanol recovery by this condensation is 650 g. per 1000 g. of tri(n-butoxy) boroxine charged to the reactor. The dodecyl alcohols are recovered as their crude borate esters after unreacted dodecane and by-product ketone have been overheaded in a continuous cyclone flasher. Ketone is removed from the dodecane by adsorption on alumina and the purified dodecane is returned to the reactor.

The flasher bottoms are hydrolyzed by a countercurrent stream of water under pressure at 120° C., giving quantitative yield of crude free dodecyl alcohols together with some n-butanol and an aqueous solution of boric acid. Subsequent purification results in 730 g. of dodecyl alcohols per 1000 g. of dodecane reacted. The aqueous boric acid solution, the condensate from the reactor exit gas, and sufficient n-butanol to supply a molar ratio of butanol to boric acid of 4:1 are fed to the 20th plate of a 25-plate Oldershaw (esterification) column. The thermosyphon reboiler at the base of the column has previously been charged with n-butanol and tri(n-butyl) ortho borate in a 1:1 ratio to furnish synthetic bottoms and is heated to about 150° C. Reaction on the plates of the column forms tri(n-butyl) ortho borate, which is then bled from the thermosyphon reboiler; water/butanol being azeotroped overhead, and the butanol returned as reflux after phase separation from the water. The water from the phase separator, being saturated with n-butanol, is returned to the hydrolyzer. A 95.1% yield of tri(n-butyl) ortho borate is obtained by this step.

Tri(n-butoxy)boroxine is produced from the above tri (n-butyl) ortho borate by controlled and partial hydrolysis with nitrogen, at atmospheric pressure, containing water vapor at 150 mm. Hg. The tri(n-butyl) ortho borate is fed into a hydrolyzer, heated to 155° C., and sparged with the wet nitrogen passed at the rate of 180 ml. per min. per 100 g. of tri(n-butyl) ortho borate. This step results in 89% conversion to tri(n-butoxy)boroxine in about 5 hours, and a comparable amount of n-butanol is overheaded. This butanol is used as feed for the above esterification column. The losses of n-butanol per pass through the reactor, replaced by make-up in the feed to the esterification column, average 8% of the butanol charged as butoxy in tri(n-butoxy)boroxine. The tri(n-butoxy)boroxine produced in this partial hydrolysis is recycled to the oxidation reactor for utilization to complete the reaction cycle.

We claim as our invention:

1. The process of producing trialkoxyboroxine containing alkoxy radicals of at least 4 carbon atoms by partially hydrolyzing trialkyl ortho borate ester, wherein the alkyl is of at least 4 carbon atoms, in liquid phase at about 130 to about 225° C. in the presence of water vapor at a partial pressure no gerater than 250 mm. Hg.

2. The process of producing a paraffin solution of trialkoxyboroxine by partially hydrolyzing trialkyl ortho borate ester in paraffin solution, wherein the alkyl is of at least 4 carbon atoms and the paraffin is of from 6 to 40 carbon atoms, at about 130 to about 225° C. in the presence of water vapor at a partial pressure no greater than 250 mm. Hg.

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