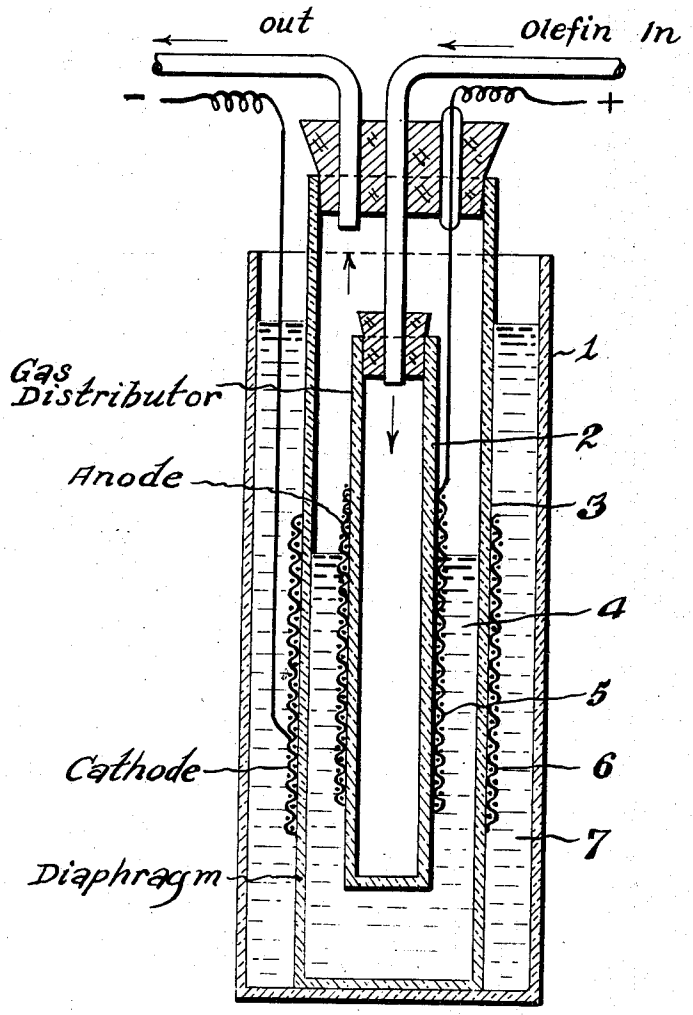
Sept. 20, 1938. P. V. ÖHMAN 2,130,813

ELECTROLYTIC PRODUCTION OF ESTERS

Filed Jan. 18, 1938



INVENTOR.
Per Valter Öhman
BY Henry C. Parker
ATTORNEY

Patented Sept. 20, 1938 2,130,813

UNITED STATES PATENT OFFICE

2,130,813

ELECTROLYTIC PRODUCTION OF ESTERS

Per Valter Öhman, Gyttorp, Sweden, assignor to Nitroglycerin Aktiebolaget, Gyttorp, Sweden, a registered company

Application January 18, 1938, Serial No. 185,623
In Sweden December 10, 1934

20 Claims. (Cl. 204—9)

This invention relates to processes for producing nitric acid esters by means of electrolytic reactions of an oxidizing nature upon unsaturated carbon compounds.

This application is a continuation-in-part of my copending application, Serial Number 51,709 filed November 26, 1935. In my acknowledged application I have described the process of electrolytically producing nitric acid esters and I have particularly illustrated the specification by examples referring to the anodic oxidation of unsaturated hydrocarbons containing an olefinic bond, in the presence of an electrolyte containing nitrate ions. The reaction is, however, by no means limited to such compounds, the faculty of forming esters at the anode during electrolysis being a property not only peculiar to olefinic hydrocarbons, it having been proven by actual tests that unsaturated carbon compounds in general which contain one or several double bonds of an unsaturated character linking carbon atoms can give rise to nitric acid esters when treated under the appropriate conditions.

The general usefulness of the various means of producing the most favorable conditions of reaction as outlined in my above copending application has also been demonstrated in these other cases. Thus a high concentration of the reacting substances in the anode film or its immediate vicinity should be aimed at and can be attained by mechanical means, e. g. by introducing the carbon compound in the anode chamber through a porous wall against which the anode e. g. in the form of a wire gauze is placed, as shown in the copending application, or, in the case of a gaseous carbon compound, by feeding it under pressure to the anode. Again, high concentrations of the carbon compound in the anolyte can be attained by using an anolyte having a high solubility for the substance to be treated. To the electrolyte is suitably added a conducting salt, preferably calcium nitrate. This is particularly useful when the reaction is carried out in a substantially water free medium. Acetic acid and acetone are suitable as solvents for the substances to be esterified or as components of the electrolyte, although other solvents in many cases may be employed as should be clear to anybody familiar with organic chemistry. The formed product may also be obtained from the anolyte in any suitable manner, e. g. by salting out, by extraction, by evaporation, etc.

To further increase the yield of the desired product this should be protected as much as possible against a continued action from the reagents, once it has formed. Thus, a so-called esterification in two-phase system may suitably be applied by the introduction into the anode compartment of a solvent for the nitric acid ester, which is immiscible with or has a low solubility in the anolyte, and which will thus immediately remove the ester from the reacting system as it is formed. When using aqueous solutions, chloroform is suitable for this purpose.

Catalysts will also in many instances greatly influence the reaction. A suitable catalyst should be preferential, i. e. favourably influence the velocity of the main reaction while being without influence or even have a depressing action upon side-reactions and on such reactions which would tend to destroy an already formed desired product. The anode per se, may also serve as such catalyst.

Since a high oxygen pressure is evidently of favorable influence upon the reaction, the discharge voltage of oxygen on the anode should be high, i. e. such conditions should be selected which have a depressing effect upon the evolution of oxygen at the anode. This may be obtained by selecting a suitable anode material, e. g. as above mentioned, smooth platinum, gold, iridium, or alloys thereof, which show a high overvoltage toward oxygen, and also by giving the anolyte a suitable composition and temperature. Another factor to be considered in this connection is the current density at the anode surface, as well as the surface condition of the latter.

The selection of anode material will often depend on the fact, that a certain material, which otherwise would be suitable, may also have such a promoting action on undesired side-reactions that it must be excluded for this reason. Thus a palladium anode will cause side-reactions to such a degree that it is unsuitable in cases where a formation of ethylene nitrate is chiefly desired. Similarly, optimum temperatures and suitable compositions of the anolyte are dependent on factors which may have an influence in various directions. The hydroxyl ion concentration should, however, as a rule be kept low at the anode.

The technical realization of these reactions require as indicated above, the best possible contact between anode surface and reacting compounds. The electrolytic cell may thus, in such cases when the carbon compound is in the gaseous state, suitably be built as a more or less gastight chamber in which the anolyte and catholyte are separated by means of a porous diaphragm.

An electrolytic cell of this type is illustrated in the accompanying drawing which represents a vertical section through a cell which is useful in conducting my process.

The cell shown in the drawing comprises three concentric cylindrical elements, the outer vessel 1, the porous diaphragm 3 and the inner gas distributing tube 2. The anode gauze 5 may be mounted on the outside of the gas distributing tube while the cathode 6 may be correspondingly mounted on the porous diaphragm 3, as shown.

The anolyte 4 is then placed between the gas distributor and the porous diaphragm, while the catholyte 7 is placed in the outer vessel and is separated from the anolyte by the porous diaphragm. A gaseous unsaturated carbon compound is introduced into the gas distributor 2 by the tube at the top, as shown by the arrow. It passes through the gas distributor into the anolyte 4 and the gas which is not absorbed passes out through the tube at the top of the anode compartment, as shown by the arrow.

This arrangement, shown in the drawing has been used in carrying out the esterifications of ethylene referred to in Example 1 below. Particularly in the case of reactions with carbon compounds in solution, an arrangement without a diaphragm or porous anode wall may also be used. It is e. g. possible to saturate the electrolyte outside the electrolytic cell with the carbon compound in question and afterwards introduce this solution in the electrolytic cell. This procedure is, of course, possible to use in the case of both gaseous, liquid, and solid carbon compounds.

The formed product may be obtained from the anolyte in any suitable manner, e. g. by a salting-out, by producing a low solubility in the electrolyte, by extraction (particularly in the case of the above mentioned two-phase reactions), by evaporation of the anolyte, etc.

As an example of reactions according to the invention the following may be mentioned:

EXAMPLE 1

Esterification of ethylene

Anode: smooth platinum gauze 100 x 80 mm., diameter of wire 0.1 mm., number of meshes per sq. cm. about 100.

Electrolyte	Catholyte	Current intensity	Potential drop of bath	Current efficiency	Content of azotemetric nitrogen in product
100 cm.³ acetone, 10 cm.³ water, 5 g. $Ca(NO_3)_2$	$Ca(NO_3)_2$ in aqueous solution.	About 0.2a.	4.0–4.7v.	Percent 67	Percent 13.34
100 cm.³ acetone, 10 g. $Ca(NO_3)_2$	do	do	4.1–4.6v.	75	13.14
100 cm.³ acetone, 5 cm.³ HNO_3 (sp. g. 1.40)	do	do	3.8–4.1v.	79	13.78
100 cm.³ acetone, 10 g. $Ca(NO_3)_2$	do	1.7–3.1	About 30v.	64	14.70

EXAMPLE 2

Esterification of butylene

Apparatus as in previous example.

100 cm.³ acetone, 10 g. $Ca(NO_3)_2$	$Ca(NO_3)_2$ in aqueous solution.	About 0.4a.	7.2–8.2v.	Percent 44	Percent 10.8

Normal butylene ($CH_3CH{:}CHCH_3$) was used in the test.

EXAMPLE 3

Esterification of propylene

Anode of Pt-gauze as above 95 x 95 mm. applied on the outside of a porous alundum tube.

100 cm.³ acetone, 10 g. $Ca(NO_3)_2$	$Ca(NO_3)_2$ in aqueous solution.	About 0.4a.	6.7–7.5v.	Percent 33	Percent 11.63

Note: By "current efficiency" is meant the obtained quantity of nitric acid esters in per cent of the theoretical maximum yield of dinitrate of ethylene, butylene, etc. ($C_2H_4(NO_3)_2$; $C_4H_8(NO_3)_2$, etc.)

The following examples will serve to demonstrate the wide scope of the invention by typifying certain general classes of compounds which may be converted into nitric acid esters by employing the reactions set forth in my above mentioned copending application, but it must at the same time be understood that these further examples by no means confine the invention to the classes of compounds specifically mentioned in the following.

Example 4.—Type: Esters containing a double bond of an unsaturated character, including unsaturated cyclic double bonds, that is, cyclic olefine esters, halogen esters and esters of organic and inorganic oxygen-acids, etc.

(*a*) Vinyl bromide $H_2C{:}CHBr$. Anolyte consisting of 5 gm. $Ca(NO_3)_2$, 5 gm. acetic acid and 90 gm. acetone containing about 1% by weight of vinyl bromide. Nitrogen content of product: 6.76%.

(*b*) Allyl bromide $H_2C{:}CHCH_2Br$. Anolyte consisting of 10 gm. allyl bromide, 10 gm. $Ca(NO_3)_2$, 10 gm. acetic acid and 100 gm. acetone. Nitrogen content of product: 3%.

(*c*) Vinyl acetate $H_2C{:}CHOOCCH_3$. Anolyte: 5 gm. $Ca(NO_3)_2$, 90 gm. acetone containing about 0.3% by weight of vinyl acetate. Rendered acid and mixed with CO_2. Nitrogen content of product: 9.7%.

Example 5.—Type: Organic acids containing a double bond of an unsaturated character, including olefinic cyclic bonds.

(*a*) Acrylic acid. $H_2C{:}CHCOOH$. Anolyte: Nitric acid of 20% strength containing about 0.3% by weight of acrylic acid. Nitrogen content of product: 10.6%.

(*b*) Crotonic acid (alpha) $H_2C{:}CHCH_2COOH$. Anolyte: 5 gm. $Ca(NO_3)_2$, 90 gm. acetone containing about 0.05% by weight crotonic acid rendered acid and mixed with CO_2. Nitrogen content of product: 9.7%.

(*c*) Maleic acid.

$$\begin{matrix} HCCOOH \\ \| \\ HCCOOH \end{matrix}$$

Anolyte: 5 gm. maleic acid, 5 gm. $Ca(NO_3)_2$ and 50 gm. acetone. Nitrogen content of product: 6.4%.

Example 6.—Type: Alcohols containing a double bond of an unsaturated character.

Allyl alcohol. $H_2C:CHCH_2OH$. Anolyte: 5 gm. $Cr(NO_3)_2$, 5 gm. acetic acid, 90 gm. acetone containing allyl alcohol in a concentration of about 0.2%. Nitrogen content of product: 10%.

Example 7.—Type: Derivatives of olefinic hydrocarbons and containing more than one double bond of an unsaturated character i. e. poly-ene compounds of aliphatic or cyclic nature also comprising partly halogen substituted compounds.

(*a*) Isoprene $CH_2:C(CH_3)CH:CH_2$. Anolyte: 5 gm. $Ca(NO_3)_2$, 90 gm. acetone containing about 0.5% of isoprene. Stirred with CO_2. Nitrogen content of product: 5.0%.

(*b*) Butadiene. $CH_2:CHCH:CH_2$. Anolyte: 0.2 gm. butadiene dissolved in 100 ccs. liquid, consisting of acetone with 10% by weight $Ca(NO_3)_2$ acidified with acetic acid. The anode consisted of a rotating platinum gauze. The sample exploded when dissolved in sulphuric acid.

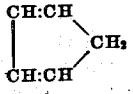
(*c*) Di-methyl-butadiene $CH_3CH:CHCH:CHCH_3$.

(*d*) Allene $CH_2:C:CH_2$. Anolyte: Acetone containing 10% by weight $Ca(NO_3)_2$ and 10% concentrated acetic. Anode:—Platinum-gauge on the outside of a diaphragm, through which the allene was slowly fed into the anolyte. Nitrogen content of product: 9.6%.

(*e*) Chloroprene $H_2C:CClCH:CH_2$. Polymerized chloroprene, so called Duprene was depolymerized by dry distillation. 0.5 gm. of the received product was dissolved in 100 ccs. anolyte consisting of acetone with 10% $Ca(NO_3)_2$. A rotating anode of platinum-gauze was used. The product contained 3.2% of chlorine and exploded when dissolved in concentrated sulphuric acid. The nitrogen content of the product was 1.6% N or more.

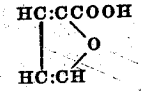
(*f*) Phorone $(CH_3)_2C:CHCOCH:C(CH_3)_2$. Anolyte: 5 gm. phorone, 10 gm. acetic acid, 10 gm. $Ca(NO_3)_2$ diluted with acetone to 200 cm^3. Nitrogen content in product: 3.5%.

(*g*) Cyclo-pentadiene



Anolyte: 10 gm. $Ca(NO_3)_2$, 10 gm. acetic acid and 180 gm. acetone containing about 0.1% cyclopentadiene. Nitrogen content of product: 7.5% (product in liquid state) 8.4% (product solid).

(*h*) Pyromucic acid



Anolyte 5 gm. $Ca(NO_3)_2$, 5 gm. acetic acid, and 95 gm. acetone containing about 0.3% pyromucic acid. Nitrogen content of product: 5.6%.

The nitrogen content was in all cases determined in an azotometer in the usual way. In all examples given above, the anode consisted of a platinum gauze but, as described in my copending application, Serial Number 51,709, the selection of the best anode material must be governed by several considerations. The process is thus by no means restricted to using a platinum anode.

It has proven of particular advantage to use a catholyte containing a fairly high amount of acetic acid and also suitably containing nitrate ions e. g. as calcium nitrate, especially in cases where the anolyte contains organic solvents e. g. acetone. When using a diaphragm, the acetic acid has a cleansing action upon this due to its faculty for keeping such organic bodies, coming from the anode compartment, in solution, which otherwise have a tendency to precipitate when mixed with catholytes containing higher percentages of water. For this reason it is also advisable to keep the catholyte in a slow streaming motion through the diaphragm in direction towards the anode compartment.

In order to prevent, as much as possible, a formation of undesired bodies in the cathode compartment e. g. by reduction of nitrates, etc. in the vicinity of the cathode, such conditions near this should be chosen which tend to counteract reducing reactions e. g. introduction of oxidizing agents, such as air, oxygen or other suitable chemical bodies near the cathode, as well as selecting a cathode material which serves the same purpose.

As should be plain from the numerous examples given, the process also applies to aromatic compounds having unsaturated side chains of the same character as stated above.

The nitric acid esters obtained by the anodic oxidation process are particularly usefus as explosives or admixtures to shock sensitive products used as explosives as already set forth in my above mentioned copending application, Serial Number 51,709.

As there shown, when aqueous solutions and ethylene are employed in my process, various side reactions occur resulting in the formation of polyglycol nitrates, one of which has the formula:

$$CH_2NO_3—CH_2—O—CH_2—CH_2NO_3.$$

These polyglycol nitrates possess explosive characteristics similar to those of glycol nitrate, for which reason it is not necessary to separate them from the reaction products. The same is true of a number of other bodies which are formed in a similar manner by way of side reactions. In the manufacture of the so-called safety explosives an admixture of polyglycol nitrate has even been found of direct advantage due to its low sensitivity to shock. The reaction products obtained by my method are less sensitive to shock than pure glycol nitrate owing to the inclusion of these side reaction products. If it should be desired to suppress these side reactions, the reaction medium should, of course, be as free from water as possible.

I claim:

1. The process of making nitric acid esters which comprises the step of submitting an unsaturated organic compound, containing at least one olefinic double bond of unsaturated character linking carbon atoms, to anodic oxidation in the presence of an electrolyte containing nitrate ions.

2. The process of claim 1 wherein said unsaturated organic compound is a gaseous hydrocarbon of the olefin series.

3. The process of claim 1 wherein said unsaturated organic compound is ethylene.

4. The process of claim 1 wherein said unsaturated organic compound containing at least one olefinic double bond is selected from a group of such compounds consisting of organic acids, alcohols, poly-ene compounds, ketones, hydro-

carbons, halogen esters, and esters of organic oxy-acids and inorganic oxygen-acids.

5. The process of claim 1 wherein said unsaturated organic compound is chloroprene.

6. The process of claim 1 wherein said unsaturated organic compound is maleic acid.

7. The process of claim 1 wherein said electrolyte contains an inert organic solvent for said unsaturated organic compound.

8. The process of claim 1 wherein said electrolyte comprises a non-aqueous organic electrolyte containing a solvent for said unsaturated organic compound.

9. The process of making nitric acid esters which comprises introducing an unsaturated organic compound, containing at least one olefinic double bond of unsaturated character linking carbon atoms, into an aqueous electrolytic bath containing a highly conducting nitrate in solution, passing an electric current through said bath between an anode and a cathode, the anode being of a metal producing high oxygen over-voltages, and recovering the resulting nitric acid esters from said electrolyte.

10. The process of claim 9 wherein a solvent for said nitric acid esters is added to said bath, said solvent being substantially insoluble in said bath, whereby said solvent dissolves said nitric acid esters when formed, said esters being then recovered from said solvent.

11. As a new composition of matter, a product containing a dinitrated derivative of a low-molecular unsaturated carbon compound containing an olefinic bond, dinitrated poly-compounds of said unsaturated carbon compound and other side-reaction products of said unsaturated carbon compound; said composition being less sensitive to shock than the pure dinitrated derivative of said unsaturated carbon compound and constituting the reaction products obtained by subjecting said unsaturated carbon compound to anodic oxidizing conditions in the presence of an electrolyte containing nitrate ions.

12. As a new composition of matter a product containing ethylene nitrate, polyglycol nitrate and other side-reaction products of ethylene; said composition being less sensitive to shock than pure ethylene nitrate and constituting the reaction products obtained by subjecting ethylene to anodic oxidizing conditions in the presence of an electrolyte containing nitrate ions.

13. The process of preparing nitric acid esters which comprises supplying a feed of a gaseous, lower membered, olefinic hydrocarbon to an anode while passing an electric current through an anolyte, containing acetone and nitrate ions, to said anode to establish an oxidizing condition at the interface between said anode and said anolyte.

14. The process of preparing nitric acid esters which comprises saturating a liquid containing nitrate ions with a gaseous, lower membered, olefinic hydrocarbon under pressure and maintaining said liquid under pressure while subjecting it to electrolytic oxidizing conditions using an anode which produces high overvoltage toward oxygen and under such conditions that evolution of oxygen at the anode is suppressed.

15. The process of preparing nitric acid esters which comprises subjecting a low-molecular unsaturated hydrocarbon containing an olefinic bond to anodic oxidizing conditions in the presence of an anolyte containing nitrate ions and hydrogen ions and of low hydroxyl ion concentration, said anolyte comprising a component having high solvent power for said hydrocarbon.

16. In the process as set forth in claim 15 the use of an anolyte comprising acetone and calcium nitrate.

17. The process of preparing nitric acid esters which comprises an unsaturated olefinic hydrocarbon to anodic oxidizing conditions in the presence of an anolyte containing nitrate ions, using a noble metal anode while producing such conditions near the cathode that the reducing action of this latter is at least partly counteracted.

18. A process for electrolytic production of nitric acid esters comprising using in an electrolytic cell a suitable cathode and an anode of a material and surface condition producing high overvoltage toward oxygen in contact with an anolyte containing ethylene, nitrate ions and a component having high solvent power for ethylene, adjusting the acidity of said anolyte so that a low hydroxyl ion concentration is obtained in the vicinity of said anode, effecting a high conductivity of said anolyte and a suitable catholyte contained in said cell substantially by means of the addition of calcium nitrate thereto, circulating ethylene gas through said anolyte, said anolyte being separated from the catholyte of the cell by means of a suitable membrane; and passing a direct electric current through said cell from anode to cathode while maintaining said conditions.

19. The process of claim 9 wherein said anode and said cathode are separated by a porous diaphragm and the catholyte is maintained slowly streaming through said diaphragm towards said anode.

20. The process of claim 9 wherein an oxidizing gas is introduced into said bath in the vicinity of said cathode.

PER VALTER ÖHMAN.