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(54) PROCESS FOR PREPARING DIACETYLBENZENE

(71) We, ASAHI KASEI KOGYO KABUSHIKI KAISHA, a corporation organized under the laws of Japan, of 25—1, Dojimahamadori 1-chome, Kita-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for preparing diacetylbenzene from diethylbenzene, ethylacetophenone or a mixture thereof by a liquid phase oxidation reaction using a molecular oxygen-containing gas.

Diacetylbenzene is used as an intermediate, for example, for preparing divinylbenzene which is a cross-linking agent for high molecular weight polymers, by a hydrogenation and a dehydration, and for preparing an aromatic diamine by an oximation and a Beckmann rearrangement. Also, diacetylbenzene is a starting material for preparing heat resistant polymers and is generally one of the promising compounds in the chemical industry.

In general, in the liquid phase oxidation of an ethyl group bonded to a benzene nucleus, the corresponding carboxylic acid is readily produced. Accordingly, in order selectively to produce an acetyl substituted benzene, which is an intermediate compound in the oxidation of the ethyl substituted benzene to the corresponding carboxylic acid, not only are there restrictions on the starting materials, but also it is necessary to take special precautions in the choice of catalysts and of reaction conditions.

Furthermore, in the production of diacetylbenzene, which is a difunctional compound, the following further restrictions are imposed on the reaction conditions and purification methods in addition to those mentioned above.

A first restriction originates from the reactivity of ethylacetophenone. In general, in the autoxidation reaction of an alkylbenzene, the reactivity is in accordance with the Hammett rule and its reaction constant ρ is a negative value. Thus, it is more difficult to oxidize the ethyl group of ethylacetophenone whose acetyl group exhibits a strong electron attraction, and the reaction conditions become more rigorous. As a result, the selectivity to diacetylbenzene tends to decrease, and more severe restrictions on the choice of catalysts and of reaction conditions are imposed.

A second restriction arises from the need to suppress the formation of compounds which hinder the oxidation reaction as the oxidation reaction proceeds, and the oxidation reaction tends to stop. For this reason, the oxidation reaction is carried out at a low conversion in most cases. Thus, when diacetylbenzene is prepared from diethylbenzene at a low conversion rate, the yield per volume of the reactor is reduced and the quantity of heat needed to separate the products from the starting material is remarkably increased. Furthermore, since the oxidation reaction of diethylbenzene to diacetylbenzene is a sequential reaction through ethylacetophenone as an intermediate, at low conversions, the oxidation reaction stops at the ethylacetophenone stage, and as a result very little diacetylbenzene is formed. Thus, in this oxidation reaction, the formation of compounds which hinder the oxidation reaction must be suppressed to achieve a high conversion.

A third restriction arises in the purification of diacetylbenzene. Since diacetylbenzene is a difunctional compound having a high boiling point, the decomposition and polymerisation of diacetylbenzene take place when diacetylbenzene is distilled in the presence of the catalyst, and therefore the catalyst must be removed prior to the distillation of the diacetylbenzene.

A fourth restriction is due to the selectivity to diacetylbenzene. Since diacetylbenzene is a difunctional compound, various by-products can be formed, and some of them have boiling points which are very close to each other. Thus, since it becomes more difficult to obtain a product of high purity, the selectivity to the products must be high.

Accordingly, in preparing diacetylbenzene from diethylbenzene as a starting material on an industrial scale, the purification system must be taken into account in addition to the oxidation reaction system. More specifically, a technique must be established in which the oxidation reaction at a high conversion of the starting material can be achieved while the formation of compounds hindering the oxidation reaction is suppressed, the selectivity to the product at a high conversion of the starting material is increased, and a regenerable catalyst can be efficiently separated from the reaction mixture liquid.

It is known that diacetylbenzene can be prepared by the liquid phase oxidation of diethylbenzene as a starting material using an oil-soluble metal salt catalyst such as a naphthenate of a transition metal. However, according to this method, the decomposition of diacetylbenzene partially takes place in the separation procedure using a distillation after the oxidation reaction and it is difficult to obtain the product in a high purity and in a high yield. On the other hand, Japanese Patent Application (OPI) No. 72231/1974 describes a method of purifying diacetylbenzene which comprises treating the reaction mixture, which has been obtained by the liquid phase oxidation of diethylbenzene using oxygen or an oxygen-containing gas and which contains, as the main component, diacetylbenzene, as such or after a flash distillation, with an alkali, and distilling the reaction mixture thus treated. When the catalyst is removed according to this invention, it is necessary to provide another step in the regeneration of recovered catalyst for reuse.

According to the present invention there is provided a process for preparing diacetylbenzene by a liquid phase oxidation reaction which comprises contacting a heterogeneous mixture of (A) 98 to 25 percent by volume of an organic liquid phase containing at least one of diethylbenzene and ethylacetophenone and (B) from 2 to 75 percent by volume of an aqueous liquid phase containing, as a catalyst, at least 0.01 mol/l of at least one water-soluble salt of a metal consisting of manganese, cobalt, nickel, chromium, copper or iron and having a pH of from 1 to 6, with a molecular oxygen-containing gas at a temperature of from 100°C to about 180°C under a pressure of from 1 to 50 Kg/cm^2 to effect the liquid phase oxidation reaction; separating the resulting reaction mixture liquid into the aqueous liquid phase and the organic liquid phase, and recovering diacetylbenzene from the separated organic liquid phase by distillation.

Suitable starting materials which may be employed in this invention include the para-, meta- and ortho-isomers of diethylbenzene and ethylacetophenone and any mixtures thereof. In general, a mixture of the para-isomer and meta-isomer of diethylbenzene in a weight ratio of from 30 to 70, which is a by-product of the preparation of ethylbenzene, can be advantageously employed. Also, *p*-ethylacetophenone which is obtained in the acetylation of ethylbenzene and is easily available can be quite suitably used as a starting material, and *p*-diacetylbenzene can be prepared therefrom.

In preparing diacetylbenzene from diethylbenzene according to this invention, first, one of the two ethyl groups of the diethylbenzene is oxidized to form ethylacetophenone and, second, the ethyl group of the resulting ethylacetophenone is oxidized to form diacetylbenzene. Thus, two oxidation steps are involved in the preparation of diacetylbenzene from diethylbenzene and accordingly two processes are possible. One process is a two-step method comprising isolating, as an intermediate, the ethylacetophenone obtained in the first oxidation step and converting the ethylacetophenone into diacetylbenzene in the second oxidation step. The other process is a one-step method comprising conducting the two oxidation steps sequentially without isolating the ethylacetophenone as an intermediate. According to the two-step method, the isolated ethylacetophenone contains α-ethylphenylethanol which is the corresponding alcohol derivative but this compound can be ultimately converted into diacetylbenzene. In general, the two-step method requires the use of more complicated equipment for preparing diacetylbenzene than the one-step method.

Appropriate catalysts which are employed in this invention include water-soluble salts of manganese, cobalt, nickel, chromium, copper and iron. Of these water-soluble metal salts, manganese salts and cobalt salts are preferred. Suitable water-soluble salts which can be used include organic acid salts and inorganic acid salts. Examples of organic acid salts include, for example, the acetates and propionates, and examples of inorganic acid salts include, for example, the sulfates, nitrates and chlorides. Of these salts, the acetates are preferred. With regard to the oxidation state of the metal in the salts, manganese (II), cobalt (II), nickel (II), chromium (III), copper (II) and iron (III) are preferred.

Specific examples of suitable catalysts include manganese (II) acetate, manganese (II) chloride, cobalt (II) acetate, cobalt (II) propionate, cobalt (II) sulfate, cobalt (II) nitrate, cobalt (II) chloride, nickel (II) acetate, nickel (II) propionate, nickel (II) sulfate, nickel (II) nitrate, nickel (II) chloride, chromium (III) acetate, chromium (III) propionate, chromium (III) sulfate, chromium (III) nitrate, chromium (III) chloride, iron (III) acetate iron (III) propionate, iron (III) sulfate, iron (III) nitrate and iron (III) chloride and any mixtures thereof.

The catalysts used in the process of this invention are employed in the form of an aqueous solution thereof.

The concentration of the catalyst in the aqueous liquid phase which is required in the process of the present invention is at least 0.01 mol/l. When the concentration of the catalyst is less than 0.01 mol/l the rate of the oxidation reaction is reduced and the selectivity to diacetylbenzene is decreased. A preferred concentration of the catalyst is less than 0.01 mol/l or more, and a more preferred concentration of the catalyst ranges from 0.1 to 1.0 mol/l.

The presence of an aqueous liquid phase in the oxidation reaction is essential in the process of this invention. The presence of the aqueous phase not only facilitates separation of the catalyst in the recovery process for the catalyst after the oxidation reaction but also suppresses the formation of by-products to provide a high selectivity to the products at a high conversion. Thus, the amount of the aqueous liquid phase, based on the total volume of the liquid, which is necessary in this invention is at least 2 percent by volume. When the amount of the aqueous liquid phase is less than 2 percent by volume, a stable emulsion tends to form and the separation and recovery of the catalyst after the oxidation reaction becomes difficult. Also, from the viewpoint of productivity, the amount of the aqueous liquid phase is at most 75 percent by volume. A preferred amount of the aqueous liquid phase ranges from 5 to 60 percent by volume and a more preferred amount ranges from 10 to 50 percent by volume.

The pH of the aqueous liquid phase is adjusted with an acid whose anion corresponds to the anion of the catalyst alone or with sulfuric acid or an aqueous solution of ammonia to prevent the formation of precipitates due to the decomposition of the catalyst. The pH of the aqueous liquid phase used in the process of this invention ranges from 1 to 6. When the pH of the aqueous liquid phase is lower than 1, the rate of the oxidation reaction is increased but the selectivity to diacetylbenzene is reduced. On the other hand, when the pH of the aqueous liquid phase is higher than 6, precipitates are formed by the hydrolysis of the catalyst. A preferred pH of the aqueous liquid phase ranges from 3 to 5.

The molecular oxygen-containing gas which is employed as an oxidizing agent in the process of this invention may be pure oxygen or oxygen diluted with an inert gas such as nitrogen and/or carbon dioxide. Air is preferably employed as the molecular oxygen-containing gas. The oxidation reaction according to the process of this invention proceeds smoothly with at least one percent by volume of molecular oxygen based on the total gas volume in a reactor. However, the amount of the molecular oxygen present in the gas in the reactor is preferably at most 15 percent by volume from the viewpoint of avoiding explosions. A more preferred amount of molecular oxygen ranges from 2 to 10 percent by volume.

The oxidation reaction according to the process of this invention is carried out at a temperature ranging from 100°C to 180°C. In general, when the oxidation reaction temperature is lower than 100°C, the rate of the oxidation reaction is low, and on the other hand, when the temperature is higher than 180°C, the selectivity to the product is reduced. The preferred temperature depends upon factors such as e.g. the choice of catalyst, the concentration of catalyst chosen, and the pH of the aqueous liquid phase employed. When cobalt (II) acetate or manganese (II) acetate is employed in a concentration of 0.2 mol/l and the aqueous liquid phase containing the cobalt (II) acetate or manganese (II) acetate has a pH of 3 to 5, a preferred oxidation reaction temperature with regard to cobalt (II) acetate ranges from 120°C to 150°C and with regard to manganese acetate (II) ranges from 130°C to 160°C.

The effect of the oxidation reaction pressure on the oxidation reaction according to the process of this invention is smaller than that of the oxidation reaction temperature. In general, the rate of the oxidation reaction temperature increases with higher pressures. The present invention requires a pressure sufficient to prevent the reaction mixture solution from volatilizing, and from the viewpoint of apparatus restrictions a lower pressure is preferred. The oxidation reaction pressure according to the process of this invention ranges from 1 to 50 Kg/cm². A preferred pressure ranges from 2 to 30 Kg/cm² and a more preferred pressure ranges from 3 to 20 Kg/cm².

In the present invention, in order to promote the contact of the starting material with the molecular oxygen-containing gas, fine bubbles are preferably maintained in the reaction mixture liquid with sufficient stirring. The oxidation reaction according to the process of this invention will proceed smoothly by maintaining the amount of bubbles in the reaction mixture liquid in a range which is typically from 3 to 30 percent by volume, and preferably from 5 to 20 percent by volume.

The material of the reactor affects the oxidation reaction of the process of this invention, and a reactor which is corrosion-resistant to the reaction mixture liquid is preferred. For example, when a reactor composed of iron is employed, the rate of the oxidation reaction is low and the oxidation reaction stops at a low conversion, and, furthermore, the selectivity to diacetylbenzene is remarkably reduced. Preferred materials for the reactor are titanium and glass or reactors lined with titanium or glass. Reactors in which the areas contacting the reaction mixture liquid are lined with titanium or glass are also preferred.

The process according to this invention can be carried out batchwise, semi-continuously or continuously. In the batchwise process, a mixture of an organic liquid phase containing diethylbenzene or ethylacetophenone or both of these materials and an aqueous liquid phase containing a specific catalyst as described above is charged in a reactor, and a molecular oxygen-containing gas is fed therein at a specific temperature as described above under a specific pressure as described above with vigorous stirring. In the continuous process, the starting material is fed at a constant rate as the oxidation reaction progresses, while the contents of the reactor are withdrawn at a constant rate.

In the batchwise process, the concentration of the starting material, i.e., the diethylbenzene and/or the ethylacetophenone, in the organic liquid phase fed in a reactor is typically 100 percent by weight, and, when the concentration of diacetylbenzene reaches a level of from 5 to 70 percent by weight, and preferably a level of 10 to about 50 percent by weight, the reaction mixture liquid is withdrawn from the reactor. In the continuous process, the concentration of the diethylbenzene and/or the ethylacetophenone as the starting material in the organic liquid phase of a reactor is at least 10 percent by weight from the viewpoint of the rate of the oxidation reaction. Also when the concentration of the diacetylbenzene produced is less than 5 percent by weight, the quantity of heat necessary for recovering the diacetylbenzene produced from the organic liquid phase becomes too large. Thus, the concentration of the diethylbenzene and/or ethylacetophenone in the organic liquid phase in a reactor typically ranges from 10 to 95 percent by weight, and preferably ranges from 30 to 90 percent by weight.

The reaction mixture liquid which is collected is separated into the organic liquid phase and the aqueous liquid phase. The separation of the organic liquid phase from the aqueous liquid phase can be effected using conventional methods such as a coalescer, settling or centrifuging. The removal of the catalyst is essentially completed in this separation of the organic liquid phase from the aqueous liquid phase, and then the product is recovered from the organic liquid phase by distillation. Where distillation is used as a product recovery method, the decomposition and polymerization of diacetylbenzene and ethylacetophenone, which are observed in the case of an oil-soluble catalyst, are not observed.

According to the process of this invention, the selectivity to the product is increased and, as a result, the formation of by-products having a high boiling point due to side reactions is reduced. More specifically, in the distillation of the organic liquid phase separated from the aqueous liquid phase, the distillation residue based on the total weight of the diethylbenzene, the ethylacetophenone and the diacetylbenzene fed is at most 3 percent by weight. Thus, the amount of diacetylbenzene which is lost together with the distillation residue is low, and the recovery rate of diacetylbenzene by distillation based on the weight of the diacetylbenzene fed approaches 95 to 98 percent by weight. These high values show that hardly any decomposition and polymerization of diacetylbenzene occur in the distillation.

Furthermore, if necessary or if desired, the organic liquid phase separated from the aqueous liquid phase after the oxidation reaction is treated with either an aqueous acidic solution or an aqueous alkaline solution, either alone or successively with both of these solutions, to remove a minute amount of the catalyst and the by-produced carboxylic acids remaining in the organic liquid phase, and, subsequently, in recovering the diacetylbenzene by distillation, the resulting organic liquid phase is distilled with a higher distillation efficiency. Suitable aqueous acidic solutions which can be used include, for example, dilute aqueous solutions of hydrochloric acid and/or sulfuric acid. Suitable aqueous alkaline solutions of sodium hydroxide and/or potassium hydroxide.

The distillation of the organic liquid phase in recovering the diacetylbenzene according to the process of this invention may be conducted either at atmospheric pressure or under reduced pressure such as at from 760 mmHg to 1 mmHg. The boiling points of diethylbenzene, ethylacetophenone and diacetylbenzene are from 180°C to 184°C/760 mmHg, from 120°C to 126°C/20 mmHg and from 153°C to 155°C/10 mmHg, respectively.

The diethylbenzene and ethylacetophenone recovered by distillation can be reused in the oxidation reaction step of the process of this invention as a starting material without any decrease in the rate of the oxidation reaction and the selectivity to the products. Also, the aqueous liquid phase separated from the organic liquid phase, if the catalyst concentration is sufficiently high, can be reused without any decrease in the rate of the oxidation reaction and the selectivity to the products, as compared with a newly prepared aqueous catalyst solution. However, in the oxidation reaction step of the process of this invention, two moles of water based on one mole of diacetylbenzene are formed, and, as a result, the concentration of the catalyst in the aqueous liquid phase is reduced. Thus, in continuously carrying out the oxidation reaction step in the process of this invention, the water formed during the oxidation reaction must be removed to maintain the concentration of the catalyst constant. Accordingly in the process of this invention, the aqueous liquid phase separated from the organic liquid phase can be reused for the oxidation reaction step after the concentration of the catalyst in the aqueous liquid phase and the pH of the aqueous liquid phase have been adjusted.

Thus, according to a particular embodiment, the process according to the invention comprises adjusting the concentration and pH of the aqueous liquid phase separated from the organic liquid phase after the liquid phase oxidation reaction to at least 0.01 mol/l and from 1 to 6, respectively, and reusing the resulting aqueous liquid phase for the liquid phase oxidation reaction.

The oxidation reaction step can be monitored using gas chromatographic analysis of the organic liquid phase after the oxidation reaction step. The concentration of the oxygen in the discharged gas can be continuously measured by passing the discharged gas through a meter for measuring the oxygen concentration, and, from this result, the partial pressure of the oxygen during the oxidation reaction can be calculated. Also, from the results of gas chromatography, the first order reaction rate constants, k'_1 and k'_2, the selectivities to the products S_M, S_D, S_1 and S_2 and the conversion of the starting material can be obtained as shown below:

$$[\mathrm{DEB}] \xrightarrow[k'_1]{O_2} [\mathrm{MAB}] \xrightarrow[k'_2]{O_2} [\mathrm{DAB}]$$

$$\frac{d[\mathrm{DEB}]}{dt} = -k'_1[\mathrm{DEB}]$$

$$\frac{d[\mathrm{MAB}]}{dt} = -k'_2[\mathrm{MAB}]$$

$$S_M(\%) = \frac{[\mathrm{MAB}]}{[\mathrm{DEB}]_0 - [\mathrm{DEB}]} \times 100$$

$$S_D\,(\%) = \frac{[DAB]}{[DEB]_o - [DEB]} \times 100$$

(S_M and S_D are selectivity indices in the batchwise process)

$$S_1\,(\%) = S_M + S_D$$

$$S_2\,(\%) = \frac{[DAB]}{[DEB]_o - [DEB] + [MAB]_o - [MAB]} \times 100$$

(S_1 and S_2 are selectivity indices in the continuous process).

$$\text{Conversion}\,(\%) = \frac{[DEB]_o - [DEB]}{[DEB]_o} \times 100$$

wherein [DEB], [MAB] and [DAB] respectively represent the molar concentrations of diethylbenzene, ethylacetophenone and diacetylbenzene in the organic liquid phase after the oxidation reaction, and $[DEB]_o$ represents the molar concentration of diethylbenzene in the starting organic liquid.

According to the process of this invention, diacetylbenzene can be prepared with a high selectivity at a high conversion of the starting material by particularly employing a specific catalyst, a specific concentration range for the catalyst in an aqueous phase, a specific pH range for the aqueous liquid phase, and a specific oxidation reaction temperature range and pressure range as described above. Also, the separation of the catalyst used in the oxidation reaction can be easily and effectively carried out by employing, as a reaction system, a heterogeneous system of the organic liquid phase containing the starting material and the aqueous liquid phase containing the catalyst.

The present invention will now be illustrated in greater detail by the following Examples.

Example 1.

In a 500 ml titanium reactor equipped with two baffle plates, a stirrer, a gas inlet nozzle, a sampling nozzle, a reflux condenser, a thermometer, a pressure gauge, a gas flow meter and a meter for measuring oxygen concentration there were charged 240 g of diethylbenzene (para-isomer:meta isomer weight ratio = 30:70) and 60 g of a 0.2 mol/l aqueous solution of each of the various catalysts as set forth in Table 1 below whose pH had been adjusted to 4 with an acid whose anion corresponded to the anion of the catalyst alone or with sulfuric acid and an aqueous solution of ammonia.

After the air in the reactor was replaced by gaseous nitrogen, the temperature was increased to the temperature set forth in Table 1 below, and the pressure in the reactor was adjusted to 15 Kg/cm² with stirring at a rate of 1,200 r.p.m. The oxidation reaction was carried out by continuously feeding air as the molecular oxygen-containing gas into the reactor while maintaining the concentration of oxygen in the discharged gas at a level of 3 to 5 percent by volume and controlling the oxidation reaction temperature within ±2°C of the temperature set forth in Table 1.

During the reaction, the reaction mixture liquid was sampled at intervals, each of the samples was separated into the organic liquid phase and the aqueous liquid phase, and the organic liquid phase separated was gas chromatographed. The results obtained are shown in Table I. The values of the conversion, S_M, S_D and S_1 are those when the amount of diethylbenzene became nearly constant.

TABLE I.

Run No.	Catalyst	Reaction Temperature (°C)	k'_1 (sec^{-1})	Conversion (%)	S_M (%)	S_D (%)	S_1 (%)
1	Manganese (II) acetate	140	2.1×10^{-4}	87	52	25	77
2	Cobalt (II) acetate	140	4.7×10^{-4}	96	51	31	82
3	Copper (II) acetate	140	1.5×10^{-4}	42	74	12	86
4	Chromium (III) acetate	140	1.1×10^{-4}	58	60	16	76
5	Nickel (II) acetate	140	0.65×10^{-4}	55	56	10	66
6	Iron (III) acetate	140	0.65×10^{-4}	46	42	8	50
7	Manganese (II) sulfate	160	1.8×10^{-4}	70	53	18	71
8	Manganese (II) chloride	160	0.93×10^{-4}	56	30	8	38
9	Manganese (II) nitrate	140	1.5×10^{-4}	75	47	21	68
10	Manganese (II) propionate	140	1.9×10^{-4}	81	50	20	70

Example 2.

Using the same type of reactor as described in Example 1, the same procedures as described in Example 1 were repeated except that the concentration of the catalyst in the aqueous liquid phase was varied as set forth in Table II below and the concentration of the oxygen in the discharged gas was adjusted to a level of from 2 to 10 percent by volume.

The results obtained are shown in Table II below. The values of the conversion, S_M, S_D and S_1 are those when the amount of diethylbenzene became nearly constant.

TABLE II

Run No.	Catalyst	Concentration of Catalyst (mol/l)	k'_1 (sec^{1})	Conversion (%)	S_M (%)	S_D (%)	S_1 (%)
1	Manganese (II) acetate	0.01	0.1×10^{-4}	50	35	4	39
2	—do—	0.04	3.9×10^{-4}	84	48	19	67
3	—do—	0.2	6.7×10^{-4}	94	51	35	86
4	—do—	0.4	8.5×10^{-4}	92	37	33	70
5	—do—	0.8	6.6×10^{-4}	90	28	34	62
6	—do—	1.6	6.7×10^{-4}	87	38	28	66
7	Cobalt (II) acetate	0.01	0.05×10^{-4}	45	31	11	42
8	—do—	0.04	0.44×10^{-4}	83	36	15	51
9	—do—	0.2	3.1×10^{-4}	91	47	38	85
10	—do—	0.8	3.2×10^{-4}	91	47	45	92
11	—do—	1.5	3.5×10^{-4}	94	45	42	87

Reaction temperature: Manganese (II) acetate: 160°C
Cobalt (II) acetate : 130°C

Example 3.

Using the same type of reactor as described in Example 1, the same procedures as described in Example 1 were repeated except that the pH of the aqueous liquid phase was varied as set forth in Table III below. The pH was adjusted with acetic acid if such were possible to obtain the pH shown; otherwise, sulfuric acid or an aqueous solution of ammonia was used.

The results obtained are shown in Table III below. The values of the conversion, S_M, S_D and S_1 are those when the amount of diethylbenzene became nearly constant.

TABLE III.

Run No.	Catalyst	pH of Aqueous Phase	k'_1 (sec^1)	Conversion (%)	S_M (%)	S_D (%)	S_1 (%)
1	Cobalt (II) acetate	1.0	8.0×10^{-4}	80	27	25	52
2	—do—	3.0	2.7×10^{-4}	77	41	38	79
3	—do—	5.0	2.5×10^{-4}	91	46	40	86
4	—do—	6.0	2.4×10^{-4}	88	48	37	85
5	—do—	7.2	1.5×10^{-4}	85	55	32	87
6	Manganese (II) acetate	1.0	12.0×10^{-4}	70	32	18	50
7	—do—	2.0	9.7×10^{-4}	86	42	21	63
8	—do—	3.5	6.7×10^{-4}	93	50	36	86
9	—do—	6.5	5.7×10^{-4}	93	42	31	73

Reaction temperature: Cobalt (II) acetate: 130°C
Manganese (II) acetate: 160°C
Concentration of catalyst: 0.2 mol/l
Precipitates of the catalyst were formed in Run Nos. 5 and 9.

Example 4.

Using the same type of reactor as described in Example 1 the same procedures as described in Example 1 were repeated except that the oxidation reaction temperature was varied as set forth in Table IV below.

The results obtained are shown in Table IV. The values of the conversion, S_M, S_D and S_I are those when the amount of diethylbenzene became nearly constant. From these values in Table IV, the activation energy of the oxidation reaction was calculated and the results are as follows:

Cobalt (II) acetate: 14.8 Kcal/M

Manganese (II) acetate: 20.2 Kcal/M

TABLE IV

Run No.	Catalyst	Reaction Temperature (°C)	k'_1 (sec^{-1})	Conversion (%)	S_M (%)	S_D (%)	S_1 (%)
1	Cobalt (II) acetate	100	0.45×10^{-4}	60	43	20	63
2	—do—	120	1.39×10^{-4}	89	45	32	77
3	—do—	130	2.7×10^{-4}	91	47	38	85
4	—do—	140	4.1×10^{-4}	96	51	31	80
5	—do—	150	5.7×10^{-4}	90	43	33	76
6	—do—	180	17.3×10^{-4}	98	18	17	35
7	Manganese (II) acetate	120	0.56×10^{-4}	68	39	14	53
8	—do—	140	1.9×10^{-4}	85	46	20	66
9	—do—	150	3.6×10^{-4}	92	49	27	76
10	—do—	160	6.6×10^{-4}	94	51	35	86
11	—do—	180	15.8×10^{-4}	98	33	29	62
12	—do—	200	45.0×10^{-4}	99	13	11	24

Concentration of catalyst: 0.2 mol/l
pH of aqueous liquid phase: 3.6 to 4.0

Example 5.

Using a 500 ml glass reactor equipped with the same devices as in Example 1, the same procedures as described in Run No. 2 in Example 1 were repeated. The results obtained are as follows:

k'_1: 4.6×10^{-4}

Conversion: 93%

S_M: 49%

S_D: 36%

S_1: 85%

These values are almost the same as those obtained by using a titanium reactor.

Example 6.

Using a 500 ml SUS 32 (ASTM: A240 Type 316) reactor equipped with the same devices as in Example 1, the same procedures as described in Run No. 1 in Example 1 were repeated. The results obtained are shown in Table V.

TABLE V.

Run No.	k'_1 (sec^{-1})	Conversion (%)	S_M (%)	S_D (%)	S_1 (%)
1	4.5×10^{-4}	84	71	16	87
2	2.3×10^{-4}	75	75	8	83
3	0.7×10^{-4}	50	76	4	80

Note: Run No. 1: A newly ground reactor was employed.
Note: Run No. 2: A reactor covered with an oxidized surface in a passive state was employed.
Note: Run No. 3: A reactor covered with a corroded surface after several uses was employed.

Example 7.

Using a 500 ml titanium reactor equipped with the same devices as in Example 1, the same procedures as described in Run No. 10 in Example 4 were repeated except that either the catalyst or the diethylbenzene recovered in Run No. 10 of Example 4 was employed. The results obtained are shown in Table VI below.

TABLE VI.

Run No.	k'_1 (sec^{-1})	Conversion (%)	S_M (%)	S_D (%)	S_1 (%)
1	6.4×10^{-4}	93	50	36	86
2	6.7×10^{-4}	96	48	34	82
Example 4 Run No. 3	6.6×10^{-4}	94	51	35	86

Note: Run No. 1: Recovered diethylbenzene and newly prepared catalyst were employed.
Run No. 2: Recovered catalyst and newly prepared diethylbenzene were employed.

Example 8.

Into the same type of reactor as described in Example 1 were charged 240 g of ethylacetophenone and 60 g of 0.2 mol/l aqueous cobalt acetate solution having a pH of 4.0 which had been prepared with acetic acid, and the oxidation reaction was carried out in the same manner as described in Example 1. The results obtained are shown in Table VII.

TABLE VII.

Run No.	k'_2 (sec^{-1})	S* (%)	Conversion** (%)
1	1.28×10^{-4}	88	60
2	1.29×10^{-4}	85	55

Note: Run No. 1: The ethylacetophenone employed was that with a para-isomer:meta-isomer weight ratio = 30:70)

Run No. 2: The ethylacetophenone employed was the *p*-ethylacetophenone obtained by acylation of ethylbenzene.

$$*S = \frac{[DAB]}{[MAB]_0 - [MAB]} \times 100$$

$$**Conversion\ (\%) = \frac{[MAB]_0 - [MAB]}{[MAB]_0} \times 100$$

[DAB] and [MAB] respectively represent the molar concentrations of diacetylbenzene and ethylacetophenone in the organic liquid phase after the oxidation reaction, and $[MAB]_0$ represents the molar concentration of ethylacetophenone in the starting organic liquid phase.

Example 9.

A one liter titanium reactor was used which was equipped with two baffle plates, a stirrer, a gas inlet nozzle, a reflux condenser, a thermometer, a pressure gauge, a gas flow meter, a meter for measuring oxygen concentration, a nozzle for feeding the starting material and a nozzle for withdrawing the reaction mixture. 101 g of diethylbenzene (para-isomer:meta-isomer weight ratio = 30:70), 177 g of ethylacetophenone (para-isomer:meta-isomer weight ratio = 30:70) and 122g of diacetylbenzene (para-isomer:meta-isomer weight ratio = 30:70) and 140 g of a 0.2 mol/l aqueous cobalt (II) acetate solution having a pH of 4 were charged into the reactor. Under stirring at a rate of 1,000 r.p.m., the temperature was increased to 140°C under a nitrogen atmosphere and the pressure in the reactor was adjusted to 15 Kg/cm^2. Under these conditions, air was fed to the reactor as a molecular oxygen-containing gas at a rate of 60 l/minute (N.T.P.) and, after the absorption of oxygen had started diethylbenzene (para-isomer:meta-isomer weight ratio 30:70) was continuously fed to the reactor at a rate of 1.61 moles/hour, ethylacetophenone (para-isomer:meta-isomer weight ratio = 30:70) was fed at a rate of 1.24 moles/hour and a 0.2 mole/l aqueous cobalt (II) acetate solution was fed at a rate of 100 g/hour. During the reaction, the reaction mixture liquid was withdrawn while maintaining the level of the reaction mixture liquid in the reactor substantially constant. The oxidation reaction achieved a stationary state in 3 to 8 hours from the start of the oxidation reaction, and, in this period, diethylbenzene at a rate of 0.58 mole/hour, ethylacetophenone at a rate of 1.28 moles/hour, diacetylbenzene at a rate of 0.81 mole/hour and the aqueous liquid phase at a rate of 140 g/hour were withdrawn. At this time, the selectivity S_2 was 79% and the recovery rate of cobalt (II) acetate was 98%.

Example 10.

95.6 g of diethylbenzene (para-isomer:meta-isomer weight ratio = 30:70), 218 g of ethylacetophenone (para-isomer:meta-isomer weight ratio 30:70), 86.4 g of diacetylbenzene (para-isomer:meta-isomer weight ratio = 30:70) and 130 g of a 0.2 mole/l aqueous cobalt (II) acetate solution having a pH of 4 were charged into the same type of reactor as described in Example 9. Under stirring at a rate of 1,000 r.p.m., the temperature was increased to 125°C under a nitrogen atmosphere and the pressure in the reactor was adjusted to 15 Kg/cm^2. Under these conditions, air was fed to the reactor as the molecular oxygen-containing gas at a rate of 60 l/minute (N.T.P.), and, after the absorption of oxygen had started, diethylbenzene (para-isomer:meta-isomer weight ratio = 30:70) was continuously fed into the reactor at a rate of 1.32 moles/hour, ethylacetophenone (para-isomer:meta-isomer weight ratio = 30:70) was fed at a rate of 1.51 moles/hour and a 0.2 mole/l aqueous cobalt (II) acetate solution was fed at a rate of 100 g/hour. During the reaction, the reaction mixture liquid was withdrawn while the level of the reaction mixture liquid in the reactor was maintained substantially constant. In a period of from 3 to 8 hours after the start of the oxidation reaction, diethylbenzene was withdrawn at a rate of 0.71 mole/hour, ethylacetophenone was withdrawn at a rate of 1.49 moles/hour, diacetylbenzene was withdrawn at a rate of 0.54 and the aqueous liquid phase was withdrawn at a rate of 130 g/hour. At this time, the selectivity S_2 was 88% and the recovery rate of cobalt (II) acetate was 98%.

Example 11.

Into a 1,000 ml titanium reactor equipped with the same devices as the reactor of Example 1 were charged 480 g of diethylbenzene (para-isomer:meta-isomer weight ratio = 30:70) and 120 g of a 0.2 mol/l aqueous cobalt (II) acetate solution having a pH of 4. The oxidation reaction was carried out at 130°C with stirring at a rate of 1,000 r.p.m. in the same manner as described in Example 1.

240 Minutes after the start of the oxidation reaction the conversion of diethylbenzene became 87%, and the amount of the components of the organic liquid phase at this time determined by gas chromatography are shown in Table VIII below. Also, at this time, the reaction mixture liquid was withdrawn and separated into the organic liquid phase and the aqueous liquid phase by passing the reaction mixture liquid through a glass column of 50 mm in diameter and 20 cm in length packed with glass wool and allowing the reaction mixture liquid passed to settle. Then, the organic liquid phase separated in this manner was distilled to yield each component of the product. The results are also shown in Table VIII. The amount of cobalt in the aqueous liquid phase obtained by chelatometric titration was 0.98 mole which corresponded to 98% of the amount of cobalt fed.

TABLE VIII.

Component	Amount of Feed (g)	Amount of Product (g)	Amount of Product after Distillation (g)	Recovery Rate by Distillation (g)
DEB	480	61	61	100
MAB	0	220	217	98.6
DAB	0	201	195	97.0
Alcohols*	0	47	45	95.7
Others	0	11**	16**	—
Total	480	540	534	—

Note: DEB: Diethylbenzene
MAB: Ethylacetophenone
DAB: Diacetylbenzene
* Alcohols corresponding to MAB and DAB.
** Weight = Total weight − (DEB + MAB + DAB + Alcohols) weight
*** Distillation residue.

Example 12.

The same procedures as described in Example 11 were repeated. The conversion of diethylbenzene was 88% and a reaction mixture liquid containing an organic liquid phase of 11 percent by weight of diethylbenzene, 41 percent by weight of ethylacetophenone, 38 percent by weight of diacetylbenzene, 7 percent by weight of alcohols and 3 percent by weight of other materials was obtained. Then, the organic liquid phase was separated from the aqueous liquid phase and divided into three parts. After each part had been treated with an aqueous solution as set forth in Table IX below, the resulting solution was distilled. The results obtained are shown in Table IX.

TABLE IX.

Run No.	Aqueous Solution (ml)	Recovery Rate of DAB (%)	Amount of Distillation Residue (% by weight based on total feed in distillation)
1	0.1 N Aqueous hydrochloric acid solution (200)	98	2.5
2	0.1 N Aqueous sodium hydroxide solution (200)	98	2.0
3	0.1 N Aqueous sodium hydroxide solution (200) first and then 0.1 N aqueous hydrochloric acid solution (200)	98.5	1.0

DAB: Diacetylbenzene.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the scope thereof.

WHAT WE CLAIM IS:—

1. A process for preparing diacetylbenzen which comprises contacting with a molecular oxygen-containing gas a heterogeneous mixture of (A) from 98 to 25 percent by volume of an organic liquid phase containing at least one of diethylbenzene and ethylacetophenone and (B) from 2 to 75 percent by volume of an aqueous liquid phase containing as a catalyst, at least 0.01 mole/l of at least one watersoluble salt of a metal consisting of manganese, cobalt, nickel, chromium, copper or iron and having a pH of from 1 to 6, at a temperature of from 100°C to 180°C and under a pressure of from 1 to 50 Kg/cm^2 to effect a liquid phase oxidation reaction; separating the resulting reaction mixture liquid into an aqueous liquid phase and an organic liquid phase; and recovering diacetylbenzene from the separated organic liquid phase.

2. A process as claimed in Claim 1, wherein the water-soluble salt of a metal consists of an acetate, propionate, sulfate, nitrate or chloride of manganese (II), cobalt (II), nickel (II), chromium (III), copper (II) or iron (III).

3. A process as claimed in Claim 2, wherein the water-soluble salt of a metal is cobalt (II) acetate.

4. A process as claimed in Claim 3, wherein the oxidation reaction temperature ranges from 120°C to 150°C.

5. A process as claimed in Claim 2, wherein the water-soluble salt of a metal is manganese (II) acetate.

6. A process as claimed in Claim 5, wherein the oxidation reaction temperature ranges from 130°C to 160°C.

7. A process as claimed in any of claims 1 to 6, wherein the concentration of the catalyst in the aqueous liquid phase ranges from 0.1 to 1.0 mol/l.

8. A process as claimed in any of claims 1 to 7, wherein the pH of the aqueous liquid phase ranges from 3 to 5.

9. A process as claimed in any of claims 1 to 8, wherein the amount of the aqueous liquid phase based on the total amount of the organic liquid phase and the aqueous liquid phase ranges from 10 to 50 percent by volume.

10. A process as claimed in any of claims 1 to 9, wherein the molecular oxygen-containing gas is air.

11. A process as claimed in any of claims 1 to 10, wherein the amount of the molecular oxygen based on the total gas in a reactor ranges from 2 to 10 percent by volume.

12. A process as claimed in any of claims 1 to 11, wherein the reaction is effected in a titanium reactor or a titanium-lined reactor.

13. A process as claimed in any of claims 1 to 11, wherein the reaction is effected in a glass reactor or a glass-lined reactor.

14. A process as claimed in any of claims 1 to 11, wherein the reaction is

effected in a reactor whose parts in contact with the reaction mixture liquid are lined with titanium.

15. A process as claimed in any of claims 1 to 11 wherein the reaction is effected in a reactor whose parts in contact with the reaction mixture liquid are lined with glass.

16. A process as claimed in any of claims 1 to 15, which comprises recovering at least one of diethylbenzene and ethylacetophenone by distillation from the organic liquid phase after the liquid phase oxidation reaction, and reusing the recovered compound as a starting material for the liquid phase oxidation reaction.

17. A process as claimed in any of Claims 1 to 16, which comprises treating the organic liquid phase separated from the aqueous liquid phase after the liquid phase oxidation reaction with at least one aqueous oslution consisting of an aqueous acidic solution consisting of an aqueous acidic solution or an aqueous alkaline solution, again separating the organic liquid phase formed and recovering diacetylbenzene from the resulting organic liquid phase by distillation.

18. A process as claimed in any of Claims 1 to 17, which comprises adjusting the concentration and pH of the aqueous liquid phase separated from the organic liquid phase after the liquid phase oxidation reaction to at least 0.01 mol/l and from 1 to 6, respectively, and reusing the resulting aqueous liquid phase for the liquid phase oxidation reaction.

19. A process as claimed in claim 1, substantially as herein described with reference to any of the specific Examples.

20. Diacetylbenzene when prepared by a process as claimed in any of claims 1 to 19.

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