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Cobb et al.

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[54] ELECTROLYTE REDUCTION OF OZONOLYSIS PRODUCTS

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[58] **Field of Search** 204/72, 73

[56] **References Cited**

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[57] **ABSTRACT**

An oxygen-containing product, e.g., an alkoxyhydroperoxide, from the ozonolysis of an olefin, e.g., cyclododecene, is electrochemically reduced to a product in which the oxygen is present in aldehydic and/or ketonic form, e.g., alpha, omega-dialdehyde.

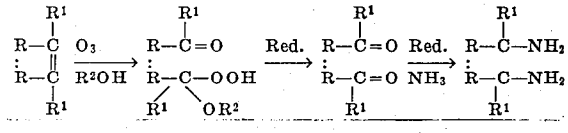
4 Claims, No Drawings

ELECTROLYTE REDUCTION OF OZONOLYSIS PRODUCTS

This invention relates to the electrochemical preparation of organic compounds. In one of its aspects the invention relates to the electrolytic reduction of an ozonolysis product, for example, an alkoxyhydroperoxide, to produce a compound in which oxygen is present in aldehydic and/or ketonic form. In another aspect the invention relates to the production of alpha, omega-dialdehydes.

Products of the invention find use as intermediates in the subsequent production of valuable products and in some instances are useful, per se, for uses to which aldehydic or ketonic compounds are put. The reduction products, for example alpha, omega-dialdehydes, can be reductively ammoniated to diamines and used in the formation of polyamide polymers.

Conversion of cyclic or acyclic olefins to other useful materials by a sequence of steps employing ozonolysis and one or more reductive steps is known and can be shown schematically by the following series of simplified reaction equations:



An important step in such a sequence is the second step, namely, the reduction of the alkoxyhydroperoxide, or ozonolysis product, to the corresponding aldehyde or ketone product. This can be done efficiently with zinc metal and acetic acid, but this is prohibitively costly for commercial use. This step can also be done by catalytic hydrogenation, but such an approach suffers from lowered yields of aldehydes because of side reactions.

In one of its concepts the invention provides a process for the efficient electrochemical reduction of an ozonated olefin such as an alkoxyhydroperoxide heretofore reduced chemically or catalytically. More specifically in a concept of the invention there is provided a process for the electrochemical reduction of an alkoxyhydroperoxide compound to produce aldehyde and/or ketone products by passing the alkoxyhydroperoxide into an electrochemical cell to the cathode thereof as more fully described herein.

We have now found that electrochemical reduction can be employed for conversion of the ozonolysis products of olefins. We have also found that such reduction can be practiced economically and to the substantial exclusion of many of the secondary reactions which frequently occur when catalytic reduction is employed.

An object of this invention is to provide a process for the production of electrochemically reduced ozonated olefins. It is another object of this invention to provide a process for reducing alkoxyhydroperoxide compounds to aldehydes and/or ketones. It is a further object of the invention to provide a process for the production of aldehydes and/or ketones by electrochemical reduction of an ozonated olefin in an electrochemical cell provided with certain features.

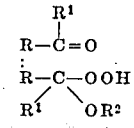
Other aspects, concepts and objects of the invention are apparent from a study of this disclosure and the appended claims.

According to the present invention there is provided a process for reducing an ozonized olefin, e.g., an alkoxyhydroperoxide, which comprises subjecting the ozonized olefin to an electric current in an organic solvent in the presence of a suitable electrolyte, as described herein, at a cathode potential in the range of −0.2 to −0.8 (in respect to saturated calomel electrode) and recovering a product of the reduction from the cell.

As solvents which can be employed for the electrolytic reduction of the ozonolysis product of an olefin according to the invention, there are included alcohols, R^2OH, wherein R^2 is an an alkyl radical having from one to three carbon atoms, and acetone. Some examples of the alcohols are methanol, ethanol, and isopropanol, and the like and mixtures thereof. Such solvents can contain minor amounts of other common solvents such as ethers.

The electrolytes which can be used in the present process, are, generally, those which have substantial solubility in the cell solvent, which provide substantial conductivity, and which are not substantially decomposed at either the anode or the cathode.

The feedstocks for the process of the invention are alkoxyhydroperoxide compounds of the formula



wherein R and R^1 are hydrogen or aromatic or saturated aliphatic hydrocarbon radicals, R^2 is an alkyl radical having from one to three carbon atoms, and wherein two hydrocarbon R groups can be joined to form a difunctional molecule, and when there is no bond between the two R groups, the feedstock can be an approximately equimolar mixture of the corresponding aldehyde and alkoxyhydroperoxide, and wherein the total number of carbon atoms in each molecule is in the range of from 2 to about 30. Preferred feedstocks are those of the difunctional group, wherein the two R groups are joined together to form an alkylene group, wherein R^1 is hydrogen only and wherein the number of carbon atoms is five to 12.

Such feedstocks are readily obtainable by the ozonation, in the presence of a participating solvent R^2OH, of one or more corresponding mono or polyolefinic hydrocarbons having from two to 30 carbon atoms per molecule. Ozonation is a well known reaction and is widely applicable for olefinic materials. Monoolefinic cyclic hydrocarbons are converted to alpha, omega-difunctional compounds. Acyclic olefinic hydrocarbons can be cleaved into two or more such difunctional or monofunctional compounds depending upon the number of double bonds initially present. Cyclic polyenes will also produce such mixtures. Typical ozonation conditions are about 1 mole of ozone per double bond, methanol solution, 0°–25 C, and reaction times of 1 hour or less. Ozone is conveniently produced by passing oxygen through conventional arc process ozone generators. The ozonides are relatively safe, particularly those containing four or more carbon atoms, and can frequently be separated and recovered in the pure state by distillation.

Some specific examples of the alkoxyhydroperoxide ozonation products are:

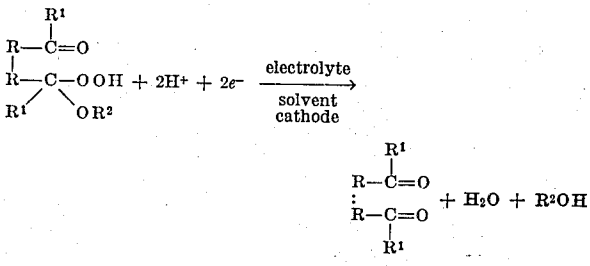
5-oxo-1-methoxypentanehydroperoxide
12-oxo-1-methoxydodecanehydroperoxide
8-oxo-1-ethoxyoctanehydroperoxide
8-oxo-5-benzyl-1-methoxyoctanehydroperoxide
6-oxo-1-methoxydecanehydroperoxide
10-oxo-5-cyclopentyl-1-methoxydecanehydroperoxide
8-oxo-8-methyl-1-ethyl-1-methoxyoctanehydroperoxide
9-oxo-1-methoxytriacontanehydroperoxide
mixture of formaldehyde and 1-methoxyheptanehydroperoxide
mixture of propionaldehyde and 1-propoxynonanehydroperoxide
mixture of heptaldehyde and 1-methoxyheptanehydroperoxide
mixture of 2,3-dimethyloctaldehyde and 1-methoxydodecanehydroperoxide

and the like, and mixtures thereof.

When ozonolysis produces mixtures of ozonated products, such as by the ozonolysis of acyclic mono- or polyenes, the aldehydes can be separated, if desired, from the alkoxyhydroperoxide compounds which must undergo reduction in the cell. However, it is convenient to subject the entire mixture of ozonated products, particularly when they are already dispersed in a solvent suitable for the electrochemical reaction, to the selectively reducing action of the cathodic invention process.

More preferred feeds for the present invention are the ozonides resulting from the ozonolysis of unsubstituted cyclic monoolefins having from five to about 12 carbon atoms per molecule, which yield, after electrochemical reduction, alpha, omega-dialdehydes having from five to about 12 carbon atoms per molecule.

The electrolytic reduction of the ozonolysis product of an olefin in an alcohol, R^2OH, may be depicted



The electrochemical cell which is suitable for use in the present invention can be of any convenient design in keeping with good electrochemical practice in regard to minimization of internal cell resistances, convenience in introducing and removing feedstocks and electrolytes, cooling or heating means to maintain the desired cell temperature, materials of construction to withstand chemical attack, control means to maintain the desired cathode potential, stirring means to insure contact of the feedstock with the cathode, and the like. Such electrochemical apparatus is known in the art.

The cell can contain an ion-permeable membrane or other conventional cell divider, if desired, to separate the catholyte from the anolyte and thus to minimize undesirable oxidation reactions at the anode. Low resistance ion exchange resins can be used for diaphragms of this type.

Platinum is the preferred anode electrode material although any convenient material such as palladium, rhodium, nickel, carbon, and the like can be used. In a preferred embodiment, the anode is depolarized with hydrogen and, consequently, anode materials, such as platinum, which are particularly effective for hydrogen oxidation are preferred. With hydrogen depolarization of the anode, the diaphragm separating the anolyte and catholyte is less desirable. The hydrogen-depolarized anode can be of any convenient configuration such as a porous structure fed with hydrogen through a feed pipe communicating with its hollow interior. Alternatively, the hydrogen can be fed by mean of a feed pipe to the cell contents in the vicinity of a non-porous anode.

The material of construction of the cathode, as is demonstrated hereinafter, is more critical. Silver cathodes have demonstrated high current density within the range cathode potential interest and with relatively small current losses to side reactions. Other metals such as tungsten, nickel, platinum, and platinized substrates can be used but at some sacrifice of efficiency. The cathodes, as well as the anodes, can be in any convenient form such as wire screen, gauze, porous metal, smooth metal, sheet, and the like, and in any convenient shape such as hollow cylinders, flat sections, and the like, depending upon the configuration of the cell.

According to the process of the invention the alkoxyhydroperoxide-containing feedstock is charged to the catholyte of a suitable cell either batchwise or continuously. The cell is equipped with an anode, preferably of silver, and with a cathode, and the cell preferably contains methanol as the solvent in which is dissolved sufficient electrolyte to provide adequate conductivity. The concentration of the feed in the cell solvent can be at any level up to about the solubility limits of the system. Generally feed concentrations of about 10 percent, based on the cell contents, or less are satisfactory.

Sufficient cell voltage is applied to the cell to provide a cathode potential, using a saturated calomel electrode as reference, in the range of from about −0.2 to about −0.8 volts, preferably from about −0.3 to about −0.6 volts. The current density will depend upon the specific combination of chemical and mechanical components of the system but will be in the range of from about 1 to about 500 ma/cm², preferably 10–100 ma/cm².

The electrochemical reaction can be carried out at any convenient temperature and pressure sufficient to maintain a suitable liquid phase in the cell, being high enough to permit operation at a satisfactory rate yet low enough to prevent significant product decomposition. Operation at room temperature is satisfactory, although temperatures up to 100°C and higher can sometimes be maintained.

Whether the electrochemical reaction is carried out batchwise or continuously, the level of feed conversion can vary as desired and can be near complete conversion. The products can be removed from the cell continuously or intermittently by draining a portion of the cell contents and subjecting it to conventional separation means to recover the product. Unconverted feed can be recycled to the cell. The cell reaction medium can be adjusted in regard to its desired composition and similarly returned to the cell.

The effect of solvent, electrolyte, cathode material and reagent concentration have been studied. Methanol was used as the preferred solvent because of the good conductivity of its solutions. Ethanol, isopropanol and acetone are not as satisfactory but can be used. Electrolytes included tetrabutyl ammonium perchlorate, paratoluene sulfonic acid, ammonium acetate, acetic acid, sodium acetate and sodium hydroxide. Because of the stoichiometry, an acidic electrolyte avoids erratic current behavior which alkalinity causes. To avoid aldol condensation in very acidic or basic solutions, a buffered system, e.g., acetic acid - sodium acetate is now preferred. At feed concentrations over about 10 weight percent, the increased viscosity produces a decrease in current. The current is clearly dependent on the nature of the cathode material, as Tables I and II illustrate. High background current is undesirable because of power loss and especially because of the implied occurrence of side reactions. Background current is the current expended on side reactions and is measured by applying the desired cathode potential to a system under reaction conditions except that the feed is absent.

TABLE I

Current dependence on cathode material and potential

		−0.3V		−0.6V	
Run No.	Cathode	Total current ma/cm²	Background current %	Total current ma/cm²	Background current %
1	Silver	33	2	52	36
2	Tungsten	5	3	26	15
3	Platinized Platinum	12	78	—	—
4	Nickel	7	11	18	88
5	Dense carbon	0.3	57	1.3	46
6	Porous carbon	—	—	1.2	70

Anode: platinum
Solvent: methanol - 6 percent tetrahydrofuran
Electrolyte: 5 percent paratoluene sulfonic acid
Temperature: ≈25°C.
Anode and cathode separated by sintered glass diaphragm.
Reagent: 0.30 moles/l of $CHO—(CH_2)_{10}—CH(OCH_3)(OOH)$. (12Oxo-1-methoxydodecane-hydroperoxide)
Product: alpha, omega-dodecanedialdehyde

TABLE II

Current dependence on cathode material and potential

Run No.	Cathode	−0.3V Total current ma/cm²	−0.3V Background current %	−0.6V Total current ma/cm²	−0.6V Background current %
7	Silver	23	2	62	2
8	Pt, Zn^{++}	14	10	48	8

(Zn^{++} plates on Pt Zn surface)

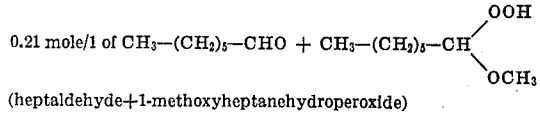
Anode: platinum

Solvent - electrolyte: methanol - 10 percent acetic acid - 4 percent sodium acetate

Temperature: 25°C.

Anode and cathode separated by a Teflon felt plug.

Reagent:



0.21 mole/1 of $CH_3-(CH_2)_5-CHO + CH_3-(CH_2)_5-CH(OOH)(OCH_3)$

(heptaldehyde+1-methoxyheptanehydroperoxide)

Product: additional heptaldehyde

Measurements are made with the aid of a potentiostat, which senses the potential difference between working electrode (cathode, here) and reference electrode, compares it to a control potential, amplifies the difference between the two and supplies power to the counter electrode (anode, here) to polarize the working electrode more, or less, so that the difference is diminished.

Table III shows the effects of electrolyte and reagent concentration on the current.

TABLE III

Electrolyte	Run No.	M reagent	−0.3V. Total current ma./cm.²	−0.3V. Background current, percent	−0.6V. Total current ma./cm.²	−0.6V. Background current, percent
A-------	9	0.06	1.5	25	4.7	17
A-------	10	0.30	2.5	25	9.4	9
B-------	11	0.06	4.5	14	7.7	18
B-------	12	0.30	8.5	8	19	8

Anode: platinum.

Solvent: methanol

Electrolyte: A: 10 percent acetic acid - 4 percent sodium acetate;

B: 5 percent paratoluene sulfonic acid - 6 percent tetrahydrofuran

Temperature: 25°C.

Cathode: silver

Reagent: $CHO-(CH_2)_{10}-CH(OCH_3)(OOH)$ (12-Oxo-1-methoxydodecanehydroperoxide)

Product: alpha, omega-dodecanedialdehyde

These data show that, increasing the concentration of the reagent (feedstock) in the cell, improves the current flow (at a given electrode potential) and generally reduces the background current.

Under the conditions now most preferred, the cathode is silver, the solvent-electrolyte is methanol - 10 percent acetic acid, 4 percent sodium acetate, the temperature is ≈ 25°C., the fuel concentration is 5–10 weight percent, there is no electrode compartment separator and the anode is depolarized with hydrogen gas, which both eliminates oxidation of other components present and reduces the overall cell polarization. Operating under these conditions, the following data were obtained for the reduction of 12-Oxo-1-methoxydodecanehydroperoxide at a cell concentration of 0.30 mole/1, using gas chromatography to analyze for the aldehyde present in the solution.

TABLE IV

Aldehyde concentration during electrolysis

Time hours	Aldehyde moles/1*	Aldehyde, M From Zn reduction	Aldehyde, M Calculated from current
0	0.37	—	—
0.4	0.475	—	—
0.65	0.525	—	—
1.05	0.57	—	—
1.65	0.60	—	—
2.0	0.59	—	—
3.0	0.605	—	—
6.0	0.64	0.64	0.63

*The chromatograph analysis of aldehyde appears to be slightly high, possibly due to some pyrolysis occuring in the chromatograph, but the results show the efficiency of the process.

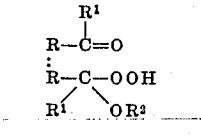
An identical sample of feedstock was reduced with powdered zinc and acetic acid, to produce the composition in the third column. The results of this chemical reduction are essentially identical to that of the present invention, thus illustrating that the present industrially promising process can reduce the ozonated materials as effectively as the highly efficient but economically prohibitive zinc process.

The value for the calculated aldehyde concentration, appearing in the fourth column of Table IV, was calculated from the integral of the current-time curve of the run. The close arrangement between this calculated value and the actual value of the test attests to the electrical efficiency of the run and of the process for producing alpha, omega-dodecanedialdehyde.

Reasonable variation and modification are possible within the scope of the foregoing disclosure and the appended claims to the invention the essence of which is that there has been provided a method for an electrochemical reduction of ozonolysis product, e.g., an alkoxyhydroperoxide, as described.

We claim:

1. A method which comprises the electrochemical reduction at the cathode in an electrochemical cell of an alkoxyhydroperoxide feed material employing a cathode potential in the approximate range 0.2–0.8 volts in respect of a saturated calomel electrode, said alkoxyhydroperoxide being selected from the group represented by the formula



wherein R and R^1 are hydrogen or aromatic or saturated aliphatic hydrocarbon radicals, R^2 is an alkyl radical having from one to three carbon atoms, and wherein two hydrocarbon R groups can be joined to form a difunctional molecule and where there is no bond between the two R's, the feed material is approximately an equimolar mixture of the corresponding aldehyde and alkoxyhydroperoxide and wherein the total number of carbon atoms in each molecule is in the range of from 2 to about 30.

2. A method according to claim 1 wherein the alkoxyhydroperoxide is dissolved in a suitable solvent-electrolyte.

3. A method according to claim 1 wherein the feed material contains 12-Oxo-1-methoxydodecanehydroperoxide and there is recovered alpha, omega-dodecanedialdehyde.

4. A method according to claim 1 wherein the feed material contains heptaldehyde and 1-methoxyheptanehydroperoxide.

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