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PRODUCTION OF METHACRYLIC ESTERS

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ABSTRACT OF THE DISCLOSURE

Process for producing methacrylic esters by the dehydrogenation of isobutyric esters with oxygen in which the dehydrogenation reaction takes place in the presence of iodine and an inert heat carrier having a mean pore radius of from 200 to 20,000 A. and an internal surface area of from 0.05 to 10 sq. m./g. The process provides high yields of methacrylic esters with high conversion rates.

This invention relates to a process for the production of esters of methacrylic acid by dehydrogenation of esters of isobutyric acid with oxygen in the presence of iodine.

It is known that olefinically unsaturated organic compounds may be prepared by dehydrogenation of the corresponding saturated compounds with oxygen in the presence of free or combined halogen. The dehydrogenation of esters of isobutyric acid into esters of methacrylic acid cannot however be carried out with satisfactory yields and conversions.

The reaction of methyl isobutyrate with oxygen in the presence of iodine at 500° to 550° C. is described in U.S. patent specification No. 2,719,171. A yield of 29% of methyl methacrylate, at a conversion of 9.5%, is achieved using quartz beads as a heat carrier, whereas a yield of 70% at a conversion of 23% is obtained in the absence of the heat carrier.

In British patent specifications Nos. 1,007,489, 977,146, 988,619, U.S. patent specifications Nos. 3,207,806 and 3,207,805 and in French patent specification No. 1,342,-464 it is stated that dehydrogenatable organic compounds may be advantageously reacted with oxygen in the presence of free or combined halogen using a solid catalyst which contains an oxide, hydroxide or salt of a metal of Group I–A, II–A, II–B, III–A, III–B, IV–A, IV–B, V–A, V–B, VI–A, VII–A, VIII or the lanthanide group of the Periodic System of Elements. The yield for the dehydrogenation of isobutyric esters are not given however. If methyl isobutyrate be dehydrogenated in accordance with the directions in Example 1 of the French patent specification No. 1,342,-464, methyl methacrylate is obtained in a yield of less than 10% of the theory. These methods have therefore not hitherto been used for industrial syntheses.

It is the object of the present invention to provide a process for the production of methacrylic esters by dehydrogenation of isobutyric esters to give high yields and high conversions.

This and other objects are achieved in a process for the production of methacrylic esters by dehydrogenation of isobutyric esters with oxygen at a temperature of from 400° to 700° C. in the presence of iodine and of an inert heat carrier which has a mean pore radius of from 200 to 20,000 A. and an internal surface area of 0.05 to 10 sq. m./g.

Yields of more than 80% are achieved at high conversions of the starting materials by the new process. The reaction, which hitherto has been only of theoretical interest, thus becomes interesting industrially and permits commercial use.

Esters of isobutyric acid are used as starting materials, particularly isobutyric esters which have a boiling point of less than 300° C. at atmospheric pressure. Esters of lower alcohols, such as methyl isobutyrate, ethyl isobutyrate isopropyl isobutyrate and butyl isobutyrate, are preferred, methyl isobutyrate being particularly suitable.

Pure oxygen is usually employed in an amount equivalent to about that theoretically calculated or in excess, particularly 0.35 to 1 mole of oxygen per mole of ester. The oxygen is advantageously metered in at such a rate that the off-gas is as free as possible from oxygen. Oxygen-containing gas, such as air, may also be used instead of pure oxygen but there is no further advantage in this.

Iodine is usually used in a small amount, generally from 1 to 10, particularly 1 to 5, mole percent on the organic compound.

Dehydrogenation is carried out in the presence of an inert heat carrier having a specific internal surface area and a specific mean pore radius. All solid materials whose surface structure does not change appreciably at the reaction temperature and under the reaction conditions are suitable. Examples of suitable heat carriers are petroleum coke, silicon carbide, porcelain, quartz powder or pumice. Heat carriers which contain at least one of the oxides, hydroxides or salts of metals of Group I–A, II–A, II–B, III–A, III–B, IV–A, IV–B, V–A, V–B, VI–A, VII–A, VIII or the lanthanide group of the Periodic System of Elements as described in British patent specifications Nos. 1,007,489, 977,146, 988,619 and in U.S. patent specifications Nos. 3,207,806 and 3,207,805 or which consist of at least one of the said hydroxides, oxides or salts may be used with particular advantage. The groups of the Periodic System of Elements are as set out in Chemiker-Kalender, Springer-Verlag, Berlin 1956, page 2. it is particularly advantageous to use substances which contain basic and acid components, the basic components, such as oxides or hydroxides of metals of groups I–A, II–A and II–B of the Periodic System of Elements not being present in stroichiometric excess with respect to the acid components, such as oxides of metals of Groups IV–A, IV–B, V–A, V–B and VI–A of the Periodic System of Elements.

Examples of such suitable heat carriers are stoichiometric and non-stoichiometric silicates, aluminosilicates and phosphates of the metals: potassium, sodium, magnesium, calcium, barium, aluminum and boron; oxides of iron, titanium, manganese, cobalt, copper, nickel, zinc, boron, tungsten, molybdenum, chromium, cerium and zirconium, and mixtures of the said compounds. Natural and synthetic products may be used, such as are obtained by coprecipitation. Examples of suitable compounds are potassium aluminosilicate, sodium aluminosilicate, calcium aluminosilicate, pumice, barium silicate, aluminum silicate, calcium phosphate, boron phosphate, aluminum phosphate, aluminum oxide and silicon dioxide. It is preferred to use silicates of the alkaline earth metals, particularly of magnesium, or products which have a high content of magnesium silicates, as for example the natural minerals: soapstone, enstatite or olivine. The suitable pore size and internal surface area of the magnesium silicates may be set up in the conventional way by roasting the raw material. Thus soapstone for example is converted by roasting at 900° to 1300° C. into steatite or protoenstatite which has a suitable porosity for the process.

It is essential for the successful performance of the reaction to use a heat carrier which has a mean pore radius of from 200 to 20,000 A., particularly from 500 to 10,000 A., and an internal surface area of from 0.05 to 10.0, particularly from 0.5 to 5, sq. m./g.

The reaction is carried out in the gas phase at temperatures of from 400° to 700° C., particularly from 450° to 580° C. Atmospheric pressure is generally used but the

reaction may be carried out at subatmospheric or superatmospheric pressure. The heat carrier is usually stationary, but a fluidized bed may be used.

(ISA); the mean pore radius in A. (MPR); the yield as a percentage of the theoretical yield (Yield); and the percentage conversion (Con.).

TABLE

Ex.	Heat carrier	ISA	MPR	Yield	Con.
2	Italian pumice	6.2	~1,310	61	42
3	SiO_2	4.3	860	70.5	51.5
4	SiO_2 + 10% P_2O_5	3.1	1,010	76	51
5	Quartz glass	0.1	~18,500	52	36
6	Petroleum coke	0.2	~5,000	62	39
7	Aluminum silicate	5.15	715	64	49
8	Aluminum phosphate	1.2	960	66	50
9	α-Al_2O_3	2.4	695	57.5	41.5
10	α-Al_2O_3 + 5% P_2O_5 + 1% Cr_2O_3	1.7	985	71.5	46
11	Chamotte ($Ml_2O_3 \cdot SiO_2$)	0.2	~6,200	70.5	49
12	Magnesium silicate + 4% Cl_2O_3 + 6% BaO + 3% Fe_2O_3	0.2	~4,500	73.5	49.5
13	SiO_2 + 5% didymia + 2.5% P_2O_5 + 5% MoO_3	1.4	~1,085	67	48.5
14	SiO_2 + 2% Bi_2O_3 + 1% Sb_2O_4 + 1% V_2O_5 + 0.5% Li_2O	0.8	990	63.5	45.5
15	SiO_2 + 5% TiO_2 + 5% P_2O_5 + 2% MnO_2 + 2% ZnO	1.1	980	68	47.5
16	SiO_2 + 1% AgO + 1% NiO + 0.5% P_2O_5	1.8	895	69	48
17	SiO_2 + 2.5% CeO_2 + 1% Nd_2O_3 + 1% B_2O_3 + 0.5% P_2O_5	0.8	~1,210	68	47
18	Inactivated pumice	<0.05	~26,000	5.5	26
19	Magnesium silicate (600° C.)	315.0	28.6	7.5	81
20	Aluminum silicate	19.8	312.5	9.2	78.5
21	θ-Al_2O_3 + 38% MnO_2 + 2% LiCl	97.4	105.7	4.5	55

The residence time of the reaction mixture in the reaction chamber is about 0.1 to 30 seconds, preferably 1 to 20 seconds. It is preferred not to use any diluent.

The reaction is carried out in the conventional way. For example iodine may be dissolved in the isobutyric ester, the solution evaporated and the gas mixture introduced with oxygen into the reaction chamber filled with heat carrier. The gaseous reaction mixture is cooled, the condensate separates into an aqueous phase and an organic phase, and the methacrylic ester formed is separated from the organic phase.

The invention is illustrated by the following examples.

EXAMPLE 1

1 mole of methyl isobutyrate, 0.025 mole of iodine and 0.67 mole of oxygen per hour are supplied at 500° C. to the bottom of a quartz reactor having a diameter of 20 mm. which is provided at the bottom with a quartz frit and which contains 300 ml. of rings of magnesium silicate (steatite magnesia) having a mean pore radius of 595 A. and an internal surface area of 1.57 sq. m./g. and whose porosity is about 12%. The residence time under the reaction conditions in contact with the rings is ten seconds. The gas leaving the reactor is cooled in an efficient cooler and the liquid fraction is condensed out. The total throughput of methyl isobutyrate is 408 g. The organic reaction product is 397 g. and has a methyl methacrylate content of 49.7% by weight and a methyl isobutyrate content of 41.5% by weight. The yield, calculated from this, is 82.8% of the theory at a conversion of 59.7%.

EXAMPLES 2–21

The procedure of Example 1 is followed but using other heat carriers. Heat carriers whose surface properties are within the ranges according to the invention are used in Examples 2 to 17, while in Examples 18 to 21 heat carriers are used whose surface properties are outside the ranges according to the invention. The following table gives the internal surface area in sq. m./g.

We claim:

1. In a process for the production of esters of methacrylic acid and lower alcohols by dehydrogenation of esters of isobutyric acid and lower alcohols with oxygen in the presence of iodine and, as an inert heat carrier, magnesium silicate at a temperature of from 400° to 600° C., a residence time of the reaction mixture in the reaction chamber of about 0.1 to 30 seconds, a mole ratio of oxygen to isobutyric ester of from about 0.35 to 1, the iodine being used in an amount of from 1 to 10 mole percent based on the isobutyric ester, the improvement which comprises: using a heat carrier which has a mean pore radius of from 200 to 20,000 A. and an internal surface area of from 0.05 to 10 sq. m./g.

2. A process as claimed in claim 1 carried out in the absence of any diluent.

3. A process as in claim 1 wherein said inert heat carrier has a mean pore radius of from 500 to 10,000 A. and an internal surface area of from 0.5 to 5 sq. m./g.

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1,342,464	9/1963	France.
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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,530,169 Dated September 22, 1970

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 57, in the references,
" 1,342,464 9/1963 France." should read
-- 1,382,523 11/1964 France. --.

SIGNED AND
SEALED
DEC 1 - 1970

(SEAL)
Attest:

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