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OXIDATION OF HYDROCARBONS

Nat C. Robertson and Robert L. Mitchell, Corpus Christi, Tex., assignors to Celanese Corporation of America, New York, N. Y., a corporation of Delaware

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1 Claim. (Cl. 260—451)

This invention relates to the production of organic compounds by oxidation reactions and relates more particularly to an improved process for the production of certain valuable organic compounds by the controlled oxidation of hydrocarbon mixtures.

The controlled vapor phase oxidation of aliphatic hydrocarbons such as propane, butane, and mixtures thereof yields many useful organic compounds such as methanol, formaldehyde, acetone, acetaldehyde, propionaldehyde, acrolein, propyl alcohol, n-butyl alcohol, isobutyl alcohol, and some 1,2-propylene oxide as well as significant amounts of various other oxygentaed organic compounds. The mixture of products obtained by vapor phase partial oxidation reactions depends to some extent on the particular hydrocarbon or hydrocarbons subjected to said vapor phase partial oxidation. The preparation of compounds having adjacent carbonyl and hydroxy groups by vapor phase partial oxidation of hydrocarbons is, we believe, quite novel. Normally, only insignificant amounts, if any, of compounds having both a carbonyl and a hydroxy group are obtained as a product of said oxidation process when the hydrocarbons are essentially paraffinic in nature. Such compounds are quite valuable, however, since they serve admirably as intermediates in the preparation of numerous other organic compounds; and development of a new process for their manufacture, along with other valuable compounds, would be highly advantageous.

It is, therefore, an important object of this invention to provide a process for the vapor phase partial oxidation of aliphatic hydrocarbons whereby the yield of oxygenated organic compounds containing both a hydroxy and a carbonyl group may be enhanced.

Another object of this invention is the provision of a process for the vapor phase oxidation of aliphatic hydrocarbons in which increased yields of other oxygenated organic compounds may also be obtained.

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

We have now found that oxygenated aliphatic compounds containing both a hydroxy and a carbonyl group, as well as other valuable oxygenated compounds normally formed in only relatively small quantities, may be obtained in substantial yields by the vapor phase oxidation of olefinic hydrocarbons, either alone or in admixture with saturated aliphatic hydrocarbons, without appreciable reduction in the overall yield of valuable compounds, such as aldehydes, alcohols,

etc., normally produced by the partial oxidation of aliphatic hydrocarbons. The type of hydroxy carbonyl compound produced can be determined by selecting the olefinic hydrocarbon which is to be subjected to partial oxidation. Thus when the olefin employed is butene-1, 1-hydroxy methyl ethyl ketone is produced. When the olefin is butene-2, 2-hydroxy methyl ethyl ketone (also known as acetoin) is produced. When the olefin is isobutylene, alpha hydroxy isobutyraldehyde is produced. When the olefin is propylene, hydroxy acetone (also known as acetol) is produced. In no case do the corresponding saturated hydrocarbons yield any appreciable quantity of the hydroxy carbonyl compound on partial oxidation.

With certain olefinic hydrocarbons, notably butene-2 and isobutylene, which olefins contain more than one methyl group adjacent to the double bond, the oxidation of the pure olefinic hydrocarbon is too slow at temperatures up to 800–900° F. and at the pressures conventionally used in partial oxidation processes to be of interest as a source of oxygenated compounds. However, when 20 to 70% by volume of a saturated aliphatic hydrocarbon of three or more carbon atoms is added to these olefinic hydrocarbons, the oxidation of the mixture proceeds readily at temperatures of 600–900° F. Butene-1 with no methyl group adjacent to the double bond and propylene with only one methyl group adjacent to the double bond can be oxidized at temperatures of 600–900° F. without any added saturated aliphatic hydrocarbon.

Organic peroxides such as ditertiary butyl peroxide in concentrations of 0.1 to 2.0% and similar substances can be used in lieu of saturated aliphatic hydrocarbons to sensitize the oxidation of butene-2 and isobutylene so that the oxidation may be more readily initiated.

In carrying out the partial oxidation of olefinic hydrocarbons or of mixtures containing both olefinic and paraffinic hydrocarbons to obtain substantial yields of compounds containing both hydroxy and carbonyl groups, optimum results are obtained when carrying out the reaction at a temperature of from 550° to 900° F. The oxidation reaction is effected by bringing the reaction mixture up to oxidation temperature, allowing the oxidation to take place for from about 0.5 second to about 6.0 seconds and then cooling the mixture of reaction products obtained to halt further oxidation. The separation of the various oxygenated organic products formed is achieved by a combination of steps including selective absorption, extraction, and distillation operations.

In order further to illustrate our invention, but without being limited thereto, the following examples are given:

Example I

A gaseous reaction mixture containing butene-1 and oxygen consisting of 30% by volume of butene-1, 3.5% by volume of oxygen and 66.5% by volume of inerts including nitrogen, carbon monoxide, and carbon dioxide is heated to a temperature of 650° F. under a pressure of about 100 pounds per square inch gauge to initiate a partial oxidation reaction. The temperature rises, due to the exothermic character of the oxidation, to a temperature of about 850 to 950° F., and, after the oxidation has continued at this temperature for about 0.5 second, further reaction is halted by passing the gaseous reaction mixture into a cascading stream of water. Upon separation of the products of reaction it is found that a yield of 15 moles of 1-hydroxy methyl ethyl ketone is obtained for each hundred moles of hydrocarbon oxidized while the yield of 1,2-butylene oxide is 8 moles for each 100 moles of hydrocarbon oxidized. When a reaction mixture comprising essentially n-butane is subjected to a vapor phase partial oxidation under the same reaction conditions, the yield of 1-hydroxy methyl ethyl ketone is less than 0.5 mole and that of 1,2-butylene oxide only 1 mole for each 100 moles of hydrocarbon oxidized.

Example II

A gaseous reaction mixture containing n-butane and butene-2 in a ratio of 1 part of n-butane to 3 parts of butene-2 and consisting of 7.5% by volume of n-butane, 22.5% by volume of butene-2, 3.5% of oxygen, and 66.5% of inerts is heated to a temperature of 675° F. under a pressure of about 100 pounds per square inch gauge to initiate a partial oxidation reaction. If pure butene-2 is used without the addition of a paraffinic hydrocarbon such as n-butane, a temperature of almost 1000° F. is required to initiate reaction under these conditions, and since the reaction is exothermic, the high final temperature attained results in decomposition of most of the valuable products. In the present example the temperature rises to about 850–900° F., and, after this temperature is attained, further reaction is halted within about 0.5 second by passing the reaction mixture into a cascading stream of water. Upon separation of the products of reaction, it is found that a yield of 5 moles of 2-hydroxy methyl ethyl ketone is obtained for each 100 moles of total hydrocarbon oxidized, while the yield of 2,3-butylene oxide is 5.5 moles for each hundred moles of hydrocarbon oxidized. When a reaction mixture comprising essentially n-butane is subjected to a vapor phase partial oxidation under the same reaction conditions, the yield of 2-hydroxy methyl ethyl ketone is only about 0.5 mole and the yield of 2,3-butylene oxide is only 1.5 moles for each 100 moles of hydrocarbon consumed.

Example III

A gaseous reaction mixture containing isobutane and isobutylene in the ratio of 1 part isobutane to 4 parts isobutylene and consisting of 6% by volume of isobutane, 24% by volume of isobutylene, 3.5% of oxygen and 66.5% of inerts is heated to a temperature of 650° F. under a pressure of about 100 pounds per square inch gauge to initiate reaction. Pure isobutylene without the addition of any isobutane, n-butane, or similar saturated aliphatic hydrocarbon or other initiator requires a temperature of almost 1000° F. to initiate reaction under the same conditions; and at the final high temperatures attained under such conditions the valuable reaction products are largely destroyed. Using the mixture of isobutane and isobutylene of this example, a final temperature of about 850–900° F. is reached, and further reaction is then halted within a period of 0.5 second by passing the gaseous reaction mixture into a cascading stream of water. Upon separation of the products of reaction, it is found that a yield of 10 moles of alpha hydroxy isobutyraldehyde is obtained for each 100 moles of total hydrocarbon oxidized while the yield of isobutylene oxide is 1.5 moles for each 100 moles of hydrocarbon oxidized. When a reaction mixture comprising essentially isobutane is subjected to vapor phase partial oxidation under the same reaction conditions, the yield of alpha hydroxy isobutyraldehyde is less than one mole per 100 moles hydrocarbon oxidized, and essentially no isobutylene oxide is produced.

Example IV

A gaseous reaction mixture consisting of 45% by volume of propylene, 3.5% by volume of oxygen, and 51.5% of inerts is heated to a temperature of 650° F. under a pressure of about 100 pounds per square inch gauge to initiate reaction. After initiation the temperature rises to about 850–900° F. and further reaction is then halted within about 0.5 second by passing the reaction mixture into a cascading stream of water. Upon separation of the reaction products it is found that a yield of 5 moles of hydroxy acetone is obtained for each 100 moles of hydrocarbon oxidized while the yield of 1,2-propylene oxide is 11.5 moles for each 100 moles of hydrocarbon oxidized. The yield of 1,2-propylene oxide from propane is only 2 moles for each 100 moles hydrocarbon oxidized, and that of hydroxy acetone is negligible.

Olefinic hydrocarbons alone may also be subjected to controlled vapor phase partial oxidation giving in general higher yield of useful oxygenated compounds, such as those enumerated previously, than does the corresponding paraffinic hydrocarbon. However, because of their wide commercial use in production of such materials as high octane rating gasoline and synthetic rubber, olefinic hydrocarbons are more valuable and expensive than their paraffinic counterparts. Therefore, any improvement in the oxidation process which duplicates the improved yields of oxygenated products obtained from olefinic hydrocarbons alone and at the same time permits a decrease in the amount of olefinic hydrocarbon required would be highly advantageous.

We have also found that if a particular olefinic hydrocarbon be diluted with a paraffinic hydrocarbon so that certain specific ratios of saturated and unsaturated hydrocarbon are present in the reaction mixture, yields of propionaldehyde and acrolein, for example, are obtained which are not only equal to but substantially greater than are obtained when the amounts of saturated and unsaturated hydrocarbons are outside of these ratios. When, for example, n-butane alone is oxidized in the vapor phase under the usual conditions employed commercially, a yield of about

0.27 part by weight of propionaldehyde and acrolein is obtained for each 5 parts by weight of n-butane. When a mixture comprising 15% by volume of n-butane and 85% by volume of butene-2 is oxidized, the yield of acrolein and propionaldehyde increases but slightly to an amount of about 0.35 part by weight for each 5 parts by weight of hydrocarbon mixture oxidized. However, when the butene-2 is diluted with n-butane to give a ratio of about 40% by volume of n-butane and 60% by volume of butene-2 for use as the hydrocarbon oxidation mixture, the yield of acrolein and propionaldehyde undergoes a very marked increase to about 0.56 part by weight for each 5 parts by weight of the hydrocarbon mixture oxidized. In addition, by employing suitable mixtures of n-butane with butene-1 or butene-2, appreciable amounts of 1,2-butylene oxide or 2,3-butylene oxide, respectively, are obtained.

While the oxidation of ethylene over a silver catalyst yields ethylene oxide, direct oxidation of butene-1 or butene-2 over a silver catalyst under the same conditions does not yield the corresponding butylene oxide, and consequently, the butylene oxides have remained relatively rare and expensive compounds. This, however, is no longer the case since appreciable yields of said butylene oxides may now be readily obtained by our novel process. It is quite apparent, therefore, that the extent of dilution of the unsaturated hydrocarbon with saturated hydrocarbon is definitely critical in its relation to the character and distribution of the products formed.

The variation in product distribution pointed out above when the hydrocarbon mixture is modified to include appreciable amounts of unsaturated hydrocarbons is also noted when a hydrocarbon mixture comprising essentially propane is modified to include varying proportions of propylene. Thus, for example, when oxidizing propane, one of the several oxidation products obtained is propylene oxide. When the reaction mixture is modified to include propylene, the yield of propylene oxide increases markedly. The use of a hydrocarbon reaction mixture containing 60% by volume of propylene and 40% by volume of propane, for example, results in four-fold increase in the amount of propylene oxide when compared to the amount of propylene oxide produced from propane alone under the same partial oxidation reaction conditions. The ability to determine, at least in some degree, the nature of the oxidation products and the distribution of said products by suitably varying the composition of the hydrocarbon reaction mixture to include appreciable amounts of olefin as well as paraffin hydrocarbons is a substantial advance in the art.

In carrying out the partial oxidation of hydrocarbon mixtures including both paraffin and olefin hydrocarbons, optimum results are obtained when the olefin hydrocarbon is diluted with paraffin hydrocarbon so that the hydrocarbon mixture contains said hydrocarbons in a ratio of 30 to 70% by volume of said paraffinic hydrocarbon and 70 to 30% by volume of said olefinic hydrocarbon. The oxidation is preferably effected at a temperature of from 600 to 900° F. and at pressures conventionally used in partial oxidation processes e. g. 50 to 200 pounds per square inch guage. The oxidation reaction is effected by bringing the reaction mixture up to oxidation temperature, allowing the oxidation to take place for from about 0.25 to 6.0 seconds and then cooling the mixture of reaction products obtained to halt further oxidation. The separation of the various oxygenated organic products formed is achieved by a combination of steps including selective absorption, extraction and distillation operations.

This feature of our novel process is illustrated by the following examples:

Example V

A gaseous reaction mixture containing a mixture of propane and propylene in a ratio of 60% propylene and 40% propane and consisting of 26% by volume of propylene, 17% by volume of propane, 3.2% by volume of oxygen, and 53.8% by volume of inerts including nitrogen, carbon monoxide and carbon dioxide is subjected to a vapor phase partial oxidation. The reaction mixture is heated to a temperature of 650° F. under a pressure of about 100 pounds per square inch gauge to initiate the reaction and the temperature rises to 850 to 900° F. The reaction mixture is permitted to remain at this temperature for about 0.5 second to effect the desired oxidation and the hot reaction gases then cooled to halt further reaction by passing said hot gases into a stream of water. On separation of the reaction mixture it is found that a yield of 4.5 moles of propionaldehyde and acrolein is obtained. When a reaction mixture comprising essentially propylene is subjected to a vapor phase partial oxidation under similar conditions a yield of 4.2 moles of propionaldehyde and acrolein is obtained. The oxidation of propane alone under the same conditions as above yields only 2.1 moles of propionaldehyde and acrolein for each 100 moles of hydrocarbon reacted.

Example VI

A gaseous reaction mixture containing a mixture of propane and propylene in a volumetric ratio of 60% propylene and 40% propane and consisting of 26% by volume of propylene, 17% by volume of propane, 3.2% by volume of oxygen, and 53.8% by volume of inerts is subjected to a vapor phase partial oxidation. The reaction mixture is heated to a temperature of 650° F. under a pressure of 100 pounds per square inch to initiate the reaction.

The reaction mixture is permitted to remain at reaction temperature for about 0.5 second and the hot mixture of reaction products then cooled by means of a stream of water to halt further oxidation. The partial oxidation products are then separated from the water by suitable distillation and extraction operations. The yield of 1,2-propylene oxide is found to be 8 moles for each 100 moles of hydrocarbon oxidized. The yield of 1,2-propylene oxide is a four-fold increase over that obtained by the partial oxidation of propane alone under the same conditions. When propylene alone is oxidized under the same conditions as above the yield of 1,2-propylene oxide is 11.5 moles for each 100 moles of propylene oxidized. This is less than the equivalent of 13.3 moles per 100 moles of propylene oxidized when mixed with propane in the ratio given above.

Example VII

A gaseous reaction mixture containing n-butane and butene-2 in a ratio of 40% n-butane and 60% butene-2 and consisting of 16% by volume of butene-2, 11% of n-butane, 3.6% of oxygen and 69.4% by volume of inerts is subjected to a vapor phase partial oxidation. The gaseous mixture is heated to a temperature of 650° F. under a pressure of 100 pounds per square inch to initiate the oxidation and the temperature rises to about 900° F. during the course of the exothermic reaction which takes place. The gaseous mixture is maintained at this temperature for 0.5 second and further reaction is halted by quenching the hot gaseous reaction mixture with water. Upon separation of the reaction products the combined yield of propionaldehyde and acrolein is found to be 11 moles for each 100 moles of hydrocarbon oxidized.

When there is employed an oxidation reaction mixture containing the same proportion of hydrocarbon but in which 85% of the hydrocarbon is butene-2 and 15% is n-butane, the combined yield of propionaldehyde and acrolein is only 6.6 moles for each 100 moles of hydrocarbon oxidized. The oxidation of n-butane alone yields propionaldehyde and acrolein in an amount of only 5.5 moles for each 100 moles of n-butane.

Example VIII

A gaseous reaction mixture containing n-butane and butene-2 in a ratio of 60% n-butane and 40% butene-2 and consisting of 16% by volume of n-butane, 11% by volume of butene-2, 3.6% by volume of oxygen and 69.4% by volume of inerts including nitrogen, carbon monoxide and carbon dioxide is subjected to a vapor phase partial oxidation. The reaction mixture is heated to a temperature of about 650° F. under a pressure of 100 pounds per square inch to initiate the reaction.

The reaction mixture is permitted to remain at reaction temperature for about 0.5 second and the hot mixture of reaction products then cooled by means of a stream of water to halt further oxidation. The partial oxidation products are then separated from the water by suitable distillation and extraction operations. The yield of 1,2-propylene oxide is found to be 2.6 moles for each 100 moles of hydrocarbon oxidized. When a reaction mixture comprising butene-2 and n-butane in the ratio of 85% butene-2 and 15% n-butane is subjected to vapor phase partial oxidation under similar conditions, a yield of only 0.6 mole of 1,2-propylene oxide is obtained. The oxidation of n-butane alone under the same conditions as above yields only 1 mole of 1,2-propylene oxide for each 100 moles of hydrocarbon oxidized.

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:

In a process for the production of oxygenated organic compounds having adjacent carbonyl and hydroxy groups by the vapor phase partial oxidation of aliphatic hydrocarbons, the steps which comprise subjecting a mixture containing 40% by volume of n-butane and 60% by volume of butene-2 to a non-catalytic partial oxidation in the vapor phase with oxygen by heating said mixture to a temperature of 650° F. and at a pressure of about 100 pounds per square inch gauge in the presence of about 70% by volume of inert diluent gas to initiate the exothermic reaction, allowing the temperature to rise to about 900° F. for ½ second, cooling by direct contact with water the mixture of reaction products obtained to halt further oxidation, and separating the reaction products from the water.

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