PROCESS FOR PREPARING BIS(ALKANESULFONYL)PEROXIDE

Abstract: A process for preparing bis(alkanesulfonyl)peroxide of the formula (I), in which ALK represents an alkyl group, characterized by the following process steps: a) mixing an alkylsulfonic acid chloride in a reaction vessel; b) with an excess of a peroxide-containing compound; c) optionally adding a basic compound if hydrogen peroxide is employed; d) allowing the mixture to react; adding water to terminate the reaction; and e) separating the reaction product obtained, bis(alkanesulfonyl)peroxide.
Process for Preparing Bisfalkanesulfonyl peroxide

The present invention relates to a process for preparing bis(alkanesulfonyl) peroxide.

Bis(alkanesulfonyl) peroxide compounds are free-radical initiators for chemical syntheses, especially for polymerization reactions and free-radical induced processes and chain reactions. The free radicals are formed by thermal, photolytic, metal-catalyzed or other excitation (e.g., microwaves) of the peroxide.

US 4,680,095 discloses the preparation of dialkanesulfonyl peroxide ($\text{RSO}_2\text{O-O-O}_2\text{SR}$) in a continuous process by electrolyzing the corresponding alkanesulfonic acid at an elevated temperature (to keep the peroxide product in solution) in a continuous-flow electrolysis cell, removing the solution from the electrolytic cell, cooling the solution to precipitate the peroxide product, and recycling the supernatant alkanesulfonic acid back to the cell.

One important representative of the bis(alkanesulfonyl peroxide) class of compounds is its methyl derivative bis(methanesulfonyl) peroxide with the CAS number 1001-62-3 and the CAS name methanesulfonic acid methylsulfonyloxy ester. Its IUPAC name is methylsulfonyloxy methanesulfonate, and it has the following formula:

It is the object of the present invention to provide a simple process for preparing bis(alkanesulfonyl) peroxide compounds that enables the preparation of the compound in high purity and high yield.
The object of the invention is achieved by a process for preparing bis(alkanesulfonyl) peroxide of the formula

\[ \text{M}_1 \text{M}_2 \text{S}_1 \text{S}_2 \text{O}_1 \text{O}_2 \]

in which ALK represents an alkyl group,

characterized by the following process steps:

a) mixing an alkylsulfonic acid chloride in a reaction vessel;
b) with an excess of a peroxide-containing compound;
c) optionally adding a basic compound if hydrogen peroxide is employed;
d) allowing the mixture to react; adding water to terminate the reaction; and
e) separating the reaction product obtained, bis(alkanesulfonyl) peroxide.

According to the process according to the invention, the alkylsulfonic acid chloride may be selected from the group consisting of methylsulfonic acid chloride, ethylsulfonic acid chloride, propylsulfonic acid chloride, or butylsulfonic acid chloride.

It may be advantageous to charge the alkylsulfonic acid chloride in a cooled condition in step a).

The order of process steps a) to c) can be permuted. Thus, the sequence of the process steps can be, in particular: a), b), c); a), c), b); b), a), c); b), c), a); c), a), b); or c), b), a).

According to the invention, reaction steps a) to d) are typically performed with cooling by ice/iced water.

According to the invention, the peroxide-containing compounds may be inorganic or organic peroxide compounds. Said peroxide-containing inorganic compounds, in
particular, are selected from the group consisting of hydrogen peroxide, especially as a 60-70% by weight hydrogen peroxide solution, or its alkali or alkaline earth metal salts, or so-called superoxides and ozonides. Also, perboric acids and hydrogen peroxide adducts can be employed. Said peroxide-containing organic compounds, in particular, are selected from the group consisting of aryl and alkyl peroxides, for example, cumene hydroperoxide, dibenzoyl peroxide, percarboxylic acids, for example, peracetic acid, amine oxides, for example, piperidine oxides or peroxonitrites, or organometallic peroxo reagents, for example, copper oxidation catalysts.

Said basic compound is typically an inorganic or organic base. Said inorganic base, in particular, may be selected from the group consisting of sodium hydrogen carbonate, aqueous sodium hydroxide, sodium carbonate, sodium phosphate, calcium carbonate. Said organic base, in particular, may be selected from the group consisting of triethylamine, DBU (diazabicycloundecene), DABCO (triethylene diamine), and/or ethanolamine. In particular, the basic compound is added dropwise with cooling.

The process according to the invention is further illustrated in the following Example by means of the preparation of bis(methanesulfonyl) peroxide.

Example:

Into a Schlenk flask purged with nitrogen and placed in an ice bath, 0.10 mole of methanesulfonic acid chloride was weighed. Thereafter, an excess of 70% (w/w) hydrogen peroxide was added, and triethylamine was added dropwise. After the solution had been stirred with a magnetic stirrer with cooling for 2 h, an excess of iced water was added, and the precipitated white solid was filtered off. It was pure bis(methanesulfonyl) peroxide. The yield was about 60%.
CLAIMS

1. A process for preparing bis(alkanesulfonyl) peroxide of the formula in which ALK represents an alkyl group, characterized by the following process steps:

   a) mixing an alkylsulfonic acid chloride in a reaction vessel;
   b) with an excess of a peroxide-containing compound;
   c) optionally adding a basic compound if hydrogen peroxide is employed;
   d) allowing the mixture to react; adding water to terminate the reaction; and
   e) separating the reaction product obtained, bis(alkanesulfonyl) peroxide.

2. The process according to claim 1, characterized in that said alkylsulfonic acid chloride is selected from the group consisting of methylsulfonic acid chloride, ethylsulfonic acid chloride, propylsulfonic acid chloride, or butylsulfonic acid chloride.

3. The process according to claim 1 or 2, characterized in that said alkylsulfonic acid chloride is charged in a cooled condition in step a).

4. The process according to at least one of claims 1 to 3, characterized in that said steps a) to c) are performed in the order of a), b), c); a), c), b); b), a), c); b), c), a); c), a), b), or c), b), a).
5. The process according to at least one of claims 1 to 4, characterized in that said reaction steps a) to d) are performed with cooling by ice/iced water.

6. The process according to at least one of claims 1 to 5, characterized in that said peroxide-containing compounds are inorganic or organic peroxide compounds.

7. The process according to claim 6, characterized in that said peroxide-containing inorganic compounds are selected from the group consisting of hydrogen peroxide, especially as a 60-70% (w/w) hydrogen peroxide solution, or its alkali or alkaline earth metal salts, or so-called superoxides and ozonides.

8. The process according to claim 6, characterized in that said peroxide-containing organic compounds are selected from the group consisting of aryl and alkyl peroxides, for example, cumene hydroperoxide, dibenzoyl peroxide, percarboxylic acids, for example, peracetic acid, amine oxides, for example, piperidine oxides or peroxonitrites, or organometallic peroxo reagents, for example, copper oxidation catalysts.

9. The process according to at least one of claims 1 to 8, characterized in that said basic compound is an inorganic or organic base.

10. The process according to claim 9, characterized in that said inorganic base is selected from the group consisting of sodium hydrogen carbonate, aqueous sodium hydroxide, sodium carbonate, sodium phosphate, and calcium carbonate.

11. The process according to claim 9, characterized in that said organic base is selected from the group consisting of triethylamine, DBU (diazabicycloundecene), DABCO (triethylene diamine), and ethanolamine.
### A. CLASSIFICATION OF SUBJECT MATTER

**INV. C07C409/44 C07C407/00**

**ADD.**

According to International Patent Classification (IPC) or to both national classification and IPC.

### B. FIELDS SEARCHED

- Minimum documentation searched (classification system followed by classification symbols): C07C
- Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched.

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Date of the actual completion of the international search

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17/02/2015

Name and mailing address of the ISA:

European Patent Office, P.O. 5818 Patentlaan 2 NL - 2280 HV Rijswijk

Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer

Mates Valdzielso, J
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