

This invention relates to a process for the preparation of alkyl isothiocyanic acid esters by the reaction of N-alkyl-dithiocarbaminates with aqueous hydrogen peroxide.

Many processes have become known for the preparation of
5 alkyl isothiocyanic acid esters, also known as alkyl isothiocyanates or alkyl mustard oils, see Ullmanns Enzyklopädie der technischen Chemie, 4th Edition, Volume 23, pages 154-159 and DE-OS 21 05 473. With the exception
10 of the process disclosed in DE-PS 21 05 473, none of the known processes has gained entrance into technology, either because the preparation of the starting materials is too expensive or because the yields of pure alkyl isothiocyanates are too low.

The process according to DE-OS 21 05 473 for the prepara-
15 tion of methyl isothiocyanate, which is increasingly used as intermediate product for organic syntheses and as nematocide and fungicide, has gained a position of technical importance. In the process according to DE-OS 21 05 473 for the preparation of alkyl isothiocyanic acid
20 esters of the general formula $R-N=C=S$ wherein R stands for a lower alkyl group, 1 mol of an aqueous solution of an N-alkyldithiocarbamate of the general formula $R-NH-C(S)-SMe$ wherein R has the meaning indicated above and Me may stand for an alkali metal atom, an ammonium
25 group or an alkylammonium group is reacted at a temperature of from 50 to 120°C with at least 1 mol of a 20 to 70% by weight aqueous hydrogen peroxide solution at pH

5 to 9 and the alkyl isothiocyanic acid ester formed is isolated in known manner. According to the Claims, from 2.3 to 2.5 mol of hydrogen peroxide were preferably used per mol of dithiocarbamate and a pH of from 6 to 8 was maintained. The use of a highly concentrated dithiocarbamate solution was regarded as particularly advantageous. When a molar ratio of dithiocarbamate to hydrogen peroxide of about 1 to 2.5 per mol of alkyl isothiocyanate is used in this known process, half a mol of sulphur and half a mol of sulphate are formed as by-products. Whereas these by-products can simply be separated off when the process is carried out on a laboratory scale, the removal of sulphur entails problems in a large scale technical process because the sulphur is partly obtained in the form of hard lumps and incrustations are formed in the reactor. Frequent and often prolonged production stoppages are required for removing the lumps and incrustations. This considerably reduces the volume/time yield of the process.

It is an object of the present invention to improve the process for the preparation of alkyl isothiocyanic acid esters of the formula $R-N=C=S$, wherein R denotes a methyl or ethyl group, from an aqueous solution of an N-alkyldithiocarbamate of the formula $R-NH-C(S)-S-Me$, wherein R stands for a methyl or ethyl group and Me stands for an alkali metal atom or an ammonium or alkyl ammonium group, and an aqueous hydrogen peroxide solution which is used in a quantity of at least 1 mol of hydrogen peroxide per mol of N-alkyldithiocarbamate, the reaction being carried out at a temperature of from 95 to 130°C and the alkylisothiocyanic acid ester formed being removed in known manner from the reaction mixture, the purpose of this improvement being that the process should be carried out with an increased volume/time yield and reduced effort for

cleaning the reactor while a high yield and high degree of purity of the alkyl isothiocyanate are maintained.

This object is achieved by reacting the aqueous N-alkyl-dithiocarbamate solution with a 20 to 40% by weight aqueous hydrogen peroxide solution in a volumetric ratio of from 1 : 1 to 0.8 : 1 while a pH of from 1.5 to 4.5 is maintained. The subclaims are directed towards preferred embodiments.

The combination of the features characterising the process according to the invention surprisingly results in sodium thiosulphate being formed in the reaction and hardly any elementary sulphur. As shown in the Examples, the quantity of sulphur formed is only 5 to 10% of the quantity which was expected under the reaction conditions of the previously known process. Removal of the sulphur suspended in the aqueous phase of the sump of the reactor entails no problems since the quantity is so small. The process according to the invention can therefore be carried out uninterruptedly both as a continuous and as an intermittent process so that for a given size of reactor the conversion in mol per hour can be almost doubled without any reduction in yield. According to the invention, methyl and ethyl isocyanate are obtained with a degree of purity of about 98% and in a yield of about 80 to 95%.

Reaction of the aqueous N-alkyldithiocarbamate solution with the aqueous hydrogen peroxide solution is carried out at 95 to 130°C, preferably at 100 to 120°C. At least 1 to 3 mol of hydrogen peroxide, preferably 2 to 2.5 mol, are used per mol of N-alkyl-dithiocarbamate. The H₂O₂ concentration is in the range of from 20 to 40% by weight. Aqueous H₂O₂ solutions containing from 25 to 35% by weight of H₂O₂ are preferably used; these can easily be obtained

by diluting more highly concentrated solutions, e.g. 50 to 70% by weight solutions. This dilution may be carried out while the hydrogen peroxide solution is introduced into the reaction chamber, for example by simultaneously
5 spraying in a concentrated hydrogen peroxide solution and water to result in a concentration according to the claims.

The concentration of the aqueous N-alkyldithiocarbamate solution is preferably in the range of from 30 to 45% by
10 weight. The pH of the solution is adjusted to 9.5 - 12.0. Such solutions are prepared in known manner. The solution of sodium-N-alkyldithiocarbamate, which is preferably used, may be obtained from the alkylamine, carbon disulphide and sodium hydroxide solution.

15 The reaction of the two solutions is carried out in the volumetric ratio claimed so that a pH of from 1.5 to 4.5, preferably 2.0 to 4.0, is maintained in the aqueous phase of the reaction mixture. In the known process of DE-PS
21 05 473, in which the pH should be from 5 to 9, no
20 volumetric ratio of N-alkyldithiocarbamate solution to hydrogen peroxide solution was mentioned but the examples show that the ratios are from 1 : 0.45 to 1: 0.75, which is outside the range of the process claimed here.

The reaction between the two solutions may be brought
25 about by introducing the two solutions into a reactor from separate inlets. At the reaction temperature of 95 to 130°C, the alkyl isothiocyanate is generally separated in vapour form, immediately after its formation, from the aqueous phase containing the by-products. The carbon
30 disulphide which is formed by slight decomposition of dithiocarbamate is recovered quantitatively by distillation of the crude alkyl isothiocyanate and may be returned

returned to the preparation of the dithiocarbamate.

Isolation of the alkyl isothiocyanic acid ester is carried out in known manner, e.g. by extraction, for example with ketones, aliphatic or aromatic hydrocarbons, methylene chloride, chloroform, carbon tetrachloride, carbon disulphide, ethers, esters or nitrobenzene. It is preferable, however, especially if the process is carried out continuously, to separate the product by azeotropic distillation. This may be carried out with the addition of steam, whereby the yield may be significantly increased. The very large amount of heat produced in the reaction of the dithiocarbamate with hydrogen peroxide may also be utilized. This quantity of heat is so great that no additional energy is required for the distillation of the isothiocyanic acid ester.

In a particularly preferred embodiment, the aqueous N-alkyldithiocarbamate solution and the aqueous hydrogen peroxide solution are reacted together in the form of droplets, in particular very finely divided droplets. The apparatus conventionally used for converting a liquid into droplet form are suitable. Fine subdivision of the components is advantageously obtained by means of nozzles, either one-material or multimaterial nozzles. One or more nozzles may be arranged in the reactor, for example in the lid and/or in the upper part of the wall.

Depending on the size of the reactor, the spray angle of the nozzles is adjusted so that the main reaction takes place at the centre of the upper third of the reactor in order to avoid condensation on the internal wall. Before the onset of the reaction, the reactor is filled with water to about 1/8 to about 1/3, depending on the volume of the reactor. When the process is carried out contin-

uously, the by-products formed are continuously removed from the reactor and if necessary replaced by water.

The invention is further disclosed in the Examples.

Example 1

A heatable and coolable reactor equipped with a spray device for the solutions which are to be reacted together, a stirrer, a vapour discharge, a sump discharge and pH and temperature measuring devices is filled with water to 15% of its volume. After the water in the reactor has been heated to about 98°C, 3 mol (770 ml) of an aqueous 42% by weight N-methyldithiocarbamate solution prepared in known manner from methylamine, carbon disulphide and sodium hydroxide and adjusted to pH 10 are reacted within 90 minutes with 7.5 mol (700 ml) of a 32.5% by weight aqueous hydrogen peroxide solution. For this purpose, the aqueous N-methyldithiocarbamate solution and the aqueous hydrogen peroxide solution are brought together in a volumetric ratio of 1 : 0.91 (molar ratio 1 : 2.5), using a nozzle with an internal diameter of 2 mm from which they are sprayed into the reactor in a very finely divided form. The methyisothiocyanate formed is distilled off immediately after its formation. The pH of the liquid phase (reactor sump) and the temperature at the vapour discharge are monitored during the reaction (see Table 1).

Table 1

	Time (min)	pH	Temperature (°C)
25	15	2.1	100.6
	30	2.4	100.1
	45	2.6	100.7
	60	2.5	101.6
	75	2.5	102.9
30	90	2.0	102.8

The heat evolved in the reaction between dithiocarbamate and hydrogen peroxide is so great that no additional energy is required for distillation of the methyl isothiocyanate. The temperature of the condenser is
5 adjusted to 35 - 38°C to ensure that the methyl isothiocyanate separates in a liquid form. About 5 to 7% of methyl isothiocyanate are still dissolved in the water which distils over at the same time. This methylisothiocyanate is separated by extraction with n-hexane
10 (separation may alternatively be carried out by partial distillation of the aqueous phase).

2.6 Mol of 98% methyl isothiocyanate, corresponding to a yield of 87%, are obtained. The aqueous phase (reactor sump) contains 4 g of sulphur in suspension, in other
15 words only 8.3% of the quantity expected in the previously known process.

Example 2

The following are reacted together in a manner analogous to Example 1: 770 ml (3 mol) of 42% by weight aqueous
20 N-methyl dithiocarbamate solution adjusted to pH 11.0 and 650 ml (7.5 mol) of a 35% by weight aqueous hydrogen peroxide solution, corresponding to a volumetric ratio of the solutions of 1 : 0.84 and a molar ratio of the reactants of 1 : 2.5. The pH of the liquid phase and the
25 temperature at the vapour discharge during the reaction are shown in Table 2.

Table 2

	Time (min)	pH	Temperature (°C)
5	15	3.9	99
	30	4.2	99
	45	3.6	100
	60	3.6	100
	75	3.6	101
	90	3.7	101

- 10 2.51 Mol of 98% methyl isothiocyanate are obtained, corresponding to a yield of 84%; the aqueous phase contains 5 g of sulphur (10.4% of the theoretically possible quantity).

Example 3

- 15 The following are reacted together analogously to Example 1: 770 ml (3 mol) of 42% by weight N-methyl-dithiocarbamate solution adjusted to pH 10 and 644 ml (6.9 mol) of a 32.5% by weight aqueous hydrogen peroxide solution, corresponding to a volumetric ratio of the solutions of 1
- 20 : 0.84 and a molar ratio of the reactants of 1 : 2.3. The pH of the liquid phase and the temperature at the vapour outlet during the reaction are shown in Table 3.

Table 3

	Time (min)	pH	Temperature (°C)
25	15	4.5	99
	30	4.2	100
	45	4.4	101
	60	4.3	101.5
	75	4.3	102
	90	4.3	103

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2.45 Mol of 98% methyl isothiocyanate are obtained, corresponding to a yield of 82%; the aqueous phase contains 3.7 g of sulphur (7.7% of the theoretically possible quantity).

5 Example 4

The following are reacted together analogously to Example 1: 770 ml (3 mol) of 42% by weight aqueous N-methyldithiocarbamate solution adjusted to pH 10 and 760 ml (7.5 mol) of a 30% by weight aqueous hydrogen peroxide solution, corresponding to a volumetric ratio of the solutions of 1 : 0.99 and a molar ratio of reactants of 1 : 2.5. The pH and the temperature during the reaction are shown in Table 4.

Table 4

15	Time (min)	pH	Temperature (°C)
	15	4.0	100
	30	3.5	101
	45	3.2	101.5
20	60	3.2	101.5
	75	2.5	102
	90	2.8	102.5

About 2.45 mol of 98% methyl isothiocyanate are obtained, corresponding to a yield of 82%; the aqueous phase contains 3 g of sulphur (6.2% of the theoretically possible quantity).

Example 5

The following are reacted together analogously to

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Example 1: 770 ml (3 mol) of 42% by weight aqueous N-methyldithiocarbamate solution adjusted to pH 10 and 700 ml (7.5 mol) of a 32.5% by weight aqueous hydrogen peroxide solution, corresponding to a volumetric ratio of the solution of 1 : 0.91 and a molar ratio of the reactants of 1 : 2.5. In addition, 350 g of steam are injected into the reaction chamber during the reaction. The pH and the temperature during the 90 minutes' reaction are shown in Table 5.

10 Table 5

	Time (min)	pH	Temperature (°C)
	15	2.2	100.5
	30	2.3	100.6
15	45	2.0	101.2
	60	1.9	101.8
	75	2.1	102.3
	90	2.0	102.5

2.7 Mol of 98% methyl isothiocyanate are obtained, corresponding to a yield of 90%; 3.5 g of sulphur (7% of the theoretically possible quantity) are suspended in the aqueous phase.

Example 6

515 ml (1.5 mol) of 36% by weight aqueous N-ethyldithiocarbamate solution adjusted to pH 10 and prepared in known manner from ethylamine, carbon disulphide and sodium hydroxide solution are atomised together with 410 ml (3.75 mol) of 31% by weight aqueous hydrogen peroxide solution within 90 minutes analogously to Example 1. The volumetric ratio of N-ethyldithiocarbamate to the hydrogen peroxide

solution is 1 : 0.8 and the molar ratio of the reactants is 1 : 2.5. The pH of the liquid phase (reactor sump) and the temperature at the vapour discharge during the reaction are shown in Table 6.

5 Table 6

	Time (min)	pH	Temperature (°C) discharge
10	15	3.2	100.2
	30	3.0	100.7
	45	2.9	101
	60	3.0	101.6
	75	2.8	102
	90	2.9	102.3

15 1.38 Mol of 98% ethyl isothiocyanate, corresponding to a yield of 92.4%, and 2 g of sulphur (8.3% of the theoretically possible quantity) are formed.

Patent claims

1. A process for the preparation of alkyl isothiocyanic
5 acid esters of the formula $R-N=C=S$, wherein R denotes a
methyl or ethyl group, from an aqueous solution of an N-
alkyl-dithiocarbamate of the formula $R-NH-C(S)-S-Me$,
wherein R stands for a methyl or ethyl group and Me for an
alkali metal atom or an ammonium or alkyl ammonium group,
10 and an aqueous hydrogen peroxide solution, at least one
mol of hydrogen peroxide being used per mol of N-alkyl-
dithiocarbamate, the reaction being carried out at a
temperature of from 95 to 130°C and the alkyl
isothiocyanic acid ester formed being separated from the
15 reaction mixture in known manner, characterised in that
the aqueous N-alkyl-dithiocarbamate solution is reacted
with a 20 to 40% by weight aqueous hydrogen peroxide
solution in a volumetric ratio of from 1:1 to 0.8:1 while
a pH of from 1.5 to 4.5 is maintained.

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2. A process according to claim 1, characterised in that
a 25 to 35% by weight aqueous hydrogen peroxide solution
is used.

25 3. A process according to claim 1 or claim 2,
characterised in that a 30 to 45% by weight aqueous N-
alkyl-dithiocarbamate solution preferably adjusted to a
pH of from 9.5 to 12 is used.

30 4. A process according to one or more of claims 1 to 3,
characterised in that the reaction is carried out at a
temperature of from 100 to 120°C.

5. A process according to one or more of claims 1 to 4,
35 characterised in that from 2 to 2.5 mol of hydrogen

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peroxide are used per mol of N-alkyl-dithiocarbamate.

6. A process according to one or more of claims 1 to 5, characterised in that a pH in the range of from 2.0 to 4.0 5 is maintained in the reaction mixture.

7. A process according to one or more of claims 1 to 6, characterised in that the aqueous N-alkyl-dithiocarbamate solution and the aqueous hydrogen 10 peroxide solution are reacted together in the form of droplets.

8. A process according to claim 7, characterised in that the reaction is carried out substantially in fine droplets 15 which are obtained by atomising the solutions, using one or more one-material or two-material nozzles and the resulting alkyl-isothiocyanic acid ester is withdrawn from the reaction chamber in vapour form.

20 9. A process according to one or more of claims 1 to 8, characterised in that the process is carried out continuously by removing the alkyl-isothiocyanic acid ester formed and the by-products which are volatile under the reaction conditions from the reaction chamber in 25 vapour form immediately after their formation and removing the nonvolatile by-products from the reaction chamber with the aqueous phase and, if necessary, maintaining the liquid level in the reactor by the addition of water.

30 10. A process according to one or more of claims 1 to 9, characterised in that additional steam is injected into the reactor during the reaction.

