

UNITED STATES PATENT OFFICE

2,376,674

METHOD FOR OXIDATION OF AROMATIC
HYDROCARBONS

William S. Emerson and Josef W. Heyd, Dayton,
Ohio, assignors to Monsanto Chemical Com-
pany, a corporation of Delaware

No Drawing. Application July 24, 1943,
Serial No. 496,078

15 Claims. (Cl. 260—592)

This invention relates to a process for oxidizing aromatic hydrocarbons and more specifically comprises an improved process for obtaining ketones and carbinols by the catalytic oxidation of aromatic hydrocarbons, having alkyl substituents of at least 2 carbon atoms, in the liquid phase by means of an oxygen-containing gas in the presence of an oxidizing catalyst comprising in part cobalt carbonate.

It has heretofore been proposed, as in the Binapfl Patent No. 1,813,606 to effect the catalytic oxidation of such hydrocarbons as ethylbenzene in the presence of metallic oxide catalysts in order to obtain carbinols and ketones. We have found, however, that when oxidations are effected according to the process described in that patent, carboxylic acids are also formed in such quantities as to lower the yields of carbinols and ketones and also render the reaction product corrosive to the reaction equipment employed. This is also true of other known methods for the oxidation of aralkyl hydrocarbons to ketones and carbinols. For example, in the Loder Patent No. 2,245,528, the liquid phase oxidation of ethylbenzene in the presence of cobalt acetate and acetic acid gave a 58% yield of acetophenone, but there was obtained at the same time a 25.6% conversion to benzoic acid. Also, Senseman and Stubbs (Ind. Eng. Chem. 25, 1286 (1933)), employing a manganese dioxide catalyst, found when the oxidation was carried far enough to obtain appreciable yields of oxidation products that the oxidation of ethylbenzene with air often gave greater conversion to benzoic acid than to the carbinol and that the yield of acetophenone decreased as conversion to benzoic acid was decreased.

Now we have found that production of acid in the liquid phase oxidation of aralkyl hydrocarbons may be considerably suppressed, or even entirely eliminated by the use of cobalt carbonate in conjunction with metallic oxide catalysts. While even comparatively small proportions of cobalt carbonate with a metal oxide catalyst are instrumental in decreasing formation of carboxylic acids in the liquid phase oxidation of aralkyl hydrocarbons, we prefer to use amounts of cobalt carbonate in quantities which are at least equivalent by weight to the amount of metallic oxide employed. Particularly good results with respect to suppression of acid are obtained by using higher ratios of cobalt carbonate to metallic oxide; a 4:1 ratio of cobalt carbonate to metallic oxide has been found to be especially desirable. We find, for example, that a catalyst consisting of one part of a metal oxide such as chromium sesquioxide, Cr_2O_3 , and 4 parts of cobalt carbonate, CoCO_3 , effects good conversion of ethylbenzene into acetophenone and phenylmethylcarbinol and only 0.01% of benzoic acid; on the

other hand when the oxidation is conducted under similar conditions but in the presence of chromium sesquioxide, alone, as catalyst, the amount of benzoic acid formed is 2.1%. Ordinarily it is preferred to employ from 2% to 10% total weight of catalyst based upon the weight of hydrocarbon treated, although generally from 3% to 5% is sufficient.

The effect of cobalt carbonate in suppressing the formation of acid in the catalytic liquid phase oxidation of aralkyl hydrocarbons is surprising in that the results obtained appear to be specific for this particular carbonate. We have investigated the effect of other carbonates in this respect and have found, for example, that the use of chromium sesquioxide with manganese carbonate or with calcium carbonate results in the production of 2.4% and 1.2% of acid, respectively. That the use of cobalt carbonate with the same metal oxide under the same reaction conditions results in the formation of only 0.01% of acid was entirely unexpected.

The invention is further illustrated, but not limited, by the following examples:

Example 1

This example illustrates the liquid phase oxidation of ethylbenzene at atmospheric pressures in the presence of catalysts comprising various oxides in the presence and in the absence of cobalt carbonate.

The apparatus used for the oxidation consisted of a 1-liter, 3-necked flask, having standard-taper joints and being fitted with a thermometer, aluminum disperser thimble gas inlet and a spiral reflux condenser. The condenser was connected to a second spiral condenser at the bottom of which was fitted a 500 cc., 24/40 flask having a tube inlet from a water-pump.

The ethylbenzene and the catalyst employed were charged to the flask, air was led through the ethylbenzene-catalyst mixture, and the temperature of the reaction mixture was raised to about 120° C. by means of an oil-bath. Air was passed through the reaction mixture for approximately 28 hours, during which time the temperature varied from 115° C.—125° C.

400 g. of ethylbenzene was used for each run. The catalyst employed in each run amounted to 5% by weight of the ethylbenzene employed and consisted of 4 parts by weight of cobalt carbonate and 1 part by weight of the metal oxide or oxide mixture.

The constituents of the reaction mixture were separated in the following manner: Upon completion of the oxidation, i. e., after passage of air through the ethylbenzene-catalyst mixture, the reaction mixture was allowed to cool to room temperature, diluted with benzene, and filtered in order to remove the catalyst. The filtrate was

then treated with a 1% sodium hydroxide solution just to neutralization and the sodium benzoate solution, after concentration, was acidified, filtered and the benzoic acid was dried to constant weight. The material remaining after separating out the sodium benzoate was subsequently dried over potassium carbonate, filtered and submitted to fractional distillation. Upon separation of the benzene, the fraction boiling at 197° C.-202° C., and representing a mixture of acetophenone and methylphenylcarbinol was collected. Except in run No. 2, given below, the refractive index of this fraction corresponded to substantially pure acetophenone. The refractive index of the fraction collected in run No. 2 indicated that 4% conversion to the carbinol had been obtained.

The following results were obtained in a number of tests:

reaction product was worked up as in Example 1. The following results were obtained:

	Per cent
Conversion to ketone+carbinol	11.5
Conversion to carbinol	0.5
Conversion to acid	0.3
Ethylbenzene recovered	72.0
Minimum yield	41.2
Maximum yield	92.8

Pressure oxidation of ethylbenzene as described above in the presence of chromium sesquioxide alone results in a 2.0% conversion to acid.

Example 3

This example provides a comparison of results obtained with respect to decrease in conversion to acid by using as catalysts mixtures of various carbonates with metal catalysts. Ethylbenzene

Test No.	Catalyst used with CoCO ₃	Per cent converted to ketone and carbinol	Per cent converted to acid	Ethylbenzene recovered	Yield of ketone and carbinol	
					Minimum yield	Maximum yield
1	Cr ₂ O ₃	18.4	0.01	75.5	70.4	89.0
2	V ₂ O ₅	10.6	0.09	81.0	55.5	89.9
3	Cr ₂ O ₃ +CoO ₂	25.2	0.13	66.1	74.0	90.5
4	Pb benzoate	24.4	0.00	52.7	51.5	88.8

In the absence of cobalt carbonate, however, the oxide catalysts give the following yields of acid under the same reaction conditions:

	Per cent converted to acid
Test No. 1 without CoCO ₃	2.10
Test No. 2 without CoCO ₃	1.75
Test No. 3 without CoCO ₃	1.70
Test No. 4 without CoCO ₃	1.70

In the tests, the minimum yields indicated the per cent theoretical yield of acetophenone or a mixture of acetophenone and methylphenylcarbinol based on the unrecovered ethylbenzene. Material balanced showed, however, that some mechanical loss occurred during the oxidation, for example, by volatilization of either the ethylbenzene or the product. The maximum yields shown above take such losses into consideration and represent the yield expected in a plant provided with efficient recovery means. The unconverted ethylbenzene may, of course, be returned to the reactor for further treatment.

Example 2

This example illustrates the liquid phase oxidation of ethylbenzene under superatmospheric pressure in the presence of a catalyst consisting of 4 parts of cobalt carbonate and 1 part of chromium sesquioxide.

Oxidation was effected in an autoclave at a pressure of 250 pounds gauge and a temperature of 130° C. for a time of 6 hours. 400 g. of ethylbenzene and 20 g. of the catalyst mixture was charged into the autoclave, and air was led into it continuously with stirring and continuously bled out while maintaining the pressure indicated above. At the end of the run, the autoclave was allowed to cool to room temperature, and the

was oxidized as in Example 1, except that the following catalysts were employed:

	Catalyst (4 parts carbonate; 1 part oxide)	Per cent conversion to acid
45	V ₂ O ₅ +CaCO ₃	2.30
	V ₂ O ₅ +CoCO ₃	0.09
	Cr ₂ O ₃ +MnCO ₃	2.40
	Cr ₂ O ₃ +CaCO ₃	1.20
	Cr ₂ O ₃ +CoCO ₃	0.01
	Pb benzoate+CaCO ₃	1.80
	Pb benzoate+CoCO ₃	0.00
50	Cr ₂ O ₃ +Co(OH) ₂ +CaCO ₃	4.70
	Cr ₂ O ₃ +Co(OH) ₂ +CoCO ₃	0.30

The use of cobalt carbonate as a component of the oxidizing catalyst thus appears to have a specific effect in decreasing formation of acid in the liquid phase oxidation of ethylbenzene.

Example 4

This example shows the liquid phase oxidation of isopropylbenzene, employing the procedure used in Example 1, but using isopropylbenzene instead of ethylbenzene and maintaining the reaction temperature at 130° C.-140° C. instead of at temperatures used in Example 1. In order to show the specific effect of cobalt carbonate as a constituent of the catalyst, tests were made in the presence of chromium sesquioxide, alone, and in the presence of a mixture consisting of 1 part of chromium sesquioxide and 4 parts of cobalt carbonate.

Catalyst used	Per cent converted to ketone and carbinol	Per cent converted to acid	Iso-propylbenzene recovered	Minimum yield	Maximum yield
Cr ₂ O ₃ -----	16.6	1.20	66.3	49.7	78.0
Cr ₂ O ₃ +CoCO ₃ ---	16.6	0.10	77.0	72.2	83.7

Yields were calculated as in Example 1.

When oxidizing isopropylbenzene, the products obtained are acetophenone and dimethylphenylcarbinol. When a carboxylic acid is found, as in the absence of cobalt carbonate, such acid is benzoic acid.

The use of cobalt carbonate in admixture with other known oxidation catalysts, for example, the oxides or hydroxides of copper, manganese, cobalt, lead, cerium, uranium, etc., also results in suppressing the formation of acid in the liquid phase oxidation of aralkyl hydrocarbons having an alkyl group of at least 2 carbon atoms.

While the present process has been illustrated, particularly with ethylbenzene and isopropylbenzene, it is likewise applicable to liquid phase oxidation of other aralkyl hydrocarbons in which there is present at least one alkyl group of two or more carbon atoms, for example, the diethylbenzenes, n-propylbenzene, isobutylbenzene, cymene, the ethyl- or isopropyl-naphthalenes, etc. The use of cobalt carbonate in admixture with the usual catalysts of oxidation likewise results in the suppression or entire elimination of reactions leading to the formation of acids and a consequent production of the corresponding ketones and carbinols in good yields.

As will be apparent to those skilled in the art, the selection of optimum temperature, pressure and other reaction conditions will vary with the aralkyl hydrocarbon which is to be oxidized. Generally, conditions which give optimum yields of ketone and carbinol in the presence of the known catalysts of oxidations give good results when operating in the presence of mixtures of such catalysts with cobalt carbonate.

The temperature employed for oxidation should preferably be maintained at a point above the decomposition temperature of peroxides which may form at temperatures below 80° C. or 85° C. Suitable temperatures for the reaction, when it is carried out at atmospheric pressure, may be within the range of from 100° C. to the boiling point of the hydrocarbon at atmospheric pressure which, in the case of ethylbenzene, is 135° C. at atmospheric pressure and in the case of isopropylbenzene is 145° C. It is, of course, not necessary that the process be restricted to operation at atmospheric pressure since satisfactory operation may also be obtained at pressures below normal atmospheric pressure as well as at pressures above atmospheric. Hence by the employment of pressures it is possible to employ temperatures above the normal boiling point of the hydrocarbon to be oxidized. Such temperatures, should generally, however, be maintained below 165° C.

Reaction may be effected in presence or absence of a diluent of either the hydrocarbon employed or the oxidizing medium. Also, while we prefer to use air as the oxidizing medium we may use pure oxygen or a prepared mixture of oxygen with an inert gas.

What we claim is:

1. In the process of oxidizing aralkyl com-

pounds in which the alkyl group contains at least 2 carbon atoms and in which process the oxidation is effected in the liquid phase by means of gaseous oxygen, the improvement which comprises carrying out the oxidation in the presence of cobalt carbonate.

2. In the process of oxidizing the alkyl group in aralkyl hydrocarbons, and in which process said alkyl group contains at least 2 carbon atoms, the improvement which comprises carrying out the oxidation in the liquid phase by means of gaseous oxygen in the presence of a metal oxide oxidation catalyst and cobalt carbonate.

3. In the process of oxidizing ethylbenzene in the liquid phase by means of gaseous oxygen the improvement which comprises contacting said ethylbenzene with oxygen, in the presence of cobalt carbonate.

4. The process of oxidizing an alkylbenzene to an aryl ketone, which comprises contacting said alkylbenzene in the liquid phase with gaseous oxygen in the presence of a metal oxide oxidation catalyst and cobalt carbonate.

5. The process of producing acetophenone which comprises contacting ethylbenzene in the liquid phase with oxygen in the presence of a metal oxide oxidation catalyst and cobalt carbonate.

6. The process defined in claim 1 in which the oxidation is effected at a temperature above 100° C. but below the boiling point of said aralkyl compound.

7. The process defined in claim 5 in which the oxidation is effected at a temperature between 100° C. and 165° C.

8. The process for producing a mixture of acetophenone and methylphenylcarbinol which comprises contacting ethylbenzene in the liquid phase with gaseous oxygen in the presence of a metal oxide oxidation catalyst and cobalt carbonate.

9. The process for producing a mixture of acetophenone and methylphenylcarbinol, which comprises contacting ethylbenzene in the liquid phase with gaseous oxygen in the presence of an oxidation catalyst comprising a mixture of Cr₂O₃ and CoCO₃.

10. The process defined in claim 9 in which the oxidation catalyst consists of 4 parts by weight of CoCO₃ and 1 part by weight of Cr₂O₃.

11. The process defined in claim 9 in which the oxidation is carried out at temperatures between 100° C. and 165° C.

12. The process for producing a mixture of acetophenone and dimethylphenylcarbinol, which comprises contacting isopropylbenzene in the liquid phase with gaseous oxygen in the presence of a metal oxide oxidation catalyst and cobalt carbonate.

13. The process for producing a mixture of acetophenone and dimethylphenylcarbinol, which comprises contacting isopropylbenzene in the liquid phase with gaseous oxygen in the presence of an oxidation catalyst comprising a mixture of Cr₂O₃ and CoCO₃.

14. The process defined in claim 13 in which the oxidation catalyst consists of 4 parts by weight of CoCO₃ and 1 part by weight of Cr₂O₃.

15. The process defined in claim 13 in which the oxidation is carried out at temperatures between 100° C. and 165° C.

WILLIAM S. EMERSON.
JOSEF W. HEYD.