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DECOMPOSING THE PEROXIDE IN THE OXIDATE RESULTING FROM THE OXIDATION OF α,β UNSATURATED ALDEHYDES TO THE ACIDS

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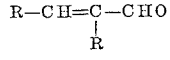
This invention relates to an improved process for the production of polymerizable unsaturated aliphatic acids. More particularly, it relates to an improved method for the recovery of unsaturated acids by the processing of liquid oxidates containing unreacted feed and peroxides.

When unsaturated aliphatic aldehydes are oxidized in the liquid phase with molecular oxygen a mixture of products is obtained in the oxidate. The oxidate contains the unreacted aldehydes, the corresponding acid product, and various peroxides of unsaturated acids and aldehydes. Previous attempts to obtain high yields of the unsaturated acids from the oxidate have resulted in the formation of large percentages of polymer rather than predominantly the unsaturated acid.

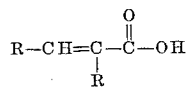
According to this invention a method has been discovered for recovering large percentages of the unsaturated acid with only small amounts of polymer formation. In its broadest aspects the invention comprises a process for combining the oxidate with a solvent which is at a temperature higher than the boiling point of the unreacted unsaturated aldehyde present in the oxidate, whereby the aldehyde is distilled off and whereby simultaneously the peroxides are decomposed to the acids.

The oxidate which is treated according to this invention may be prepared by the oxidation in the liquid phase of an ethylenically unsaturated aliphatic aldehyde. Any method for the preparation of the oxidate may be employed which results in a liquid phase containing relatively high amounts of the peroxides of mono-ethylenically unsaturated aliphatic aldehydes and acids together with mono-ethylenically unsaturated aldehydes.

Useful feed materials are compounds of the general formula



wherein R is either hydrogen or a lower alkyl group. The alkyl group may contain, for example, from one to four carbon atoms. The preferred feed materials are methacrolein and acrolein. Mixtures of feed materials may be used. Some of the corresponding acids of the formula



are produced as such.

The oxidation is preferably carried out on the feed material in bulk, that is, with essentially no diluent or solvent present. If any solvent or diluent is used, it should be essentially inert to the oxidation under the defined reaction conditions. The solvents or diluents, if any, which may be used include saturated acids such as formic acid and acetic acid; esters such as methyl acetate and ethyl acetate; aliphatic or aromatic halides, such as carbon tetrachloride and chlorobenzene; the saturated hydrocarbons such as heptane and nonane; petroleum hydrocarbon fractions such as petroleum naphtha or gasoline; and aromatic hydrocarbons such as benzene or xylene. The solution to be oxidized will preferably contain at least 75 weight percent of aldehyde and more preferably will contain at least 90 weight percent of the aldehyde. The best results were obtained by oxidizing the aldehyde in bulk.

While the oxidation reaction may be conducted without the addition of a catalyst, the rate of reaction may be increased by the use of light or by the use of an oxidation catalyst. These catalysts may be finely divided polyvalent metals which have an atomic number of about 22 to about 82. Compounds of metals are also useful, including the oxides, and the inorganic or organic salts. Examples of the types of catalyst that may be employed are the metals such as cobalt, vanadium, cerium, copper, manganese, silver and uranium and the combination of these metals with organic, nitric or phosphoric acids. Particularly desirable as catalysts are the halides of the metals such as the chlorides. Specific examples of useful compounds are cobaltic acetylacetonate, cobalt naphthenate, cobaltous acetate, magnesium oxide, manganese acetate, manganese chloride, barium acetate and barium butyrate. The preferred catalysts are cobalt, manganese and nickel salts, including cobaltic acetylacetonate, cobalt naphthenate, cobaltous acetate, manganese oleate and nickel oleate. Mixtures of catalysts may be used.

Oxygen may be added either as pure oxygen or as oxygen diluted with inert diluents such as nitrogen or helium. Either air or air enriched with oxygen may be used under certain conditions. Preferably the gaseous mixture should contain at least 70 mols percent of molecular oxygen and more desirably the gas should contain at least 95 mol percent molecular oxygen. Best results were obtained when essentially no diluent was used with the oxygen. The oxygen may be contacted with the reaction mixture by admixture with the aldehyde or olefin in any convenient manner. The oxygen may simply be bubbled through the reaction mass, or equipment particularly adapted to gas-liquid mixing may be used. Mixers such as bubble towers, turbo-absorbers, jets, scrubbers, and devices for re-circulating through towers or nozzles are useful. Generally, the reaction mass should be agitated by mechanical stirrers or other means. The oxidation may be conducted either batch-wise or continuously. The gas and liquid flow may be in the same direction or counter-current. The reaction may be conducted at any desirable temperature, but better results have been observed when temperatures of about —10° C. to 50° C. are used. The preferred range is from about 0° C. to 35° C. Temperatures in excess of 50° C. should be avoided as lower yields of the unsaturated acid are obtained at higher temperatures.

The oxidations may be conducted in the liquid phase at either subatmospheric, atmospheric or superatmospheric pressure. When more volatile aldehydes are employed as the feed, it may be desirable to use pressure higher than atmospheric to avoid loss of feed material through vaporization. Atmospheric pressure may be used, although higher conversions sometimes are achieved at higher pressures. Pressures from about atmospheric to 50 p.s.i.g. are preferred.

The oxidate contains a mixture of unsaturated acids, acid peroxides, aldehyde peroxides and aldehydes. For example, when methacrolein is oxidized, the oxidate will contain some methacrolein peroxide, some permethacrylic acid, and some methacrylic acid.

The oxidate will generally contain from about 30 to 70 weight percent of unreacted feed and from about 90 to 30 weight percent of reaction products such as unsaturated acid product and the peroxides, based on the total weight of the oxidate. The various peroxides generally will be present from about 20 to 80 weight percent of the total weight of the oxidate. According to this invention, the desired unsaturated acid product may be recovered from the oxidate by feeding the oxidate into a liquid which is maintained at a temperature higher than the boiling point of the unreacted unsaturated aldehyde

present in the oxidate. Upon contact of the oxidate with the hot liquid, the aldehyde and other low boiling products will be distilled off and may be taken off overhead. The remainder of the oxidate is retained in the liquid body into which it is fed. The process may be operated continuously by continuously feeding the various ingredients and continuously distilling off the lower boiling point materials. The peroxides present in the oxidate decompose to the acid product. By this process very little polymer is formed.

The hot liquid into which the oxidate is fed should preferably be a solvent for both the peroxides and for any polymer which is formed. Use of non-solvents should be avoided as the precipitation of explosive peroxides may result. Any solvent which does not react with the oxidate and does not precipitate the explosive peroxides will be satisfactory, with the limitation that the boiling point of the solvent is higher than that of the unreacted aldehydes which boil off. Preferably, the solvent will not precipitate any of the polymer. The solvent may have a boiling point either higher or lower than the unsaturated acid produced, but a solvent with a higher boiling point is preferable. Suitable solvents are the alcohols such as ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, ethyleneglycol, diethyleneglycol and cyclohexanol; heterocyclic solvents such as 1,4 dioxan; dimethyl formamide; aliphatic or aromatic halides such as carbon tetrachloride; hydrocarbons such as benzene, the xylenes; water and mixtures of solvents. The lower aliphatic alcohols of from one to six carbon atoms have given good results. If a solvent is already present in the oxidate, the same solvent may be used as the liquid into which the oxidate is fed, provided the enumerated requirements for the solvent used in the acid recovery are met. The amount of solvent present is normally at least about 0.75 part of solvent per part of the dissolved oxidate. Best results are obtained when the solvent is present in an amount from about 1.0 to 3.0 parts per part of the oxidate. Of course, when the oxidate is first being fed into the solvent, the ratio of solvent to oxidate will be high.

Although lower amounts of polymer formation result from the process steps of this invention, it is generally desirable to have present a polymerization inhibitor. Suitable polymerization inhibitors are compounds such as those containing aromatic nucleus as hydroquinone, pyrogallol, phloroglucinol, p-methoxyphenol, cresol, resorcinol and phenol. Mixtures of inhibitors may be used. The weight of polymerization inhibitor should be between about 0.01 and 1.0 weight percent of the oxidate and normally will be between 0.02 and 0.10 weight percent of the oxidate.

The oxidate should preferably be combined with the hot solvent in such a manner that the concentration of the ethylenically unsaturated acid does not exceed about 60 weight percent of the total weight of the solution and generally does not exceed 40 weight percent. The concentration of acid may be maintained by stopping the process when the concentration of acid has reached the desired point or by continuously distilling off the acid. Best results have been obtained when the oxidate has been combined with the solvent at a rate of about 0.10 to 3.0 parts by volume of oxidate per part by volume of solvent per hour. Generally the rate of combination is about 0.20 to 1.0 part by volume of oxidate per parts by volume of solvent per hour.

As one feautre of this invention it has been found that if a highly ionized strong acid is present in the hot solvent into which the oxidate is combined that higher yields of monomeric unsaturated acid are obtained. This result is unexpected as it might have been expected that a strong acid would have catalyzed the formation of polymer. Acids with an ionization constant (Ka) of 1×10^{-3} or greater when measured in a .1 N solution in water at 25° C. have given good results. The preferred acids have an ionization constant of 1×10^{-2} or greater. Acids such as perchlorous, perchloric, p-toluene sulfonic, benzene sulfonic, sulfuric, hydrochloric, p-azo benzene sulfonic and nitric may advantageously be used. Acidic or acid impregnated ion exchange resins may also be used. The acid catalyst should be present from about .01 to .25 weight percent based on the final weight of the solvent. Better results were obtained when the acid was present at a concentration of from about .05 to 0.20 weight percent of the solvent.

The process of this invention for the peroxide decomposition and the simultaneous distillation of the unreacted feed may be conducted at atmospheric, subatmospheric or superatmospheric pressure. However, the best results have been obtained at either atmospheric or subatmospheric pressures. Lower operating temperatures may be utilized if the decomposition is conducted under vacuum. The result of operating at lower temperatures is to further decrease the percentage of polymer formed.

The peroxide decomposition and the simultaneous distillation of the unreacted feed may be operated over a range of temperatures. A critical feature is that the temperature of the solvent for the oxidate must be at a temperature as high as the boiling point of the unreacted feed. Acrolein is the lowest boiling point unreacted aldehyde to be recovered according to this invention. The boiling point of acrolein at atmospheric pressure is 52.5° C. Therefore, the temperature of the solvent must be at least equivalent to 52.5° C. at atmospheric pressure. At reduced pressures, this figure of 52.5° C. will be correspondingly adjusted to the boiling point of acrolein at the reduced pressure. At superatmospheric pressures the minimum temperature will be adjusted upward in like manner. Of course, lower boiling degradation by-products of the oxidation will also be distilled off together with the unreacted feed. The preferred temperatures of decomposition and distillation are at the reflux temperatures of the solution of oxidate in the solvent.

The vaporous mixture of unreated feed and oxidation by-products which distills off from the solution of oxidate may be separated as by fractional distillation or equivalent means as the mixture is distilled from the solvent. The separated unreacted feed may be returned as feed to the oxidation reactor.

The unsaturated aliphatic acid product may be recovered from the solvent in any conventional manner as by extraction or distillation. If the solvent has a boiling point higher than the acid, the acid may simply be distilled off overhead at the completion of the peroxide decomposition process. If a continuous process is employed, the acid may be continuously distilled off either from the same vessel wherein the peroxide decomposition is taking place or else from a second vessel into which the solution is continuously fed. In batch operations the solution of oxidate from which the unreacted feed has been distilled is generally refluxed for a period of about ⅓ to 3 hours to insure the complete decompostion of the peroxides before the final distillation to separate the acid product. When the solvent for the acid has a lower boiling point than the acid, the solvent may be distilled off, for example, at atmospheric pressure followed by the distillation of the acid under reduced pressures of less than 400 mm. of Hg and generally less than 50 mm. of Hg.

The product acids such as methacrylic acid and acrylic acid have many well known commercial uses such as monomers and comonomers for synthetic resins.

Example 1

200 ml. of freshly distilled methacrolein and 0.1 wt. percent of iodine is charged to a 500 ml. three-necked reaction flask. The flask is fitted with a gas inlet tube, reflux condenser, thermometer, high speed magnetic stirrer and stirring bar. Agitation is begun and the temperature

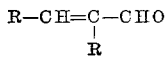
maintained at 15° C. by circulating water from a constant temperature bath through the water jacket of the reactor. Oxygen, measured by a wet test meter in the inlet system, is admitted to the reaction so as to maintain an off gas flow of 10 to 15 ml. per minute. The off gas is passed through a dry ice trap to collect all condensables present and then flow through an ascarite trap for removal of carbon dioxide, a second wet test meter and finally a rotometer for regulation of off gas flow. The dark yellow brown color imparted to the solution by the iodine gradually lightens in intensity during an induction period of about 140 minutes. The oxidation proceeds smoothly and is terminated after approximately 0.25 mole of oxygen has been absorbed per mole of aldehyde charged; this represents 50% of the theoretical oxygen. This takes 20 hours and gives an aldehyde conversion of 22.4% as shown by gas chromatography. The product contains peroxide by iodimetric titration (77.6% yield on methacrolein consumed) and free methacrylic acid. According to this invention, the methacrylic acid was recovered by feeding the reaction product into a 100 ml. three neck flask containing 75 ml. of absolute ethyl alcohol and 0.1 g. of para-toluene sulfonic acid and 0.01 g. hydroquinone. The flask was fitted with a micro Vigreaux column, about 8 inches long and 1 inch wide, and a micro distillation head capable of total reflux. A dropping funnel containing 50 ml. of the reaction product was fitted to the other neck. The alcohol was heated to reflux with a flask temperature of 78° C. The reaction product was added dropwise to the refluxing alcohol over a two-hour period. During this addition methacrolein is recovered overhead along with some alcohol. Upon the completion of this addition the reaction mixture is refluxed for 1 hour to insure complete peroxide decomposition. The distillation is then continued at atmospheric pressure to recover the alcohol and completed under reduced pressure, 5 mm. of Hg, to recover the methacrylic acid. The individual fractions obtained were analyzed by gas chromatography. The yields of ester and free methacrylic acid, based on the amount of aldehyde charged which was consumed in the process, are 4.97% and 91.6% respectively.

Example 2

The experiment in Example 1 was repeated without the use of para-toluene sulfonic acid. The yields of ethyl methacrylate and methacrylic acid obtained are 5.38% and 78.6% respectively.

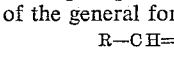
We claim:

1. A process for the preparation of ethylenically unsaturated aliphatic acids which comprises oxidizing with oxygen in the liquid phase a feed material which is a compound of the general formula



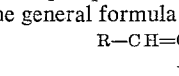
wherein R is selected from the group consisting of hydrogen and a lower alkyl group of 1 to 4 carbon atoms to produce an oxidate containing unreacted feed material and peroxides, feeding said oxidate into a hot liquid solvent for the oxidate, said solvent being at a temperature as high as the boiling point of the said feed material whereby the unreacted feed material of the oxidate is distilled off and whereby the peroxides are decomposed to form the ethylenically unsaturated aliphatic acid, the said oxidate being fed to the said hot liquid solvent whereby the concentration of the said ethylenically unsaturated aliphatic acid does not exceed about 60 weight percent of the total weight of the solution, the said solvent having a boiling point higher than the said unreacted feed material which is boiled off and being present in an amount of at least 0.75 part of solvent per part of the dissolved oxidate.

2. A process for the preparation of ethylenically unsaturated aliphatic acids which comprises oxidizing with oxygen in the liquid phase a feed material which is a compound of the general formula



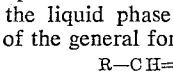
wherein R is selected from the group consisting of hydrogen and a lower alkyl group of 1 to 4 carbon atoms to produce an oxidate containing unreacted feed material and peroxides, feeding said oxidate into a hot liquid solvent for the oxidate, said solvent being at a temperature as high as the boiling point of the said feed material whereby the unreacted feed material of the oxidate is distilled off and whereby the peroxides are decomposed to form the ethylenically unsaturated aliphatic acid, the said oxidate being fed to the said hot liquid solvent whereby the concentration of the said ethylenically unsaturated aliphatic acid does not exceed about 60 weight percent of the total weight of the solution, the said solvent containing from about .01 to .25 weight percent of the solvent of a strong acid catalyst and having a boiling point higher than the said unreacted feed material which is boiled off and being present in an amount of at least 0.75 part of solvent per part of the dissolved oxidate.

3. A process for the preparation of ethylenically unsaturated aliphatic acids which comprises oxidizing with oxygen in the liquid phase a feed material which is a compound of the general formula



wherein R is selected from the group consisting of hydrogen and a lower alkyl group of 1 to 4 carbon atoms to produce an oxidate containing unreacted feed material and peroxides, feeding said oxidate into a hot liquid solvent for the oxidate, said solvent being at a temperature as high as the boiling point of the said feed material whereby the unreacted feed material of the oxidate is distilled off and whereby the peroxides are decomposed to form the ethylenically unsaturated aliphatic acid, the said oxidate being fed to the said hot liquid whereby the concentration of the said ethylenically unsaturated aliphatic acid does not exceed about 60 weight percent of the total weight of the solution, the said solvent containing from about .01 to .25 weight percent of the solvent of a strong acid catalyst having an ionization constant of at least 1×10^{-3} and having a boiling point higher than the said unreacted feed material which is boiled off and being present in an amount of at least 0.75 part of solvent per part of the dissolved oxidate.

4. A process for the preparation of ethylenically unsaturated aliphatic acids which comprises oxidizing with oxygen in the liquid phase a feed material which is a compound of the general formula

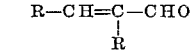


wherein R is selected from the group consisting of hydrogen and a lower alkyl group of 1 to 4 carbon atoms to produce an oxidate containing unreacted feed material and peroxides, feeding said oxidate into a hot liquid solvent for the oxidate selected from the group consisting of ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, ethylene glycol, diethylene glycol, cyclohexanol, 1,4 dioxan, dimethyl formamide, carbon tetrachloride, benzene, xylene, water and mixtures thereof, said solvent being at a temperature as high as the boiling point of the said feed material whereby the unreacted feed material of the oxidate is distilled off and whereby the peroxides are decomposed to form the ethylenically unsaturated aliphatic acid, the said oxidate being fed to the said hot liquid solvent in a manner whereby the concentration of the said ethylenically unsaturated aliphatic acid does not exceed about 60 weight percent of the total weight of the solution, the said solvent having a boiling point higher than the said unreacted feed material which is boiled off and being present in an amount of at least 0.75 part of solvent per part of the dissolved oxidate.

5. A process for the preparation of methacrylic acid which comprises oxidizing methacrolein with oxygen in the liquid phase to produce an oxidate containing unreacted methacrolein and peroxides, feeding said oxidate into a hot aliphatic alcohol solvent for the oxidate, said aliphatic alcohol containing from about .01 to .25 weight percent of the solvent of a strong acid catalyst having an ionization constant of at least 1×10^{-3} and solvent being at a temperature as high as the boiling point of the said feed material whereby the unreacted methacrolein of the oxidate is distilled off and whereby the peroxides are decomposed to form the methacrylic acid, the said oxidate being fed to the said aliphatic alcohol in a manner whereby the concentration of the said methacrylic acid does not exceed about 60 weight percent of the total weight of the solution, the said aliphatic alcohol having a boiling point higher than the said unreacted feed material which is boiled off and being present in an amount of at least 0.75 part of aliphatic alcohol per part of the dissolved oxidate.

6. A process for the preparation of methacrylic acid which comprises oxidizing methacrolein with oxygen in the liquid phase to produce an oxidate containing unreacted methacrolein and peroxides, feeding said oxidate into a hot ethyl alcohol solvent for the oxidate, said ethyl alcohol containing hydroquinone and from .01 to .25 weight percent para-toluene sulfonic acid and being at a temperature as high as the boiling point of the said feed material whereby the unreacted methacrolein of the oxidate is distilled off and whereby the peroxides are decomposed to form the methacrylic acid, the said oxidate being fed to the said hot ethyl alcohol in a manner whereby the concentration of the said methacrylic acid does not exceed about 60 weight percent of the total weight of the solution, the said ethyl alcohol being present in an amount of at least 0.75 part of ethyl alcohol per part of the dissolved oxidate.

7. A process for the preparation of ethylenically unsaturated aliphatic acids which comprises oxidizing with oxygen in the liquid phase a feed material which is a compound of the general formula



wherein R is selected from the group consisting of hydrogen and a lower alkyl group of 1 to 4 carbon atoms to produce an oxidate containing unreacted feed material and peroxides, continuously feeding said oxidate into a hot liquid solvent for the oxidate selected from the group consisting of ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, ethylene glycol, diethylene glycol, cyclohexanol, 1,4 dioxan, dimethyl formamide, carbon tetrachloride, benzene, xylene, water and mixtures thereof, said solvent being at a temperature as high as the boiling point of the said feed material whereby the unreacted feed material of the oxidate is continuously distilled off and whereby the peroxides are decomposed to form the ethylenically unsaturated aliphatic acid, the said oxidate being fed to the said hot liquid solvent in a manner whereby the concentration of the said ethylenically unsaturated aliphatic acid does not exceed about 60 weight percent of the total weight of the solution, the said solvent having a boiling point higher than the said unreacted feed material which is boiled off and being present in an amount of at least 0.75 part of solvent per part of the dissolved oxidate.

8. A process for the preparation of acrylic acid which comprises oxidizing acrolein with oxygen in the liquid phase to produce an oxidate containing unreacted acrolein and peroxides, feeding said oxidate into a hot aliphatic alcohol solvent for the oxidate, said aliphatic alcohol containing from about .01 to .25 weight percent of the solvent of a strong acid catalyst having an ionization constant of at least 1×10^{-3} and solvent being at a temperature as high as the boiling point of the said feed material whereby the unreacted acrolein of the oxidate is distilled off and whereby the peroxides are decomposed to form the acrylic acid, the said oxidate being fed to the said aliphatic alcohol whereby the concentration of the said acrylic acid does not exceed about 60 weight percent of the total weight of the solution, the said aliphatic alcohol having a boiling point higher than the said unreacted feed material which is boiled off and being present in an amount of at least 0.75 part of aliphatic alcohol per part of the dissolved oxidate.

9. A process for the preparation of acrylic acid which comprises oxidizing acrolein with oxygen in the liquid phase to produce an oxidate containing unreacted acrolein and peroxides, feeding said oxidate into a hot ethyl alcohol solvent for the oxidate, said ethyl alcohol containing hydroquinone and from .01 to .25 weight percent para-toluene sulfonic acid and being at a temperature as high as the boiling point of the said feed material whereby the unreacted acrolein of the oxidate is distilled off and whereby the peroxides are decomposed to form the acrylic acid, the said oxidate being fed to the said hot ethyl alcohol whereby the concentration of the said acrylic acid does not exceed about 60 weight percent of the total weight of the solution, the said ethyl alcohol being present in an amount of at least 0.75 part of ethyl alcohol per part of the dissolved oxidate.

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