PROCESS FOR THE PRODUCTION OF OLEFIN OXIDES

Filed Oct. 12, 1967

INVENTORS:
WALTER KRÖNIG, PETER KONRAD,
This invention relates to a process for the production of olefin oxides. It is known that olefin oxides can be produced from olefins by an electrochemical process in which an aqueous solution of a metal halide is electrolysed in an electrochemical system. The olefin is introduced into the reaction in the proximity of the anode, followed by dehydrohalogenation of the halohydrin initially formed in an electrochemical system to form the olefin oxide (cf. Belgian patent specification No. 637,691 and French patent specification No. 1,375,973). In this process, the electrolyte is transferred from the anode compartment through a diaphragm into the cathode compartment, olefin halohydrin being formed from the olefin introduced into the anode compartment under the electrochemical effect. The olefin halohydrin, dissolved in the electrolyte, passes through the diaphragm and is converted into the olefin oxide in the cathode compartment under the effect of the alkaline conditions prevailing therein. Several of these anode-diaphragm-cathode systems may be combined to form a cell unit.

This process is of particular importance in cases where the starting materials used are olefins which are present in gas form in the anode compartment under the reaction conditions selected, irrespective of whether the olefins use are themselves gaseous under the temperature and pressure conditions selected, or whether an inert gas is added which reduced the vapour pressure of the olefin to be reacted to such an extent that it is gaseous under the reaction conditions.

In the various described embodiments of the process for converting gaseous olefins into olefin oxides, the gaseous olefin is introduced into the zone between the anode and the cathode or, where the diaphragm usually required is present, in the zone between the anode and the diaphragm. The gaseous olefins may be introduced into the zone described, for example at the lower end of the vertical anode, although they are preferably supplied to this zone through the anode itself by providing the anode in a poruous condition, in which case the anode may be positioned other than vertical. In each of the embodiments described, therefore, the gasiform olefin is introduced into the current-line field between the anode and the cathode. The desired electrochemical reaction may be carried out to good effect with systems such as these.

It has now been found that the process for electrochemically producing olefin oxides from olefins in a system comprising an anode, a cathode and a diaphragm wherein a metal halide-containing aqueous electrolyte is electrolyzed to produce halogen, the olefin is converted to the halohydrin form, the electrolyte passing from the anode through the diaphragm to the cathode wherein the halohydrin is dehydrohalogenated to produce the desired olefin oxide; can be improved by carrying out the process in an electrochemical cell having an anode backside compartment or zone, an anode, a zone or compartment intermediate the anode and the diaphragm, a diaphragm, a cathode, and a cathode zone or compartment all serially aligned in the sequence set forth; and further by introducing the gasiform olefin in such a manner that such is substantially only present in the anode backside compartment or zone. This can be done, for example, by supplying the olefin to the anode compartment on that side of the anode which is remote from the cathode, i.e. the anode backside compartment. In this case, the gaseous olefin need not be introduced into the intermediate zone between the anode and the cathode, but is introduced outside the intermediate zone into the anode zone which is on the side of the anode directed away from the cathode, i.e. the anode backside compartment. It has surprisingly been found that the electrochemical reaction also proceeds satisfactorily outside the current-line field.

In the process according to the invention, the olefin is introduced as a gas and is converted into the olefin halohydrin in the space outside the intermediate zone between the anode and the cathode, with the olefin halohydrin thus formed passing into the zone between the anode and the cathode, or the diaphragm, in solution in the electrolyte.

Subsequent dehydrohalogenation of the halohydrin may be carried out in different ways. For example, the electrolyte may be passed from the intermediate compartment through the diaphragm into the cathode compartment where the halohydrin is then dehydrohalogenated into the olefin oxide. It is also possible, however, to react the anolyte containing the halohydrin with the catholyte outside the cell so that the olefin halohydrin is converted into the olefin oxide there. It has surprisingly been found that, despite the absence of the gaseous olefins in the intermediate zone between the anode and the cathode, the halohydrin passing through it does not undergo any undesirable changes. One particular advantage of the novel arrangement is that the voltage drop between the anode and the cathode is lower than it is in the conventional arrangement where the olefin gas is introduced between the anode and the cathode. This particularly applies in cases where the interval between the anode and the cathode, or between the anode and the diaphragm, is considerably smaller than it is possible in conventional systems where the olefins are supplied to the zone between the anode and the diaphragm. For example, the interval between the anode and the diaphragm in the new arrangement of this invention can be reduced to between one third and one sixth of the clearance required in the conventional system. This in turn reduces the drop in voltage between the anode and the cathode by some 5% to 25%. This reduction in the voltage drop leads to a corresponding reduction in the consumption of energy which is so very important so far as the economy of the electrochemical processes is concerned. Since a considerable part of the electrical energy supplied to the cell is converted into thermal energy which can only be utilized to a very limited extent, the reduction in energy consumption also has a favourable effect on the process as a whole.
One embodiment of the process according to the invention is now discussed by way of example with reference to the accompanying drawing which is a schematic view in side elevation of an electrolytic cell according to this invention.

The drawing shown is an electrolytic cell 1 with anode 2 and a cathode 3 facing one another and with a diaphragm 4 between the electrodes. There is provided an intermediate compartment or zone 5a (anode-diaphragm) and an anode backside compartment 5b, the back wall of the anode being the anode backside compartment 5b. The two zones 5a and 5b are interconnected by slots 6 in the anode. The upper slot may be provided with a deflector 7 for purposes to be described below. An aqueous metal halide solution is supplied to the anode backside compartment 5b through a pipe 8. The catholyte leaves the cell through a pipe 9. The olefin is introduced into the anode backside compartment 5b through a pipe 10, for example, by way of a frit, and rises upwards through it. The excess, unreacted gas leaves the anode backside compartment 5b through a pipe 11 after it has been separated from the electrolyte in the upper part of the anode backside compartment. Another empty space is provided above the cathode zone 3a through which the cathode gas is exhausted, for example, by way of a pipe 12. The catholyte leaving the system through the pipe 9 is resolved to separate further quantities of cathode gas from the catholyte which cathode gas leaves the system through a pipe 13 and which catholyte leaves the system through a pipe 14.

According to the invention, the gaseous olefins may be introduced into the anode compartment in various ways. For example, the olefin gas may be introduced into the anode compartment filled with electrolyte on the side of the largest possible area of the anode backside compartment. The upward flow of the gas in the anode backside compartment is used for internally cycling the anolyte, in which case the anolyte rises with the gas in the anode backside compartment and, following separation of most of the unreacted olefinic gas, flows downwards in the now largely gas-free intermediate compartment between the anode and the diaphragm. The unreacted gas is separated for example at the upper liquid level of the anolyte by allowing the gas flowing through the liquid to pass over into a gas zone located above the liquid level, from which it can be removed for further processing as much as the gas as possible, it is advisable to widen the cross-section of the anode compartment at the point at which the circulating electrolyte changes direction. It is also advisable to prevent the gas from flowing over into the descending part of the circuit by means of deflecting channeled baffles. The arrangement in terms of apparatus should be such that no more than about 10%, and preferably less than about 3%, of the anode gas passes into the intermediate zone between the anode and the cathode or diaphragm. To enable the electrolyte to circulate, there must be connections between the anode zone and the intermediate zone. These connections may be arranged in the cell itself, although it is also possible to provide them outside the cell. In general, it is of advantage to arrange these connections at the lower and upper ends of the anode. In this case, the electrodes are advantageously arranged vertically and the olefin is remote from the cathode, i.e., in the anode backside compartment at the lower end thereof, for example, through screens, frits or similar devices, in such a way that the olefin is not introduced into the region between the anode and cathode, but only into that region of the anode compartment which is remote from the cathode. If the olefin is remote from the cathode, it is possible, for example in cases where titanium anodes are used, to use titanium anodes of the kind that are hollow over their entire area. The part of the anode facing the cathode is made non-porous and coated with a noble metal, while the part of the anode which is remote from the cathode is porous and not coated with a noble metal. In cases where solid anodes, impervious to the electrolyte and coated with a noble metal, are used to carry out the process according to the invention, it is advisable to provide the non-porous coating on the side of the anode which faces the cathode. Accordingly, the gas flows upwards along that part of the anode which is not coated, while the anolyte, largely free of gas, flows downwards along that part of the anode which is coated with noble metal.

To carry out the process according to the invention, the anode surface may be regularly divided up into regions which are permeable and impermeable to the electrolyte. If anodes with a noble metal coating are used in an arrangement of this kind, the noble metal may be applied to that side of the anode facing the cathode and/or to that side of the anode remote from the cathode and, if desired, to those areas between the faces of the anode that are accessible to the electrolyte. In this case, the anode is preferably arranged upright and the gas to be reacted is introduced into the anode backside compartment remote from the cathode. In such a system of this kind, vertical circulation of the anolyte may be dispensed with because the anolyte naturally has a free path to the cathode through the openings in the anode. Internal streams may of course also flow between the anode backside zone and the intermediate zone through the openings in the anode.

The anodes with openings for the passage of the electrolyte may differ widely in shape. Anodes which are advantageously in plate form may be provided with slots or holes. Wire gauge anodes may also be used. It is of particular advantage to use anodes of expanded metal, in which case steps are preferably taken to ensure that the largest possible effective surface is also present between the two faces of the anode. In general, it is desirable that the anode areas available for electrolysis should be at least as large as those of a compact anode of the same external dimensions.

Suitable anode materials include, for example, graphite or platinum-coated titanium or other conventional materials. Titanium anodes in which the titanium surface is coated either wholly or in part with a noble metal, are particularly suitable for the present purpose. The titanium should be provided with a protective oxide layer over those areas that are not coated with the noble metal. Although platinum is particularly suitable for use as the noble metal, it is also possible to use mixtures of platinum with other noble metals, particularly iridium and/or rhodium, for the present purpose. Wire gauges of iron or stainless steel are advantageously used as the cathode. The cathode and anode preferably have substantially the same surface area.

Gaseous mono-olefins such as ethylene, propylene and butylene, and halogenated mono-olefins such as allyl chloride, for example, are particularly suitable starting materials for producing the olefin oxides. The olefins of course contain inert constituents such as, for example, ethane, propane or butane.

Aqueous solutions of metal halides, such as for example sodium or potassium chloride or mixtures thereof are suitable electrolytes. The salt concentration of the electrolyte may amount for example to between 2% and 20% and, preferably to 3% and 15%.

If, in accordance with one possible embodiment of the process, the aqueous electrolyte is introduced into the anode compartment and then transferred through the diaphragm and the cathode into the cathode compartment at a rate of between about 10 to 100 cc. per minute of electrolyte per cm² of cathode, it should be possible to carry out this process. In addition, the catholyte issuing from the cathode compartment may then have the olefin oxide present in it removed by conventional means, such as by distillation for example, after which the catholyte may be returned to the anode compartment, thus completing the circuit.

If, in accordance with another possible embodiment of
the process, the anolyte containing the halohydrin is reacted outside the cell with the catholyte to form the olefin oxide, the electrolyte from which the olefin oxide has been removed, for example by distillation, may be returned to the anode or cathode compartment. In this case, the flow rate of electrolyte through the anode compartment may for example amount to between about 4 and 80 cc. per minute per dm.² of anode area. If secondary products, which may be formed during electrolysis, have accumulated to a certain extent in the circulating electrolyte, it is advantageous to at least periodically remove a portion of the electrolyte from the circuit and to replace it with fresh electrolyte.

It is possible, for example, to use current densities of from 2 to 50 amps/dm.² of electrode area, voltages of from 3 to 5 volts and temperatures of from 30°C to 90°C. Although it is preferred to work at normal pressure, it is also possible to use moderately elevated pressures. The throughput of olefin through the anode compartment may for example be selected in such a way that some 5% to 95% is reacted in a single passage.

Suitable diaphragms for the process according to the invention are made from inert materials such as, for example, asbestos, polynuclear hydrocarbons, polyolefins such as, for example, propylene, polyethylene, polybutylene, polyisobutene, polyacrylonitrile, polyvinyl compounds such as, for example, polyvinyl chloride or copolymers of vinyl chloride and vinylidene chloride and others. The materials may be used in the form of porous or porous plates or films, or as fibres in the form of woven or non-woven fabrics. Fabrics woven from polyacrylonitrile fibres whose pore size has preferably been reduced by heat and/or pressure treatment, for example by calendering, have inter alia proved to be particularly suitable.

The invention is illustrated by the following examples.

**EXAMPLE 1**

(a) The following electrochemical system was used:

An anode and a cathode, each with an area of 1.75 dm.², were arranged upright facing one another in an electrolytic cell (cf. figure). The anode consisted of a 2 mm. thick sheet of solid titanium which was provided on the side facing the cathode with a layer of noble metal (platinum/titanium 70:30), and with a protective acidic skin over those areas not coated with the noble metal. The cathode consisted of a wire gauge of stainless steel. A diaphragm of a polypropylene fabric 0.3 mm. thick was provided covering the cathode on the anode directed side thereof. The anode was arranged in the cell in such a way as to provide an anode compartment defined by the anode and the rear wall of the cell, and an intermediate compartment defined by the anode and the diaphragm. The gap between the anode and the diaphragm was 3.5 mm wide. The two regions were connected together by two 10 mm. tall slots in the anode arranged above and below the platinum coating. The upper slot was provided with a deflecting baffle. The electrolytic cell was filled with a 5% aqueous potassium chloride solution. Four litres/hour of this solution were delivered into the anode compartment and from there through the diaphragm into the cathode compartment. The electrolyte was regenerated after leaving the cell. The temperature of the electrolyte in the cell was 52°C. The cell worked at atmospheric pressure. 45 litres/hour of a C₂-fraction containing 93% by weight of propylene (the rest being mostly propane) were introduced into the anode compartment through a socket arranged in the lower part of the anode/rear cell wall region in such a way that the gas flowed upward in this region. The excess unreacted gas left the electrolytic cell after it had been separated from the analyte through the gas zone situated at the upper end of this region. By guiding the gas in this way, a circuit for the analyte was established in such a way that the analyte flowed upwards in the gas-containing region (anode/rear cell wall), and then, following separation of the gas, flowed downwards in the region between the anode and the diaphragm. In order to separate as much of the gas as possible and to make it difficult for the gas to pass over into the downward flowing part of the circuit, the cross-section of the anode/rear cell wall region was widened at the point at which the circulating analyte changed direction. By applying a D.C. voltage of 3.50 volts across the electrodes, a direct current with a current density of 11.2 amps/dm.² flowed over a period of 4 hours. The chlorine formed during electrolysis reacted in the anode compartment with the water and the propylene introduced into this zone to form propylene chlorohydrin which then, dissolved in the electrolyte, flowed through the diaphragm into the cathode compartment where it was dehydrohalogenated with the alkaline catholyte to form propylene oxide. Some of the propylene oxide formed left the cathode compartment in solution in the catholyte. More was removed from the cell through the cathode gas zone together with the hydrogen given off at the cathode. The gaseous and liquid reaction products leaving the cell in the excess anode gas, the cathode gas and the catholyte were analysed and used to calculate the current yield.

**Reaction Product:**

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield in current percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene oxide</td>
<td>88.7</td>
</tr>
<tr>
<td>1,2-dichloropropane</td>
<td>7.8</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>1.1</td>
</tr>
<tr>
<td>Propylene chlorohydrin</td>
<td>0.8</td>
</tr>
<tr>
<td>Other organic compounds</td>
<td></td>
</tr>
<tr>
<td>containing chlorine</td>
<td>0.9</td>
</tr>
<tr>
<td>and oxygen</td>
<td>0.6</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.1</td>
</tr>
</tbody>
</table>

(b) The electrochemical system described in Example 1a was used with the following modifications:

The anode consisted of a 1.5 mm. thick expanded titanium plate of 1.75 dm.² surface area which was arranged at a distance of 3.5 mm. from the diaphragm and which did not have any additional slots. The anode had a noble metal coating of a 70:30 platinum/iridium mixture coated on the side remote from the cathode and between the two faces, while the side facing the cathode or diaphragm was not plated. Propylene gas to be reacted was introduced into the anolyte in the lower part of the anode/rear cell wall region as described in Example 1a. The direct current flowing over a period of 4 hours at a D.C. voltage of 3.50 volts corresponded to a current density of 10.9 amps per dm.² of anode area.

The current yields of gaseous and liquid reaction products are set out in the following table:

**Reaction product:**

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield in current percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene oxide</td>
<td>88.6</td>
</tr>
<tr>
<td>1,2-dichloropropane</td>
<td>8.0</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>1.1</td>
</tr>
<tr>
<td>Propylene chlorohydrin</td>
<td>0.7</td>
</tr>
<tr>
<td>Other organic compounds</td>
<td></td>
</tr>
<tr>
<td>containing chlorine</td>
<td>0.9</td>
</tr>
<tr>
<td>and oxygen</td>
<td>0.6</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.1</td>
</tr>
</tbody>
</table>

**EXAMPLE 2**

The electrochemical system described in Example 1a was used with the modification that the anode which consisted of a 2 mm. thick sheet of solid titanium coated on the side facing the cathode with a 70:30 platinum/iridium layer, was arranged at a distance of 3.5 mm. from the diaphragm covering the cathode and directly against the rear wall of the cell so that, in this case, the anode/rear cell wall region did not exist. The propylene gas to be reacted was introduced into the anolyte in the intermediate zone through a slit at the lower end of the space between the anode and the diaphragm in such a way that the gas flowed upwards in this space. The excess unreacted gas left the anode compartment through the gas
zone situated above the anolyte level. A D.C. voltage of 4.15 volts was required to produce a direct current with a current density of 11.1 amps. per dm.² of electrode area. The voltage was applied over a period of 4 hours. The current yields of reaction products are set out as follows:

**Reaction product:**
- Propylene oxide
- 1,2-dichloropropane
- Propylene glycol
- Propylene chlorohydrin
- Organic compounds containing chlorine and oxygen
- Oxygen
- Carbon dioxide

**Yield in percent**
- 88.3
- 8.0
- 1.2
- 0.7
- 1.0
- 0.7
- 0.1

EXAMPLE 3
The electrochemical system described in Example 1b was used with the modification that the expanded titanium plate used as the anode was coated on all sides with a thin layer of platinum. The diaphragm lying on top of the cathode consisted of a 1.0 mm. thick blue asbestos paper. A 4.5% aqueous sodium chloride solution was used as the electrolyte. The direct current flowing over a period of 4 hours at a D.C. voltage of 3.7 volts corresponded to a current density of 11.5 amps/dm.² of anode area. The amounts of reaction products present in the cathode and the excess anode gas and in the catholyte were as follows in percentages of the current used:

**Reaction product:**
- Propylene oxide
- 1,2-dichloropropane
- Propylene glycol
- Propylene chlorohydrin
- Other organic compounds containing chlorine and oxygen
- Oxygen
- Carbon dioxide

**Yield in percent**
- 86.8
- 9.1
- 1.6
- 0.7
- 1.2
- 0.5
- 0.1

EXAMPLE 4
An electrochemical system of the kind described in Example 1a was used with the modification that the anode and cathode each had an area of 7.5 dm.² for a width of 100 mm., and a height of 750 mm. A diaphragm of a polyacrylonitrile fabric 0.4 mm. thick which lay on top of the cathode, was arranged between the electrodes. The interval between the anode and the diaphragm was 5 mm. The connecting slots between the regions of the anode compartment were 15 mm. tall. The electrolytic cell was filled with a 5% aqueous potassium chloride solution of which 17.5 litres/hour were delivered into the anode compartment and from there through the diaphragm into the cathode compartment. The temperature of the electrolyte in the cell was 52° C. The cell operated at atmospheric pressure, 90 litres/hour of a C₂ fraction containing 48% of ethylene (the rest being mostly ethane) were introduced into the anode/rear cell wall region of the anode compartment. 85% of the ethylene introduced was reacted on passing through the anode compartment. By applying a D.C. voltage of 3.6 volts across the electrodes, a direct current with a current density of 11.1 amps/dm.² flowed for a period of 4 hours. The gaseous and liquid reaction products leaving the cell in the cathode and the excess anode gas and in the catholyte were analysed and used to calculate the current yield:

**Reaction product:**
- Ethylene oxide
- 1,2-dichloroethane
- Ethylene glycol
- Ethylene chlorohydrin
- Other organic compounds containing chlorine and oxygen
- Oxygen
- Carbon dioxide

**Yield in percent**
- 84.8
- 6.6
- 1.0
- 5.5
- 0.8
- 0.9
- 0.4

**What is claimed is:**
1. An improved electrolytic cell for the production of olefin oxides from olefins comprising a cell casing, an anode in said casing, a cathode in said casing, a diaphragm in said casing between said anode and said cathode, means defining an anode backside zone between said anode and the side of said anode directed away from said cathode, means defining an intermediate zone between said diaphragm and the side of said anode directed toward said cathode, means for introducing gaseous olefin reactant only into said anode backside zone, and means for substantially preventing gaseous olefin reactant introduction into said intermediate zone.
2. The improved cell claimed in claim 1, wherein said olefin reactant means is directly into said anode backside zone.
3. The improved cell claimed in claim 1, wherein said anode, which separates said intermediate zone and said anode backside zone, has means therein for communication between said zones.

4. The improved cell claimed in claim 1, wherein said anode is hollow and is pervious to said olefin on the side thereof directed away from said cathode.

5. The improved cell claimed in claim 1, including deflection means associated with said anode adapted to substantially prevent the passage of gasiform olefin from said anode backside zone to said intermediate zone.

6. The improved cell claimed in claim 1, wherein said anode surface has uniformly distributed electrolyte porous and electrolyte-impervious, respectively, regions.

7. The improved cell claimed in claim 1, wherein said diaphragm is acrylonitrile polymer woven fabric.

8. The improved cell claimed in claim 1, wherein the side of said anode directed toward said cathode has a substantially electrolyte-impervious coating of solid noble metal thereon.

9. The improved cell claimed in claim 1, wherein said olefin inlet means is in said hollow anode.

10. The improved cell claimed in claim 4, including solid noble metal coating on the hollow electrolyte-impervious portions of said anode.

11. The improved cell claimed in claim 6, having solid noble metal coating on said electrolyte impervious regions.

References Cited

UNITED STATES PATENTS

3,288,692 11/1966 Leduc -------------- 204--80
3,242,059 3/1966 Cottam et al. ------ 204--266
3,124,520 3/1964 Juda -------------- 204--265
1,253,615 1/1918 McElroy -------------- 204--80

ROBERT K. MIHALEK, Primary Examiner
R. L. ANDREWS, Assistant Examiner

U.S. Cl. X.R.