Patented Oct. 9, 1945

2,386,372

UNITED STATES PATENT OFFICE

2,386,372

PRODUCTION OF CYCLIC KETONES

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No Drawing. Application April 20, 1944, Serial No. 531,995

5 Claims. (Cl. 260—586)

This invention relates to the oxidation of alicyclic hydrocarbons. More specifically, it pertains to the catalytic vapor phase oxidation of cycloparaffins having from five to six carbon atoms in the ring, namely, cyclopentane, cyclohexane, and their respective alkyl derivatives, especially methylcyclopentane and methylcyclohexane, to form the corresponding cyclic ketones.

The production of alicyclic ketones by the oxidation of alicyclic hydrocarbons has been accomplished heretofore. U. S. Patent 2,223,494 to Donald J. Loder, discloses a process in which cyclohexane is oxidized in the liquid phase at temperatures of from 100° C. to 250° C. by means of an oxygen-containing gas in the presence of cobalt naphthenate catalyst. The products comprise a mixture of cyclohexanol and cyclohexanone. Similarly, U. S. Patent 2,285,914 to Drossbach, discloses obtaining a 4 per cent yield of cyclohexanone from cyclohexane by liquid phase oxidation.

By the process of my invention the oxidation of a cycloparaffin of from five to six carbon atoms in the ring to form the corresponding alicyclic ketone is carried out in the vapor phase, thereby avoiding the high pressures necessary when operating in the liquid phase and giving rise to many advantages.

The oxidizing gases employed in my process may be air or other oxygen-containing gases of about the same oxygen content as that of air. Under certain conditions of operation, as when an especially active oxidation catalyst is being used, it may be advantageous to limit the percentage of oxygen in the oxidizing gas mixture to a value below that of ordinary air, say to 5 to 10 per cent by volume. In this way the production of higher oxidation products may be held to a minimum.

In carrying out my process, I pass a preheated mixture of the cycloparaffin vapors and oxygen-containing gas over an oxidation catalyst at a temperature in the range of 300° to 550° C. The flow rate of this gaseous mixture is adjusted so as to result in a contact time of from 0.1 to 10 seconds, depending upon the activity of the catalyst, the temperature, and the oxygen content of the mixture. It is preferred to operate at relatively short contact times, recycling any unchanged hydrocarbons and intermediate oxidation products which may be found in the reaction effluent. In this way the production of higher oxidation products may be minimized and ultimate yields increased.

Catalysts which may be employed in my process include the following metals or other oxides, or mixtures thereof: silver, copper, vanadium, chromium, manganese, iron, cobalt, nickel, platinum, and palladium. These may be employed in the form of screen or gauze, or may be supported on inert carriers such as asbestos. Silver oxide is the preferred catalyst.

As an aid in controlling the reaction temperature, steam may be introduced either with the oxygen-containing gas or separately into the catalyst zone.

It has been found that by the use of the above specified conditions the reaction which is otherwise very difficult to control so as to avoid obtaining large amounts of higher oxidation products than the desired alicyclic ketones, the oxidation of the present invention is very easily kept under control and gives very good yields of the cyclic ketones.

Following is a specific non-limiting example of the practice of the present invention:

Example

Methylcyclohexane vapors and air, in the ratio 1:5 by volume, were preheated to 300° C. and passed over a silver oxide catalyst maintained at a temperature of 400–450° C. The catalyst was supported on asbestos and was contained in a copper tube 5 mm. in diameter and 20 cm. in length. Contact time was 0.3 second. The effluents were cooled, and separated by fractional distillation, yielding a fraction boiling between 160 and 170° C. which consisted largely of the three methylcyclohexanone isomers.

I claim:

1. The method of oxidizing cycloparaffins having from five to six carbon atoms in the ring to the corresponding cyclic ketone which comprises passing a vaporous feed consisting of said cycloparaffin and air over an oxidation catalyst consisting of silver oxide at a temperature of from 300 to 550° C., and recovering the corresponding cyclic ketone from the resulting effluent.

2. The method of oxidizing methylcyclohexane to methylcyclohexanone which comprises passing a vaporous feed consisting of methylcyclohexane and air over an oxidation catalyst consisting of silver oxide at a temperature of from 300 to 550° C. and for a contact time of from 0.1 to 10 seconds, and recovering methylcyclohexanone from the resulting effluent.

3. The method of oxidizing methylcyclohexane to methylcyclohexanone which comprises passing a vaporous mixture consisting of methylcyclohexane vapor and air in the ratio of 1:5 by

volume over an oxidation catalyst consisting of silver oxide at a temperature of from 400 to 450° C. and for a contact time of 0.3 second, and recovering methylcyclohexanone from the resulting effluent.

4. The method of oxidizing cycloparaffins having from five to six carbon atoms in the ring to the corresponding cyclic ketone which comprises passing a vaporous mixture of said cycloparaffin and an oxygen-containing gas over an oxidation catalyst consisting of silver oxide at a pressure such as to maintain vapor phase and at a temperature of from 300 to 550° C. and for a contact time of from 0.1 to 10 seconds, and recovering said corresponding cyclic ketone from the resulting effluent.

5. The method of oxidizing cycloparaffins having from five to six carbon atoms in the ring to the corresponding cyclic ketone which comprises passing a vaporous mixture of said cycloparaffin and a gas containing from 5 to 10 per cent by volume of oxygen over an oxidation catalyst consisting of silver oxide at a pressure such as to maintain vapor phase and at a temperature of from 300 to 550° C. and for a contact time of from 0.1 to 10 seconds, and recovering said corresponding cyclic ketone from the resulting effluent.

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