

## UNITED STATES PATENT OFFICE

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## OXIDATION PROCESS

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This invention relates to the oxidation of hydrocarbons and relates more particularly to the oxidation of aliphatic hydrocarbons in the liquid phase whereby valuable oxygenated organic compounds are obtained.

An object of this invention is to provide an improved process for the catalytic liquid phase oxidation of lower aliphatic hydrocarbons.

Another object of this invention is the provision of an improved process for the catalytic liquid phase oxidation of lower aliphatic hydrocarbons wherein high yields of aliphatic acids, alcohols, ketones and esters may be obtained.

A further object of this invention is the provision of an improved catalytic liquid phase oxidation process for the oxidation of lower aliphatic hydrocarbons wherein high yields of desirable oxygenated organic compounds are obtained but in which the production of formic acid is held to a minimum.

Other objects of this invention will appear from the following detailed description.

The direct oxidation of aliphatic hydrocarbons such as propane, butane, iso-butane, pentane, etc., or mixtures of these hydrocarbons, with air or oxygen to obtain alcohols, aldehydes, ketones, acids, etc. has been the subject of considerable study, and a substantial amount of research has gone into developing commercially feasible hydrocarbon oxidation processes. Although many processes for the liquid phase oxidation of the aliphatic hydrocarbons mentioned above have been proposed, few, if any, have been commercially successful. On the other hand, the oxidation of said aliphatic hydrocarbons wherein the oxidation is carried out in the vapor phase has been highly successful and now constitutes a major source of many valuable organic chemicals.

However, processes for the liquid phase oxidation of such aliphatic hydrocarbons are very attractive from the point of view that they do not consume as much heat as vapor phase operations and, in addition, do not generally form as great a variety of products. In order to improve liquid phase oxidation operations to the end that they may be employed for commercial operation, various expedients have been suggested. The use of various catalysts, such as finely divided metals or the organic or inorganic acid salts of the metals, has been mentioned as a means whereby lower and more effective reaction temperatures may be employed. It has also been proposed that various inert liquids, such as acetic acid, propionic acid, butyric acid, iso-

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butyric acid, etc., be employed as solvents for the aliphatic hydrocarbon during the oxidation reaction. This expedient has been held to offer some advantages. However, one disadvantage in the catalytic liquid phase oxidation processes heretofore employed for the production of oxygenated organic compounds from lower aliphatic hydrocarbons is the fact that, in addition to the valuable acids, esters and ketones formed, appreciable amounts of formic acid are also produced as a product of said oxidation process. The highly corrosive action of formic acid on stainless steel equipment makes the presence of appreciable concentrations of this acid in the reaction product highly undesirable. Up to the present time no effective means has been found for selectively controlling the oxidation reaction so as to minimize the formation of formic acid.

We have now found that if the liquid phase oxidation of lower aliphatic hydrocarbons is carried out employing a bismuth compound soluble in the reaction mixture as the catalyst, the production of formic acid is greatly minimized without adversely affecting the yield of the more desirable oxygenated organic compounds such as, for example, acetic acid, acetone, methyl ethyl ketone, methyl alcohol, methyl acetate, ethyl acetate, etc. As examples of soluble bismuth compounds which may be employed as the catalyst in our improved hydrocarbon oxidation process there may be the soluble organic salts of bismuth such as bismuth acetate, bismuth propionate, bismuth butyrate, bismuth benzoate and bismuth acetyl acetonate, as well as inorganic salts such as the nitrate, chloride, etc.

The catalytic liquid phase oxidation of lower aliphatic hydrocarbons such as propane, n-butane, iso-butane, pentane, etc. is carried out most advantageously at temperatures of 135 to 232° C. and under pressure of 200 to 2000 pounds per square inch absolute employing air, oxygen, or oxygen diluted with any suitable inert gas as the oxidizing agent. Preferably, we also employ a solvent during said liquid phase hydrocarbon oxidation process. Acetic acid has been found to be the most suitable solvent when oxidizing propane, n-butane, isobutane or pentane, although other oxidation-resistant solvents such as methyl acetate, ethyl acetate, benzene, diphenyl or mixtures containing two or more of these solvents in any proportion may also be employed.

The bismuth oxidation catalyst may be employed during the oxidation process in an amount of from 0.05 to 2% by weight on the weight of the solvent present in the reaction mixture.



While the liquid phase catalytic oxidation of said lower aliphatic hydrocarbons may be carried out in batch-wise operations, it is preferably carried out in a continuous manner. Thus, a suitable reaction vessel may be charged with the solvent to be employed, the desired catalyst added to the solvent in a predetermined amount, and the hydrocarbon and oxidizing gas then introduced at the desired, controlled rate while maintaining the temperature and pressure within the above-mentioned ranges. The reaction conditions employed are preferably such that the oxygen introduced into the reactor will be completely consumed by the formation of oxygenated reaction products. Accordingly, the gaseous residue of the oxidation reaction will ordinarily be free of unreacted oxygen.

In order to condense the overhead vapors from the oxidation reaction, a condenser is provided which is maintained at a temperature which is sufficiently low to ensure the condensation of all of the condensable components in the vapors. A condenser temperature of 5 to 120° C. may be utilized, but a condenser temperature of say 10 to 15° C. is usually satisfactory. The overhead vapors comprise water, unreacted hydrocarbon and hydrocarbon oxidation products. The fixed gases, such as nitrogen and carbon dioxide, are vented to the atmosphere and any uncondensed water-solubles are absorbed in a suitable water absorber. The condensate is permitted to settle out into two phases, an upper hydrocarbon and a lower aqueous phase. The reaction products present partition between the phases. The aqueous phase comprises the water of reaction and a portion of the water-soluble oxidation products. The remainder of the oxidation products which distill over dissolve in the hydrocarbon phase. The aqueous phase is subjected to suitable treatment to recover the oxidation products dissolved therein. The hydrocarbon phase, without any treatment to separate the oxidation products which are present therein, is returned directly to the reactor where the unreacted hydrocarbon and certain of the ketone, ester, alcohol and aldehyde oxidation products undergo further oxidation. If desired, certain of the oxidation products present may be separated from the hydrocarbon phase before it is returned.

The volumetric ratio of oxygen to hydrocarbon introduced into the system is generally maintained at from about 0.5 to 10 volumes of oxygen for each volume of additional hydrocarbon introduced, the respective volumes being calculated at standard conditions of temperature and pressure, i. e. 0° C. and 760 mm. The recycled hydrocarbon may be from 5 to 50 parts by weight for each part by weight of fresh hydrocarbon introduced.

In order further to illustrate the novel process of our invention, the following example is given:

#### Example

365 parts by weight of glacial acetic acid are charged into a pressure reactor provided with suitable inlets for the introduction of hydrocarbon and air as well as a suitable outlet for reaction products. 1.9 parts by weight of bismuth acetate are added to the glacial acetic acid so as to give a catalyst concentration of about 0.5% by weight based on the weight of the solvent. Normal butane in liquid form is introduced into the pressure reactor at a rate of 0.75 part by weight per minute together with 1.6 parts by

weight per minute of air while maintaining the pressure at 815 pounds per square inch absolute and the temperature at about 168° C. The volumetric ratio of hydrocarbon to air which is employed is 0.23 volume of hydrocarbon for each volume of air, measured at standard conditions. An oxidation of the n-butane to valuable oxygenated organic compounds takes place in the pressure reactor.

The vapors coming overhead from the pressure reactor are condensed in a condenser maintained at a temperature of about 10° C. The uncondensed or vent gas, consisting essentially of nitrogen, gaseous decomposition products and a small amount of unreacted hydrocarbon, is passed through a water absorber where any uncondensed oxygenated products are recovered. The remaining gases may be metered when a check on reaction efficiency is desired. The condensate obtained by condensation of the overhead vapors is permitted to phase out in a decanter into an upper hydrocarbon phase and a lower aqueous phase containing water-soluble oxidation products. The lower aqueous phase is continuously removed while the hydrocarbon phase is continuously recycled back to the pressure reactor. The aqueous phase is suitably treated to effect recovery of the oxygenated products. Under the reaction conditions described, for each gallon of n-butane oxidized, only 0.06 pound of formic acid is produced while acetic acid is obtained in a yield of 4.66 pounds per gallon. Employing cerium acetate as a catalyst, for example, and under the same reaction conditions, the formic acid produced amounts to 0.16 pound per gallon of n-butane while the yield of acetic acid is barely 4.0 pounds per gallon. Aluminum nitrate yields 0.32 pound of formic acid per gallon of butane while zinc acetate yields 0.37 pound of formic acid per gallon when said compounds are employed as oxidation catalysts under the same reaction conditions.

It is to be understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of our invention.

Having described our invention, what we desire to secure by Letters Patent is:

1. In a process for the oxidation of lower aliphatic hydrocarbons with an oxygen-containing gas to produce oxygenated organic compounds, the step which comprises effecting said oxidation in the liquid phase while employing a soluble bismuth compound as catalyst for said oxidation.

2. In a process for the oxidation of lower aliphatic hydrocarbons with an oxygen-containing gas to produce oxygenated organic compounds, the steps which comprise effecting said oxidation in the liquid phase at a temperature of 135 to 232° C. and under a pressure of 200 to 2000 pounds per square inch absolute while employing a soluble bismuth compound as catalyst for said oxidation.

3. In a process for the oxidation of lower aliphatic hydrocarbons with an oxygen-containing gas to produce oxygenated organic compounds, the steps which comprise effecting said oxidation in the liquid phase at a temperature of 135 to 232° C. and under a pressure of 200 to 2000 pounds per square inch absolute while employing a soluble bismuth compound as catalyst for said oxidation, condensing the overhead distillate, allowing the condensate to separate into a



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hydrocarbon phase and an aqueous phase, and returning the hydrocarbon phase to the reaction.

4. In a process for the oxidation of lower aliphatic hydrocarbons with an oxygen-containing gas to produce oxygenated organic compounds, the steps which comprise effecting said oxidation in the liquid phase in a reaction medium containing an oxidation-resistant solvent for the hydrocarbon being oxidized while employing a soluble bismuth compound as catalyst for said oxidation.

5. In a process for the oxidation of lower aliphatic hydrocarbons with an oxygen-containing gas to produce oxygenated organic compounds, the steps which comprise effecting said oxidation in the liquid phase in a reaction medium containing an oxidation-resistant solvent for the hydrocarbon being oxidized at a temperature of 135 to 232° C. and under a pressure of 200 to 2000 pounds per square inch absolute while employing a soluble bismuth compound as catalyst for said oxidation.

6. In a process for the oxidation of lower aliphatic hydrocarbons with an oxygen-containing gas to produce oxygenated organic compounds, the steps which comprise effecting said oxidation in the liquid phase in a reaction medium containing an oxidation-resistant solvent for the hydrocarbon being oxidized at a temperature of 135 to 232° C. and under a pressure of 200 to 2000 pounds per square inch absolute while employing a soluble bismuth compound as catalyst for said oxidation, condensing the overhead distillate, allowing the condensate to separate into a hydrocarbon phase and an aqueous phase, and returning the hydrocarbon phase to the reaction.

7. Process for the production of oxygenated organic compounds, which comprises forming a liquid reaction mixture by adding an aliphatic hydrocarbon to an oxidation-resistant solvent for said hydrocarbon containing a soluble bismuth compound as an oxidation catalyst, passing an oxygen-containing gas through said liquid reaction mixture, allowing a part of said liquid reaction mixture including unreacted hydrocarbon, a water of reaction and other oxidation product to distill over, condensing the distillate to yield an aqueous and a hydrocarbon phase, separating the phases and returning the hydrocarbon phase to the reaction.

8. Process for the production of oxygenated organic compounds, which comprises forming a reaction mixture by continuously adding an aliphatic hydrocarbon to an oxidation-resistant solvent for said hydrocarbon containing a soluble bismuth compound as an oxidation catalyst, passing an oxygen-containing gas through said reaction mixture while maintaining the same at a temperature of 135 to 232° C. and under a pressure of 200 to 2000 pounds per square inch absolute, allowing a part of said reaction mixture including unreacted hydrocarbon, water of reaction, and other oxidation products to distill over, condensing the distillate to yield an aqueous and a hydrocarbon phase, separating the phases and returning the hydrocarbon phase to the reaction.

9. Process for the production of oxygenated organic compounds, which comprises forming a reaction mixture by continuously adding butane to glacial acetic acid containing a soluble bismuth compound as an oxidation catalyst, passing an oxygen-containing gas through said reaction mixture while maintaining the same at a tempera-

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ture of 135 to 232° C. and under a pressure of 200 to 2000 pounds per square inch absolute, allowing a part of said reaction mixture including unreacted butane, water of reaction, and other oxidation products to distill over, condensing the distillate to yield an aqueous and a butane phase, separating the phases and returning the butane phase to the reaction.

10. Process for the production of oxygenated organic compounds, which comprises forming a reaction mixture by continuously adding butane to glacial acetic acid containing 0.05 to 2% by weight of a soluble bismuth compound on the weight of the acetic acid as an oxidation catalyst, passing an oxygen-containing gas through said reaction mixture while maintaining the same at a temperature of 135 to 232° C. and under a pressure of 200 to 2000 pounds per square inch absolute, allowing a part of said reaction mixture including unreacted butane, water of reaction, and other oxidation products to distill over, condensing the distillate to yield an aqueous and a butane phase, separating the phases and returning the butane phase to the reaction.

11. Process for the production of oxygenated organic compounds, which comprises forming a reaction mixture by continuously adding an aliphatic hydrocarbon to an oxidation-resistant solvent for said hydrocarbon containing bismuth acetate as an oxidation catalyst, simultaneously and continuously passing an oxygen-containing gas through said reaction mixture while maintaining the same at a temperature of 135 to 232° C. and under a pressure of 200 to 2000 pounds per square inch absolute, allowing a part of said reaction mixture including unreacted hydrocarbon, water of reaction, and other oxidation products to distill over, condensing the distillate to yield an aqueous and a hydrocarbon phase, separating the phases and returning the hydrocarbon phase to the reaction.

12. Process for the production of oxygenated organic compounds, which comprises forming a reaction mixture by continuously adding butane to glacial acetic acid containing bismuth acetate as an oxidation catalyst, simultaneously and continuously passing an oxygen-containing gas through said reaction mixture while maintaining the same at a temperature of 135 to 232° C. and under a pressure of 200 to 2000 pounds per square inch absolute, allowing a part of said reaction mixture including unreacted butane, water of reaction, and other oxidation products to distill over, condensing the distillate to yield an aqueous and a butane phase, separating the phases and returning the butane phase to the reaction.

13. Process for the production of oxygenated organic compounds, which comprises forming a reaction mixture by continuously adding butane to glacial acetic acid containing 0.05 to 2% by weight of bismuth acetate on the weight of the acetic acids as an oxidation catalyst, simultaneously and continuously passing an oxygen-containing gas through said reaction mixture while maintaining the same at a temperature of 135 to 232° C. and under a pressure of 200 to 2000 pounds per square inch absolute, allowing a part of said reaction mixture including unreacted butane, water of reaction, and other oxidation products to distill over, condensing the distillate to yield an aqueous and a butane phase, separating the phases and returning the butane phase to the reaction.

14. Process for the production of oxygenated organic compounds, which comprises forming a



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reaction mixture by continuously adding butane to glacial acetic acid containing 0.05 to 2% by weight of bismuth acetate on the weight of the acetic acid as an oxidation catalyst, simultaneously and continuously passing air through said reaction mixture while maintaining the same at a temperature of 135 to 232° C. and under a pressure of 200 to 2000 pounds per square inch absolute, allowing a part of said reaction mixture including unreacted butane, water of reaction, and other oxidation products to distill over, condensing the distillate to yield an aqueous and a butane phase, separating the phases and returning the butane phase to the reaction.

15. Process for the production of oxygenated organic compounds, which comprises forming a reaction mixture by continuously adding butane to glacial acetic acid containing 0.5% by weight of bismuth acetate on the weight of the acetic acid as an oxidation catalyst, simultaneously and

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continuously passing air through said reaction mixture while maintaining the same at a temperature of 168° C. and under a pressure of 815 pounds per square inch absolute, allowing a part of said reaction mixture including unreacted butane, water of reaction, and other oxidation products to distill over, condensing the distillate to yield an aqueous and a butane phase, separating the phases and returning the butane phase to the reaction.

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