The ratio of dialkyl disulfide to nitric acid is preferably 80:1 (mol/mol) to 1:1 (mol/mol), 60:1 (mol/mol) to 1:1 (mol/mol), 40:1 (mol/mol) to 1:1 (mol/mol), 20:1 (mol/mol) to 1:1 (mol/mol), or 10:1 (mol/mol) to 1:1 (mol/mol).

Alternatively, it is advantageous that the ratio of dialkyl disulfide to nitric acid is always larger than 1:1 because the amount of nitric acid can thus be significantly reduced, which further improves the cost efficiency of the process according to the present invention. Since the nitric acid employed in the process is always regenerated under the reaction conditions of that process, the use of smaller amounts of nitric acid has no negative effects on the yield and the selectivity for the formation of the alkanesulfonic acid. Further, there is no significant increase in reaction time when the ratio of dialkyldisulfide to nitric acid is equal to or larger than 2:1 (mol/mol).

The ratio of dialkyl disulfide to nitric acid is therefore preferably 500:1 (mol/mol) to 2:1 (mol/mol), 200:1 (mol/mol) to 2:1 (mol/mol), 100:1 (mol/mol) to 2:1 (mol/mol), 80:1 (mol/mol), 60:1 (mol/mol) to 2:1 (mol/mol), 40:1 (mol/mol) to 2:1 (mol/mol), 20:1 (mol/mol) to 2:1 (mol/mol), or (10:1 (mol/mol).

In an alternative embodiment of the present invention, the ratio of dialkyl disulfide to nitric acid is therefore 500:1 (mol/mol) to 2:1 (mol/mol).

The process of the present invention allows the preparation of alkanesulfonic acids from the corresponding dialkyl disulfides with yields of more than 90% from safety aspects with a maximum concentration of the dialkyl disulfide in the alkanesulfonic acid of not more than 20 weight per cent. From safety aspects, however, it is even more favourable for the process of the invention to be carried out with a concentration of not more than about 10 weight per cent of the dialkyl disulfide in the alkanesulfonic acid. The reason is that in that case the development both of the temperature and of the pressure during the oxidation of the dialkyl disulfide are lower than if the concentration of the dialkyl disulfide is more than 10 weight per cent or even up to 20 weight per cent. This permits even more effective control of temperature when implementing the process of the invention.

In a further embodiment of the present invention, the concentration of the dialkyl disulfide in the alkanesulfonic acid is up to 10 +/- 1 weight per cent.

The concentration of the dialkyl disulfide in the alkanesulfonic acid is preferably about 1 to about 6 weight per cent, more preferably about 2 to about 6 weight per cent and more particularly about 4 to about 6 weight per cent.

The expression "about" in connection with weight per cent is used in the context of the present invention to refer not only to the figure explicitly given but also to those figures which deviate by +/- 10% from the figures explicitly given. The term "about 10 weight per cent", therefore, encompasses not only the integral figures of 9, 10 and 11 weight per cent but also all figures which can be expressed by real numbers and lie between inclusive of 9 and inclusive of 11 weight per cent. The

At low temperatures, however, owing to the relatively low supply of energy, the oxidation reaction is not completed until a correspondingly longer reaction time has elapsed. For instance, at a reaction temperature of 30°C or 40°C, the oxidation of dimethyl disulfide to methanesulfonic acid requires approximately three or four hours, in order to achieve virtually complete conversion of the dimethyl disulfide. Implementing the same reaction at a temperature of 70°C or 90°C leads to the virtually complete conversion of the dialkyl disulfide within a period just of well below an hour.

In a preferred embodiment of the process according to the present invention, the process is carried out at a temperature of 70°C to 90°C.

The expression "about 70°C" is used in the context of the present invention such as to also encompass values which deviate for a short time, in other words for a time period which is negligible in comparison to the reaction time, by up to -5°C from 70°C.

In the process according to the present invention, the concentration of the dialkyl disulfide to be oxidized is not more than 20 wt.-%. The weight fraction of the nitric acid in the reaction mixture can be approximately disregarded, since in the process of the invention it is used only sub-stoichiometrically relative to the dialkyl disulfide.

In the context of the present invention, the term "stoichiometric", in relation to the ratio of nitric acid to dialkyl disulfide, is used to refer to a ratio of nitric acid to dialkyl disulfide of 1:1. Correspondingly, in the context of the present invention, the term "sub-stoichiometric", in relation to the ratio of nitric acid to dialkyl disulfide, is used to refer to all ratios of nitric acid to dialkyl disulfide that lie below a ratio of nitric acid to dialkyl disulfide of 1:1 – for example, a ratio of dialkyl disulfide to nitric acid of 80:1 (mol/mol), 60:1 (mol/mol), 40:1 (mol/mol), 20:1 (mol/mol) or 10:1 (mol/mol).

In the process of the present invention, therefore, the reaction mixture may comprise 80 wt.-% of alkanesulfonic acid or more. In addition, however, it is also possible for further components, which act as solvents and are inert under the oxidizing conditions, to be present in the reaction mixture. Supplementary inert components are those which can be separated by distillation from the desired alkanesulfonic acid and that have a low vapour pressure, meaning that they do not cause explosive mixtures in the gas phase. Exemplary inert components, recited without limitation, are sulfoxide and dimethyl formamide. The fraction of the alkanesulfonic acid in the reaction mixture is preferably as high as possible, since the alkanesulfonic acid used as solvent in the reaction mixture is identical with the oxidation product and therefore, with good yields, need not be removed distillatively from the product mixture.

In a further embodiment of the present invention, the concentration of the alkane sulfonic acid used as solvent is therefore at least 80 wt.-%.

In the context of the present invention, the expression "at least 80 wt.-%" is used in such a way that it encompasses all figures from inclusive of 80 weight per cent to less than 100 wt.-%. The expression "80 wt.-%" therefore encompasses the integral figures 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98 and 99 wt.-% and also all conceivable values from inclusive of 80 to less than 100 wt.-% that can be expressed using real numbers.

The concentration of the alkanesulfonic acid in the process according to the present invention is preferably at least about 90 weight per cent, more particularly at least about 92 weight per cent, and more preferably the concentration of the alkanesulfonic acid used ranges from about 92 to about 96 weight per cent. The expressions "about 90, about 92 and about 96 weight per cent" are used in the context of the present invention to refer also to deviations of ± 2 weight per cent from the respective figure explicitly stated. The expression "at least about 90 weight per cent" therefore encompasses all figures from inclusive of 88 weight per cent to less than 100 weight per cent. These are, expressly, the integral figures 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98 and 99 weight per cent and also all conceivable values from inclusive of 88 to less than 100 weight per cent that can be expressed using real numbers. The expression "at least about 92 weight per cent" encompasses all figures from inclusive of 90 weight per cent to less than 100 weight per cent: these are, expressly, the integral figures 90, 91, 92, 93, 94, 95, 96, 97, 98 and 99 weight per cent and also all conceivable values from inclusive of 90 to less than 100 weight per cent that can be expressed using real numbers. Correspondingly, the expression "about 92 to about 96 weight per cent" encompasses all figures from inclusive of 90 to inclusive of 98 weight per cent: these are, expressly, the integral figures 90, 91, 92, 93, 94, 95, 96, 97 and 98 weight per cent and also all conceivable values from inclusive of 90 to inclusive of 98 weight per cent that can be expressed using real numbers.

In a preferred embodiment of the present invention, therefore, the concentration of the alkanesulfonic acid used as solvent is at least 90 +/- 2 weight per cent.

The process of the present invention is not fundamentally subject to any restrictions on the oxidizing agent, provided that it remains ensured that the oxidation can be carried out safely. In accordance with the invention, oxygen, both in free form and in bound form, is a suitable oxidizing agent in the process of the invention. In the context of the present invention, the term "oxygen in free form" is used in accordance with the common general knowledge of the skilled person and refers to oxygen which is not, through covalent bonds, part of an organic or inorganic compound. Oxygen in free form is, for example, molecular oxygen O_2, ozone O_3 or an oxygen radical. In accordance with this understanding, therefore, an oxygen molecule or an oxygen radical that is part of a complex or is present in coordinated form, for example, is also interpreted as oxygen in free form. Oxygen in free form used in the process of the invention may therefore include pure oxygen or an oxygen-enriched gas stream, such as oxygen-enriched air or a mixture of pure oxygen and a gas which is not reactive under the oxidizing conditions, referred to as an inert gas, nitrogen or argon, for example. Conversely, the term "oxygen in bound form" refers to any oxygen which, as a

integral and by real numbers. In the limiting case, the gas stream with a free-form oxygen content of more than 21 vol.-% is pure oxygen in free form, preferably molecular oxygen O2.

The process of the present invention is not fundamentally subject to any restrictions on the pressure at which it is performed. The setting of the pressure in the process of the present invention is accomplished typically by way of a gas stream containing oxygen in free form that is fed into the reaction mixture. In accordance with the invention this may be air, a gas stream enriched with oxygen in free form, more particularly a gas stream containing more than 21 vol.-% of oxygen in free form, or pure oxygen in free form.

The process of the present invention is not fundamentally subject to any restrictions on the pressure. The upper pressure limit is determined by the pressure resistance of the reactor employed. Since high or very high pressures necessitate complicated and costly reactors, the process of the present invention is preferably operated at pressures of not more than 100 bara. In practice, moreover, it has emerged that a pressure of 20 bara leads neither to an increase in the yield nor to more rapid completion of the reaction. In the context of the present invention, the expression "bara" is synonymous with "bar absolute" and is used as a unit for the absolute pressure. In accordance with the common general knowledge of the skilled person, the absolute pressure is measured without taking account of the prevailing air pressure, in other words absolutely relative to the zero pressure in empty space. Preferably, however, the process of the present invention is carried out at superatmospheric pressure. In the context of the present invention, the expression "superatmospheric pressure" is used in such a way that it encompasses all pressures in the range of more than 1 bar that can be expressed using integral or real numbers.

In one embodiment of the present invention, therefore, the process is carried out at a pressure of more than 1 bara to 20 +/- 2 bara.

The pressure of about 20 bara is used in the context of the present invention in such a way that it also encompasses deviations of +/- 10% from the figure explicitly stated. The expression "about 20 bara" therefore also encompasses all integral figures from inclusive of 18 bara to inclusive of 22 bara, explicitly the figures 18, 19, 20, 21 and 22 bara, and also all figures that can be expressed using real numbers, from inclusive of 18 bara to inclusive of 22 bara.

The pressures to which the reaction mixture is subjected are advantageously selected such that they lead to an increase in the product yields. On the basis of a yield for the formation of methanesulfonic acid of roughly over 96% at a pressure of more than 2 bara, such as at 3 bar, for example, a staged increase in pressure by 3 bara in each case leads, given constant temperature, to an increase in the yield to up to more than 99%.

In a preferred embodiment of the present invention, therefore, the process is carried out at a pressure of more than 2 bara to 15 +/- 2 bara.

Claims

1. Process for preparing alkanesulfonic acids of the formula $R\text{-}SO_3\text{-}H$, comprising the step of oxidizing a symmetrical dialkyl disulfide of the formula $R\text{-}S_2\text{-}R$, in solution in an alkanesulfonic acid, in the presence of catalytic amounts of nitric acid, with R denoting a $C_1\text{-}C_{12}$ alkyl radical and the alkanesulfonic acid used as solvent being identical with the alkanesulfonic acid obtained from the oxidation of the dialkyl disulfide in question, characterized in that the concentration of the dialkyl disulfide in the solution is not more than 20 weight per cent, the ratio of dialkyl disulfide to nitric acid ranges from 2000:1 (mol/mol) to 1:1 (mol/mol), and the concentration of the alkanesulfonic acid used as solvent is more than 70 weight per cent.

2. Process according to Claim 1, wherein the dialkyl disulfide is dimethyl disulfide and the alkanesulfonic acid is methanesulfonic acid.

3. Process according to Claim 1 or 2, wherein the ratio of dialkyl disulfide to nitric acid ranges from 500:1 (mol/mol) to 1:1 (mol/mol).

4. Process according to Claim 1 or 2, wherein the ratio of dialkyl disulfide to nitric acid ranges from 500:1 (mol/mol) to 2:1 (mol/mol).

5. Process according to any one of Claims 1 to 4, wherein the concentration of the dialkyl disulfide in the alkanesulfonic acid is up to 10 +/- 1 weight per cent.

6. Process according to any one of Claims 1 to 5, wherein the process is carried out at temperatures of not more than 90°C.

7. Process according to Claim 6, wherein the process is carried out at temperatures of 70°C to 90°C.

8. Process according to any one of Claims 1 to 7, wherein the concentration of the alkanesulfonic acid used as solvent is at least 80 weight per cent.

9. Process according to Claim 8, wherein the concentration of the alkanesulfonic acid used as solvent is at least 90 +/- 2 weight per cent.

10. Process according to any one of Claims 1 to 9, wherein, for the oxidation, air, a gas stream enriched with oxygen in free form, and/or pure oxygen in free form is fed in.

11. Process according to Claim 10, wherein, for the oxidation, a gas stream comprising oxygen, containing more than 21 vol.-% of oxygen in free form, is fed in

12. Process according to any one of Claims 1 to 11, wherein the process is carried out at a pressure of more than 1 bara to 20 +/- 2 bara.

13. Process according to Claim 12, wherein the process is carried out at a pressure of more than 2 bara to 15 +/- 2 bara.

14. Process according to any one of Claims 1 to 13, wherein a solubilizer between the dialkyl disulfide and the alkanesulfonic acid is used.

15. Process according to Claim 14, wherein alkanesulfonic acid *S*-alkyl ester of the formula R-SO_2-S-R is used as solubilizer between the dialkyl disulfide and the alkanesulfonic acid, with the alkyl radicals of the alkanesulfonic acid *S*-alkyl ester being identical with the alkyl radicals of the dialkyl disulfide to be converted and with the alkyl radical of the alkanesulfonic acid.