

UNITED STATES PATENT OFFICE

2,265,948

CATALYTIC OXIDATION OF LOWER ALIPHATIC HYDROCARBONS

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No Drawing. Application August 2, 1939,
Serial No. 287,961

5 Claims. (Cl. 260—451)

This invention relates to oxidation of gaseous saturated hydrocarbons and, more particularly, to the oxidation of such hydrocarbons in the liquid phase.

It is an object of the present invention to provide a process for the controlled oxidation in a liquid phase of normally gaseous saturated hydrocarbons.

It is a further and more specific object of the present invention to provide a new and improved process for the production, from normally gaseous saturated hydrocarbons, of useful acids, ketones, esters and alcohols.

Other objects and advantages of the present invention will be apparent by reference to the following specification.

I have found that oxidation of normally gaseous saturated hydrocarbons with production in good yield of useful acids, ketones, esters and alcohols can be accomplished by subjecting the said compounds to oxidation by means of an oxygen-containing gas, for example oxygen or air or air enriched with oxygen in a liquid phase. This liquid phase is obtained by dissolving the hydrocarbons in a solvent for the hydrocarbons which is substantially inert to the oxidation. Various liquids substantially inert to the oxidation and capable of dissolving the hydrocarbons such as carbon tetrachloride and benzene can be used, but I prefer to use as solvent an organic acid, such as acetic, propionic, butyric, trimethyl acetic and isobutyric, such aromatic acids as phenyl acetic, and such hydroxy acids or derivatives as methoxy acetic, and the like. Varying proportions of these acids, based upon the weight per cent. present in the solution being oxidized, may be utilized, such as from 1 to 99 per cent. by weight although I prefer to utilize about 5 to 50 per cent. Within these indicated ranges I have found it possible to effect a high yield of useful products by oxidation of the hydrocarbon.

By normally gaseous hydrocarbons, I mean to include those hydrocarbons which are gaseous under atmospheric temperatures such, specifically, as methane, ethane, propane, the butanes and pentanes.

While my process may be carried out at various temperatures ranging upward from about 100° C. to about 320° C., generally speaking the use of temperatures in the more restricted range of 125 to 200° C. tends, other conditions remaining the same, to give a higher proportion of useful products. Dependent upon the temperature utilized, the pressures employed vary within a wide range, the prime requisite being that as low

a temperature as possible is employed to assure the maximum concentration of hydrocarbon in the liquid phase.

I have further discovered two factors which, taken together, produce the optimum result but which, nevertheless, individually contribute to an improved result as will appear hereinafter. Each of these factors, or methods, facilitate oxidation at low temperatures, improved results are obtained when any one of them is employed and the best results are secured when both methods are used simultaneously.

As one of the two factors previously mentioned, I have found that the yields of acids, esters, ketones and alcohols produced according to my invention may be considerably increased by carrying on the oxidation in the presence of an oxidation catalyst, such, specifically as the solid polyvalent metals having an atomic weight between about 50 and about 200. For example, I may use such metals in the finely divided metallic state or as organic and inorganic salts or oxides including such specific metals as cerium, cobalt, copper, manganese, vanadium, uranium, and ferrous salts, with or without inorganic acids such as nitric, phosphoric and hydrochloric acids or mixtures of any two or more of these substances. In addition to the oxidation catalysts, promoters such as the alkali and alkaline earth metals may also be employed, if desired, such, for example as the barium, magnesium and potassium acetates, butyrates, propionates, and the like. As specific catalysts under the above description there may be employed vanadium, cerium and cobalt chlorides, cobalt or manganese acetate alone or together with barium acetate, barium or cobalt permanganate, sodium cobalt nitrite or mixtures of two or more of such compounds.

As a further feature of the invention I have found that, especially when operating at the lower temperatures, say 150° C. or below, the yields and efficiency of the process may be even further improved by carrying on the oxidation, whether with or without the solvents referred to, in the presence of one or more "initiators," which term I employ herein to designate substances capable of initiating attack on the hydrocarbon molecule which may itself not readily react with molecular oxygen under my preferred low temperature conditions. For example, there may be employed organic peroxides such as benzoyl peroxide; inorganic peroxides, such as sodium and hydrogen peroxide; peracids, such as peracetic and perbenzoic acids; the aldehydes,

such as acetaldehyde, propionaldehyde, and isobutyraldehyde; ketones, such as acetone, methyl ethyl ketone, diethyl ketone, and cyclohexanone; ethers, such as diisopropyl, diethyl and diamyl ethers; olefines such as cyclohexene and octylene, and, in fact, any organic compound which tends to form peroxide bodies under the reaction conditions.

The initiator may be added to the reactants at the start or continuously during the oxidation or both; or, if preferred, the oxidation may be begun at a temperature and pressure at which partial oxidation products, capable of being oxidized to or acting as oxygen carriers are formed, and the partially oxidized hydrocarbons thus produced may thereafter act as oxygen carriers capable of attacking other hydrocarbon molecules at the relatively low temperatures which I have generally outlined and will hereinafter more specifically describe. The constant maintenance of a concentration of initiator is important, however, and therefore, in general, I deliberately add the initiator to the reactants as described hereinafter. The oxygen carrier is thus able to initiate the oxidation which then may become at least partially self-sustaining at temperatures very much lower than otherwise possible.

The proportions of initiators which are desirable according to this invention range from about 0.1 to 10 per cent, based upon the weight of the hydrocarbon being treated. I do not wish to be restricted to these proportions, however, for I have found that as much as 50 per cent initiator may be utilized without deleterious effect upon progress of the oxidation and at the same time as low as 0.05 per cent initiator may be employed with an increased efficiency and yield of useful products. Although primarily applicable to ketones such as acetone, dimethyl or methyl ethyl ketones, or cyclohexanone, or mixtures thereof, these ranges describe satisfactorily the amounts of other initiators which are suitable according to my invention.

While the process is operable at pressures at which the hydrocarbon will remain dissolved in the solvent at the particular temperature utilized I may also use elevated pressures ranging upwards from about 2 atmospheres to about 100 atmospheres or more. The minimum pressure is, however, that required to permit effecting the reaction in the liquid phase, by which is meant that the hydrocarbon is preferably oxidized in the liquid or dissolved state. Pressures in excess of this minimum may be used, however, since pressure has been found to favor the reaction rate.

Having described generally some of the features of my invention, the following examples will illustrate how these features may be combined for oxidation of specific compounds.

Example 1

A solution consisting of 301.9 gm. acetic acid, 5.4 gm. diethyl ketone, and 0.3 gm. cobalt acetate was charged into a tantalum lined converter of 1200 cc. capacity, provided with suitably valved gas outlet and inlet lines at top and bottom respectively. 283.8 gm. of isobutane was injected, the mixture was raised to 100° C. and 50 atmospheres pressure, and air was bubbled through the solution at the rate of 222 liters per hour (S. T. P.) while maintaining the above pressure. Over a period of 5¼ hours the temperature was gradually raised to 155°. After 2 hours continuous injection of isobutane was begun and continued

until the end of the run. 848 gm. of isobutane were added in this manner. The exit gas was passed successively through a condenser and a series of traps cooled by dry ice.

Distillation of the products gave 793.5 gm. of unconverted isobutane, 259.7 gm. acetic acid, 40.1 gm. water, 68.8 gm. acetone, 48.2 gm. methyl acetate, 31.1 gm. 1-butyl acetate, 47.1 gm. 1-butanol, and 18.1 gm. unidentified material. The total acetic acid, including that combined in the form of esters, was 314.9 gm., a gain of 13.0 gm. over that charged.

Example 2

300.9 gm. acetic acid, 5.0 gm. diethyl ketone, and 0.3 gm. cobalt acetate were charged into a 1200 cc. tantalum lined converter provided with suitably valved gas inlet and outlet at bottom and top, respectively. In addition, 56.7 gm. n-butane was injected. The pressure was built up to 50 atmospheres at which point it was maintained throughout the run. Simultaneous injection of air and n-butane was begun when the temperature reached 150°. During a 3¼ hour period, the temperature was raised to 170-180°, air was injected at the rate of 228 liters/hr. (S. T. P.), and n-butane was injected at the rate of 79 liters/hr. (S. T. P.). The exit gas was passed through a condenser and a series of traps cooled by dry ice.

69% of the n-butane was recovered by distillation of the trap condensate. Distillation of the product gave 55.9 gm. water, 375.4 gm. acetic acid, 5.6 gm. acetaldehyde, 1.1 gm. butanone, 52.9 gm. ethyl acetate, and 9.2 gm. unidentified material.

Example 3

Into a 1200 cc. tantalum lined converter, equipped with a suitably valved gas inlet at the bottom and outlet at the top, were charged 233.2 gm. isopentane, 180.2 gm. acetic acid, 5.3 gm. methyl ethyl ketone, and 0.4 gm. cobalt acetate. For three hours this solution was held at 140-150° C. and 50 atmospheres pressure, and processed with air at the rate of 223 liters/hr. (S. T. P.). The exit gas was passed through a condenser, dry ice cooled traps, and dry ice cooled toluene scrubbers.

Distillation of the product gave 55.6 gm. isopentane, 28.9 gm. water, 213.1 gm. acetic acid, 49.7 gm. acetone, 44.1 gm. ethyl acetate, 11.0 gm. formic acid, 1.8 gm. higher esters, and 20.5 gm. unidentified material.

Example 4

214.5 gm. n-pentane, 180.4 gm. acetic acid, 5.2 gm. methyl ethyl ketone, and 0.025 gm. cobalt acetate were charged into a 1200 cc. tantalum lined converter equipped with a suitably valved gas inlet at the bottom and a gas outlet at the top. The pressure was raised to 80 atmospheres and maintained at this point during the run. The temperature was 150° at the beginning of the run, but was permitted to drop slowly to 134° during the run. Air was passed in at the rate of 244 liters/hr. (S. T. P.) for 1½ hours. The exit gas was passed through a condenser and traps cooled by dry ice.

Distillation of the product gave 104.3 gm. recovered n-pentane, 219.9 gm. acetic acid, 32.8 gm. propionic acid, 25.2 gm. water, 1.1 gm. acetaldehyde, 6.8 gm. methyl n-propyl ketone, 4.5 gm. ethyl acetate, 23.7 gm. n-propyl acetate, 11.9 gm. amyl acetate, and 4.0 gm. unidentified material.

Example 5

A mixture containing 368.8 gm. mixed pentanes, 32.8 gm. acetic acid, 5.7 gm. methyl ethyl ketone, and 0.05 gm. cobalt acetate was charged into a tantalum lined converter of 1200 cc. capacity, provided with suitably valved gas outlet and inlet lines at top and bottom, respectively. The mixture was heated to 138° C., under a pressure of 80 atmospheres and air was bubbled through the mixture for 2¼ hours at the rate of 244 liters per hour, the pressure being maintained at 80 atmospheres and the temperature at 138–152° C. The exit gas was passed through a condenser, traps cooled by dry ice, and ethyl benzene scrubbers cooled by dry ice.

Distillation of the product gave 230.0 gm. recovered pentanes, 65.4 gm. acetic acid, 18.1 gm. propionic acid, 27.5 gm. water, 21.4 gm. acetone, 35.4 gm. methyl propyl ketone, 18.8 gm. ethyl acetate, 7.0 gm. propyl acetate, 14.9 gm. amyl acetate, and 12.2 gm. unidentified material.

Example 6

A solution of 366.4 gm. mixed pentanes, 62.1 gm. acetic acid, 5.4 gm. methyl ethyl ketone, 0.05 gm. copper acetate, and 0.05 gm. silver acetate was placed in a 1200 cc. tantalum lined converter equipped with suitably valved gas inlet and outlet at bottom and top, respectively. The oxidation was carried out under 80 atmospheres pressure and at 137–168° C. Air flow was 215 liters per hour (S. T. P.) during the 2¾ hour run. Exit gas was passed through a condenser, dry ice cooled traps, and dry ice cooled ethyl benzene scrubbers.

Distillation of the product gave 192.0 gm. mixed pentanes, 99.4 gm. acetic acid, 18.2 gm. propionic acid, 38.3 gm. water, 18.4 gm. acetone, 47.4 gm. methyl propyl ketone, 32.8 gm. ethyl acetate, 24.0 gm. propyl acetate, 22.0 gm. amyl acetate, and 6.1 gm. unidentified material.

Although specific disclosure has been made in the examples of methods for carrying on my invention in a batch process, it should be understood that this invention may also be practiced in a continuous manner. Thus, after completion of the acid production, such as shown in the specific examples, the materials capable of being converted to the desired acid, plus the catalyst, solvent, and initiator may be recovered and recycled to the reaction zone together with further quantities of hydrocarbon. In a continuous process it will also be found desirable to make such additions of catalyst, solvent, and initiator as will maintain the reaction rate and yield of acid at the desired high degree.

While the process as described in the examples involves passage of the oxidizing gas through a

body of liquid, it will be understood that other means of assuring the desired liquid-gas contact may be employed, as, for example, passage of liquid and gas co-current or counter-current through a tube or tower, which may be supplied with plates, packing or other devices for enhancing contact.

I claim:

1. A method of oxidizing normally gaseous saturated hydrocarbons which comprises subjecting such compounds to oxidation in a liquid phase by means of a gas containing elemental oxygen in the presence of an oxidation catalyst, an oxidation initiator selected from the group consisting of peroxides and compounds capable of forming peroxides under reaction conditions, and a solvent for the hydrocarbon at a temperature within the range of 125 to 200° C.

2. A method of oxidizing butane which comprises subjecting butane to oxidation in a liquid phase by means of a gas containing elemental oxygen in the presence of an oxidation catalyst, an oxidation initiator selected from the group consisting of peroxides and compounds capable of forming peroxides under reaction conditions, and a solvent for the butane at a temperature within the range of 100 to 320° C.

3. A method of oxidizing pentane which comprises subjecting pentane to oxidation in a liquid phase by means of a gas containing elemental oxygen in the presence of an oxidation catalyst, an oxidation initiator selected from the group consisting of peroxides and compounds capable of forming peroxides under reaction conditions, and a solvent for the pentane at a temperature within the range of 100 to 320° C.

4. A method of oxidizing normally gaseous saturated hydrocarbons which comprises subjecting such compounds to oxidation in a liquid phase by means of a gas containing elemental oxygen in the presence of an oxidation catalyst and a solvent for the hydrocarbon, and in the presence of an oxidation initiator selected from the group consisting of peroxides and compounds capable of forming peroxides under the reaction conditions, at a temperature within the range of 100 to 320° C.

5. A method of oxidizing propane which comprises subjecting propane to oxidation in a liquid phase by means of a gas containing elemental oxygen, in the presence of an oxidation catalyst, an oxidation initiator selected from the group consisting of peroxides and compounds capable of forming peroxides under reaction conditions and a solvent for the propane, at a temperature within the range of 100–320° C.

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