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(54) Title: PROCESS FOR THE PREPARATION OF NAPHTHOQUINONES		
(57) Abstract <p>A process for the preparation of a naphtho-1,4-quinone, which process comprises oxidising a naphthalene by the action of an aqueous solution of a cerium (IV) salt and an acid, characterised in that the oxidation is conducted in the presence of toluene as an organic solvent. The cerium (IV) salt may be prepared by electrochemical oxidation of the corresponding cerium (III) salt formed during a preceding oxidation.</p>		

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PROCESS FOR THE PREPARATION OF NAPHTHOQUINONES

The present invention relates to a process for the preparation of naphthoquinones, in particular naphtho-1,4-quinone, from the corresponding naphthalenes by oxidation using certain cerium salts.

5 It is disclosed in DE 152 063 that naphthalene may be oxidized to naphtho-1,4-quinone using cerium (IV) sulphate, during which the cerium (IV) salt is reduced to cerium (III) sulphate. The cerium (III) sulphate so-formed may be converted back into cerium
10 (IV) sulphate by oxidation for economic and environmental reasons. Such an oxidation may be carried out using e.g. ozone, but electrolysis of the cerium (III) sulphate in dilute sulfuric acid is at present a particularly suitable process for this
15 purpose. In order to carry out the oxidation process as efficient as possible, especially to achieve a sufficient current efficiency during an electrolysis process, organic components have to be removed prior to oxidation.

20 A prerequisite for a simple separation is the execution of the oxidation of the naphthalene substrate with the cerium (IV) sulphate dissolved in dilute acid, especially sulfuric acid, in a biphasic reaction mixture.

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The following processes for the preparation of naphthoquinones have been disclosed in the prior art:

- 1) oxidation of finely ground, solid naphthalene without the addition of organic solvents and at a temperature sufficiently low to avoid adhesion of the naphthalene particles (DE 32 20 305).
- 2) oxidation of molten naphthalene without the addition of organic solvents at a temperature of from 80 to 100°C (DE 18 04 727).
- 3) oxidation of naphthalene in a suitable solvent that is both stable against oxidation and poorly water-miscible.

However, the processes disclosed in the prior art have a number of serious disadvantages. The first process is complicated because the starting material has to be ground to a particle size of approximately 0.1 mm, the process requires a special reactor in which reaction and filtration can alternately be carried out, the volume-time yield is low, and, additionally, the conversion of naphthalene is low (<70%; I.M. Dalrymple and J.T. Millington, J. Appl. Electrochem. 16, 885 (1986)).

Compared to the first process, operation of the second process is easier. However, the conversion of the starting material is even lower. Further, this process has to be carried out in such a way that the formed quinone does not crystallize, otherwise, the organic layer is prevented from being mixed sufficiently with the oxidating solution. Moreover, the process requires a reaction temperature of more than 80°C, at which temperature the selectivity of cerium (IV) sulphate is significantly reduced, compared with operation at lower temperatures. This reduced selectivity results in a low conversion of

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naphthalene (<50%; DE 32 20 305) and in product mixtures which are difficult to purify.

5 The third process, in which a solvent stable against oxidation and which is poorly water-miscible is added, is easy to operate and can be carried out in the optimal temperature range for oxidation (DE 18 04 727). Thus, reasonable product yields can be obtained. However, for successful and efficient operation of the process, the solvent has to meet 10 several requirements. Firstly, it has to be sufficiently stable under the oxidation conditions necessary for the naphthalene substrate. Secondly, the water miscibility of the solvent should be very low and the dissolving power for starting material and product sufficiently high. Thirdly, in oxidative 15 regeneration of the cerium (III) salt, the solvent must not induce corrosion, for example as encountered with halogenated solvents. Finally, the solvent should possess a boiling point within the suitable temperature range, a low price and be safe with 20 respect to the environment and toxicity.

Solvents disclosed in the relevant prior art suffer one or more disadvantages in that they have a low dissolving power for naphtho-1,4-quinone, for 25 example aliphatic hydrocarbons and ethers, and/or increase the corrosion of the oxidation equipment, e.g. of the anode in an electrochemical process, for example chloro hydrocarbons, and/or are toxicologically unsafe, such as benzene. Such 30 solvents are not suitable for use as solvents in the oxidation of naphthalene using cerium (IV) salts.

Toluene does not possess the aforementioned disadvantages. However, it has been generally accepted that toluene would not be stable under the 35 oxidation conditions prevailing in the preparation of

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naphtho-1,4-quinones by the aforementioned process. In particular, it has been disclosed in the prior art (DE 158 609; Tetrahedron Lett. 1966, 4493) that toluene is readily oxidized to benzaldehyde by cerium (IV) salts, and also by other mild oxidants (M.V. Bhatt and P.T. Perumal, Tetrahedron Lett. 1981, 2605; US 3,647,715; H. Kropf, E. Müller and H. Weickmann in Houben-Weyl, Methoden der organischen Chemie, 4th ed. vol. 4/1a, Stuttgart 1981).

In complete contrast to the general teaching and understanding of the prior art, it has, most surprisingly, been found that toluene is a very suitable solvent for the oxidation of naphthalenes to the respective naphtho-1,4-quinones by cerium (IV) salts.

Accordingly, the present invention provides a process for the preparation of a naphtho-1,4-quinone, which process comprises oxidising a naphthalene by the action of an aqueous solution of a cerium (IV) salt and acid, characterised in that the oxidation is conducted in the presence of toluene as an organic solvent.

The naphthalene starting material may, optionally, bear one or more substituents selected from those typical in the art. Optional substituents may, for example, be alkyl groups. Alkyl moieties present as substituents preferably have from 1 to 10 carbon atoms, more preferably 1 to 6 carbon atoms. The naphthalene starting material is preferably not substituted. However, if a substituent is present, it is preferably in the 2-position. A most preferred substituent, if present, is methyl.

The acid to be used in the process of the present invention may be every suitable acid or mixture of acids, e.g. sulphuric acid, phosphoric

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acid and hydrochloric acid, or mixtures thereof. Especially preferred is sulphuric acid, amongst others because its stability during electrochemical regeneration of cerium (III). The optimum
5 concentration of sulphuric acid is between 5 and 20% wt, preferably between 10 and 20% wt, in view of the solubility of the cerium salts, its specific gravity with regard to the separation step and its electrolytic conductivity.

10 The cerium (IV) salt used in the process may be any suitable salt. A preferred cerium (IV) salt is cerium (IV) sulphate.

The naphthalene is dissolved in toluene and then thoroughly mixed with an aqueous solution of the
15 cerium (IV) salt in dilute sulphuric acid. The pH of the reaction mixture is preferably below 3, preferably below 1. The concentration of the naphthalene in toluene is suitably between 1 and 30% wt, especially between 10 and 15% wt.

20 The concentration of cerium salt is suitably between 0.01 and 1M, especially between 0.10 and 0.5M.

As discussed above in relation to the prior art processes, the selectivity of the cerium (IV) salt
25 oxidation is reduced as the temperature at which the process is conducted increases. It is a particular advantage of the process of the present invention that it can be operated efficiently at relatively low temperatures. Thus, the process is preferably
30 operated at a temperature below about 75°C. Preferably, the reaction is carried out at a temperature in the range from 55°C to 65°C.

After completion of the reaction, the two phases of the reaction mixture are separated and the

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naphtho-1,4-quinone product recovered by usual methods from the organic layer.

The aqueous cerium (III) salt solution obtained may, if desired, be subjected to electrochemical oxidation or oxidation using ozone, during which particular advantages of the process according to the invention may be realised. The electrolysis serves to oxidise the cerium (III) salt formed during the process to the corresponding cerium (IV) salt, for further use in the process. This electrolysis stage is facilitated by the aforementioned advantages of using toluene as the solvent in the process.

The process may be carried out either in batches or, advantageously, in a continuous flow operation.

Toluene meets the aforementioned requirements of a solvent for the process, in that it has sufficient chemical stability under the oxidation conditions, poor water-miscibility, high dissolving power for the starting material and product, no stimulation of corrosion, low toxicity and hence a high level of environmental safety, a suitable boiling point and an economic price.

The present invention will be further understood from the following illustrative examples.

EXAMPLES

Example 1

Preparation of naphtho-1,4-quinone by oxidation of naphthalene using an aqueous cerium (III) and cerium (IV) sulphate solution acidified with sulphuric acid

The solution used for the oxidation of naphthalene contained the following compounds:

0.60 mol/l cerium (IV) sulphate (= 0.60 M Ce^{4+})
0.10 mol/l cerium (III) sulphate (= 0.20 M Ce^{3+})

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1.0 - 1.2 mol/l sulphuric acid.

Naphthalene (11.5g, 0.090 mol) dissolved in toluene (120 ml) was thoroughly stirred at 50°C with the aforementioned solution (2.4 l), until the concentration of cerium ions determined by iodometric titration had dropped to 0.36 - 0.38 M (after about 50-60 min.). The layers were then separated and the aqueous layer extracted with toluene (120 ml). The collected organic layers were washed with water (120 ml) containing a small amount of hydrogen peroxide. The wash water and the aqueous layer of the reaction mixture were collected and evaporated in vacuo at a maximum temperature of 50°C to the original volume (2.4 l).

The washed toluene solution was evaporated in vacuo at max. 60°C as far as possible. The residue was subjected to a steam distillation in vacuo, whereby toluene and unreacted naphthalene distilled with the water. Almost pure naphtho-1,4-quinone and water remained in the still. Toluene was added and the organic layer was evaporated in vacuo after separation of the water. Analysis by thin layer chromatography (silica gel, acetone/heptane, 1:1) proved the product to be pure.

Yield: 12.0 g (84% of theoretical referred to naphthalene; 82% of th. referred to Ce(IV) ions)

Mp.: 117-123°C (after sintering: 111°C)

Example 2:

Preparation of naphtho-1,4-quinone by oxidation of naphthalene using an aqueous cerium (III) and cerium (IV) solution acidified with sulphuric acid, followed by electrolytic regeneration of the cerium salt solution:

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A solution of naphthalene (13.0 g, 0.10 mol) in toluene (100 ml) was thoroughly stirred with a solution (5 l) containing $\text{Ce}(\text{SO}_4)_2$ (0.122 mol/l) and $\text{Ce}_2(\text{SO}_4)_3$ (0.02 mol/l, electrolytically regenerated cerium sulphate solution) in aqueous sulphuric acid (20%) at 58-60°C for 40 min. Subsequently, the layers were separated and the aqueous layer extracted with toluene (100 ml).

The collected organic layers were washed with water (50 ml) and then evaporated in vacuo at 60°C bath temperature until a small amount of product precipitated. The evaporation was stopped and the residue chilled in an ice bath, whereby the major part of the formed naphtho-1,4-quinone crystallized and the unreacted naphthalene remained completely dissolved. After 20-30 minutes of cooling, the precipitate was collected by vacuum filtration and dried in a circulating air drier. The mother liquor was used for the following batch.

The aqueous layer of the reaction mixture was electrolyzed on a PbO_2 anode. The amperage was regulated such that only a small amount of oxygen was formed at the anode. When the concentration of cerium (III) ions was about 0.04 mol/l, the electrolysis was stopped.

For the following batch, the electrolytically oxidized solution was stirred with toluene (100 ml) containing the material of the mother liquor of the first batch and additional naphthalene (11 g, 0.086 mol). Work-up was carried out as described above for the batch.

Yield: 85% of th. referred to naphthalene
Purity: >99%.

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Example 3:

Preparation of 2-methyl naphtho-1,4-quinone by oxidation of 2-methyl naphthalene using a cerium (IV) sulphate solution acidified with sulphuric acid:

5 A solution of 2-methyl naphthalene (1.42 g, 10 mmol) in toluene (30 ml) was thoroughly stirred with a solution of cerium (IV) sulphate (30 g, 75 mmol) and concentrated sulphuric acid (60 ml) in water (600 ml) at 70°C for 9 hours. Subsequently,
10 the layers were separated, the organic layer twice washed with water and then evaporated in vacuo to dryness. The crystalline residue was recrystallized from methanol.

 Yield: 1.5 g (87% of th. calculated on the
15 2-methyl naphthalene)
 Mp.: 101-103°C

CLAIMS

1. A process for the preparation of a naphtho-1,4-quinone, which process comprises oxidising a naphthalene by the action of an aqueous solution of a cerium (IV) salt and an acid, characterised
5 in that the oxidation is conducted in the presence of toluene as an organic solvent.
2. A process according to claim 1, characterised in that the oxidation is conducted at a temperature below 75°C.
- 10 3. A process according to claim 2, characterised in that the oxidation is conducted at a temperature in the range of from 55°C to 65°C.
4. A process according to any preceding claim, characterised in that the cerium (IV) salt is
15 cerium (IV) sulphate.
5. A process according to any preceding claim, characterised in that the cerium (IV) salt is prepared by oxidation of the corresponding cerium (III) salt produced during a preceding
20 oxidation.
6. A process according to claim 5, characterised in that the oxidation process is an electrochemical process.

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7. A process according to any of the preceding claims, characterised in that the napho-1,4-quinone is napho-1,4-quinone.
- 5 8. A process according to any of the preceding claims, characterised in that the acid is sulfuric acid.
9. A process according to claim 1, which is carried out substantially as hereinbefore described having reference to any one of Examples 1 to 3.
- 10 10. A naphtho-1,4-quinone whenever produced by a process according to any preceding claim.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 91/01958

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C07C46/04; C07C50/10; C07C50/12		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C07C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	CHEMICAL ABSTRACTS, vol. 104, 1986, Columbus, Ohio, US; abstract no. 232913, TAKAHASHI, YOJIRO ET AL.: 'ELECTROCHEMICAL OXIDATION OF AROMATIC COMPOUNDS.' page 528 ;column 2 ; see abstract & JP,A,6 152 382 (NIPPON SHOKUBAI KAGAKU KOGYO CO.,LTD.) 15 March 1986 ---	1-10
Y	US,A,3 510 498 (LE ROI E. HUTCHINGS) 5 May 1970 see column 6, line 17 - line 31; claims 1,2 ---	1
Y	US,A,4 632 782 (TATSUYOSHI ET AL.) 30 December 1986 * Column 3; Column 8, line 11-line 14 * ---	1
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IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
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		JP-B- 2002956	19-01-90
US-A-3510498	05-05-70	None	
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		CA-A- 1225095	04-08-87
		SE-B- 463417	19-11-90
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