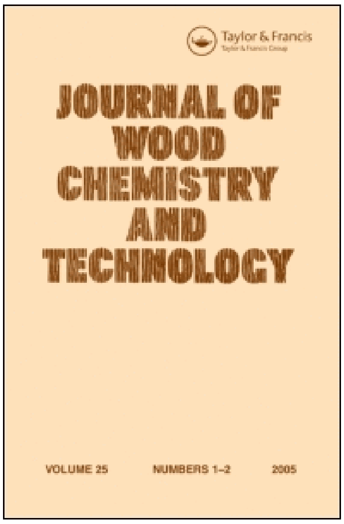

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REACTIONS OF METHYL MERCAPTAN WITH POLYSULFIDE OR POLYTHIONATE - IDENTIFICATION OF PRODUCTS BY ^{1}H NMR

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ABSTRACT

The products formed when methyl mercaptan reacts with polysulfide in an alkaline solution have been identified, using ^{1}H NMR, as dimethyldisulfide, dimethyltrisulfide, dimethyltetrasulfide and methyldisulfide anion (CH_3SS^-). Analogously, methyl mercaptan and polythionate were found to give methylthiosulfate anion ($CH_3SSO_3^-$), in addition to these dimethylpolysulfides. The reactions are interpreted in terms of nucleophilic displacements of the S_N2 type. The formation of these anionic products constitutes the basis for the potential use of polythio compounds for reduction of air pollution in the kraft pulping process.

INTRODUCTION

A serious drawback of the kraft pulping process is the release of malodorous gases. One of the major components responsible for the evil smell is methyl mercaptan originating from the reaction between hydrosulfide anions and methoxyl groups in lignin[1].

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It has recently[2,3] been shown that the partial pressure of methyl mercaptan above an alkaline solution can be drastically reduced by adding polysulfide or polythionate ions. This offers a possibility of reducing air pollution in the kraft process. The influence of the reaction conditions on the extent of reaction was studied[3] and it was found that polysulfide reacts with methyl mercaptan only when the latter is in the dissociated (methyl mercaptide) form. Alkalinity affecting the dissociation of the methyl mercaptan and lowering the mean size of the polysulfide chains, temperature, ionic strength and concentration of hydrogen sulfide anions were identified as important reaction parameters. It was also found that addition of sodium sulfide or sulfite to the reaction mixtures releases methyl mercaptan.

The aim of the present work was to determine the chemical structures of the products formed when methyl mercaptan is reacted with polysulfide or polythionate and to describe the reactions involved.

RESULTS AND DISCUSSION

Reaction of Methyl Mercaptan with Polysulfide

When polysulfide with a high mean chain length ($n=4-5$) was added, GC-analysis of the gas phase over an alkaline solution of methyl mercaptan ($pOH=2.5$, 60°C) showed a decrease in partial pressure of methyl mercaptan by two orders of magnitude[2,3].

Since polysulfide derivatives are often thermally labile at elevated temperatures, and sensitive towards a decrease in pH, direct NMR-analysis of the reaction mixture was used in the present study to obtain correct information about the reaction products formed and about their relative amounts. Considerably higher concentrations of mercaptan and polysulfide than in the previous experiments[3] were chosen in order to facilitate the NMR-analysis.

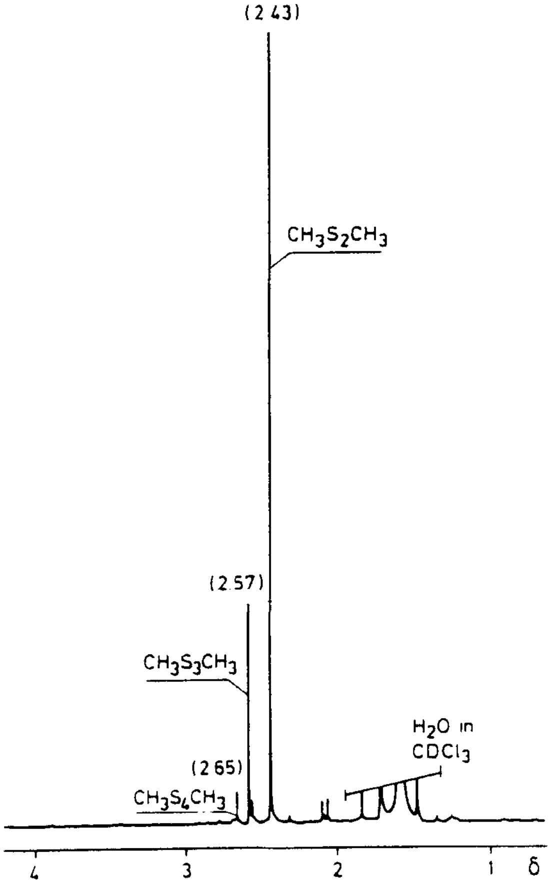


FIGURE 1. ^1H NMR spectrum of the $CDCl_3$-extractable compounds formed when methyl mercaptan is reacted with polysulfide.

The ^1H NMR spectrum (Fig. 1) of a $CDCl_3$-extract of a methyl mercaptan/polysulfide mixture shows the presence of dimethyldisulfide (CH_3SSCH_3), dimethyltrisulfide (CH_3SSSCH_3) and dimethyltetrasulfide ($CH_3SSSSCH_3$) (cf. Table 1). The relative amounts of these compounds can be changed by varying the amounts of reactants and other reaction parameters. CH_3SSCH_3 and CH_3SSSCH_3 were also identified by GC-analysis of the gas collected over the dilute aqueous solution.

TABLE I

^{1}H NMR Chemical Shifts (δ-values) of Reference Compounds (cf. Experimental)

	$CDCl_3$	D_2O
CH_3SH	2.07 (d)	2.00
CH_3SSCH_3	2.42	2.42
CH_3SSSCH_3	2.56	-
$CH_3SSSSCH_3$	2.64	-

To study hydrophilic reaction products, experiments were carried out using D_2O as solvent, since this allows direct NMR-analysis of the reaction mixture with no risk of losses or transformations during work-up. The NMR spectrum (Fig. 2) contains, besides peaks for methyl mercaptan and CH_3SSCH_3, a main peak at $\delta = 2.24$ assigned to the methyldisulfide anion (CH_3SS^-). Since no authentic sample of this compound was available for comparison, this assignment is based on the following observations:

- The compound is not extractable with $CDCl_3$.
- Reference samples of CH_3SSCH_3 and CH_3SSSCH_3 react with sodium sulfide to give the same compound together with CH_3S^- (Fig. 3,4).
- Addition of excess of $CH_3SH(g)$ transforms the compound to CH_3SSCH_3.

A general reaction mechanism which explains the formation of the various products is described below.

Reaction of Methyl Mercaptan with Polythionate

The ^{1}H NMR spectrum (Fig. 5) of a $CDCl_3$-extract of a reaction mixture of methyl mercaptan and potassium tetrathionate in D_2O shows that CH_3SSCH_3, CH_3SSSCH_3 and $CH_3SSSSCH_3$ are the main products. The remaining D_2O phase gives a main peak at $\delta = 2.58$

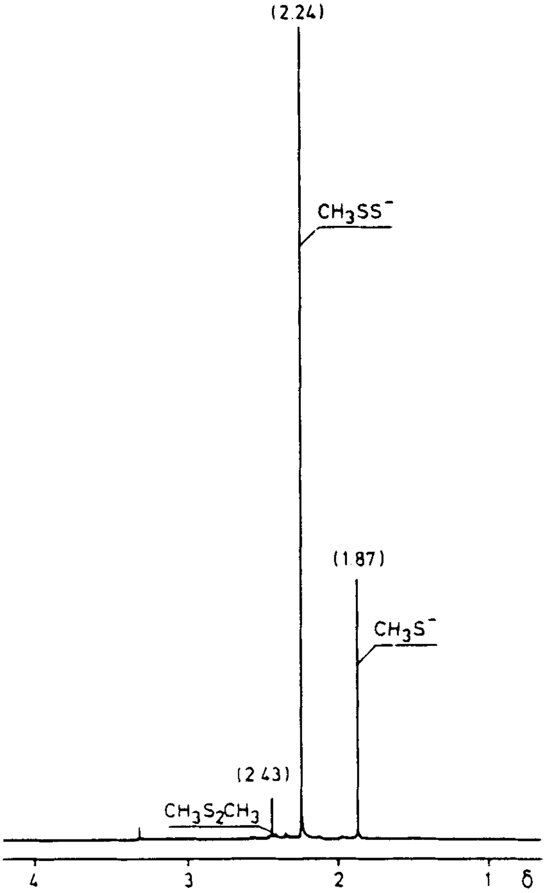


FIGURE 2. Direct NMR-analysis of the product mixture after the reaction of methyl mercaptan with polysulfide in D_2O. The main peak at $\delta = 2.24$ is assigned to CH_3SS^-.

assigned to $CH_3SSO_3^-$ (Fig. 6). This assignment is based on the following findings:

- The compound is not extractable with $CDCl_3$ in contrast to CH_3SSSCH_3 which has the same chemical shift.
- Addition of sodium sulfite to CH_3SSCH_3 or CH_3SSSCH_3 affords the same compound together with CH_3S^- (Fig. 7,8).

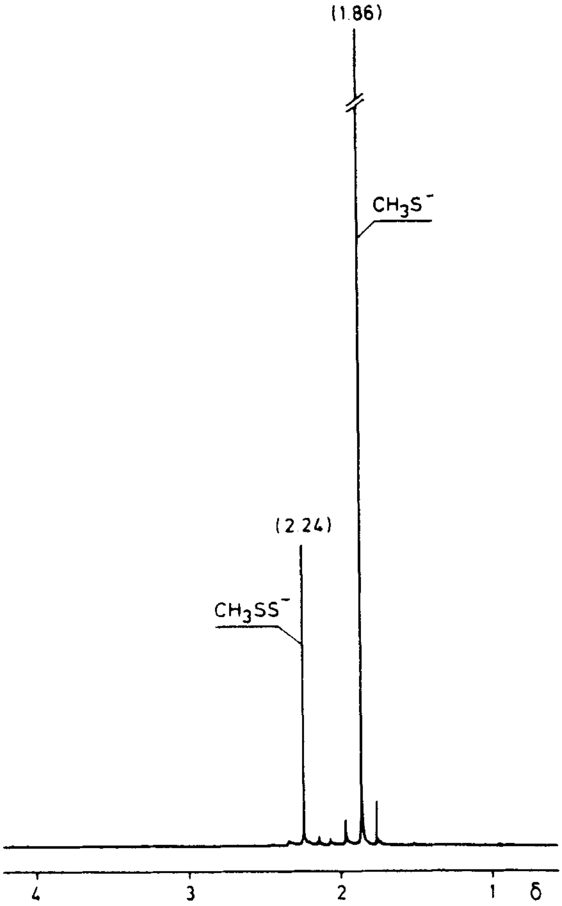


FIGURE 3. ^{1}H NMR spectrum after addition of sodium sulfide to a reference sample of CH_3SSCH_3 in D_2O.

- Addition of excess of CH_3SH (g) transforms the compound to CH_3SSCH_3.

Together with the peak assigned to $CH_3SSO_3^-$ less intense peaks, which are probably due to higher sulfur homologues, are observed at higher δ-values.

Depending on the composition of the reaction mixtures (e.g. alkalinity and ionic strength), large variations in the chemical

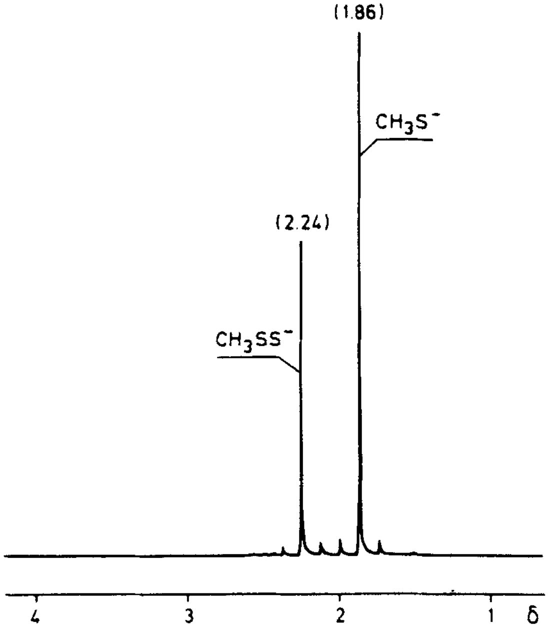


FIGURE 4. ^{1}H NMR spectrum after addition of sodium sulfide to a reference sample of CH_3SSSCH_3 in D_2O.

shifts (up to 0.1 δ-units) were sometimes obtained. However, the relative distances between the different peaks remained constant. This phenomenon has previously been reported for polysulfides[4].

Mechanism

The results obtained in the present NMR-studies of the reactions between methyl mercaptan and polysulfide or polythionate are in agreement with results from earlier studies on the chemistry of bivalent sulfur[5-8]. Foss[9] was the first to state clearly that in polythio compounds the sulfur atoms are in an unbranched chain. Strong evidence for this has been accumulated by studies of dipole moments, UV-, Raman-and IR-spectra, electron and X-ray diffraction.

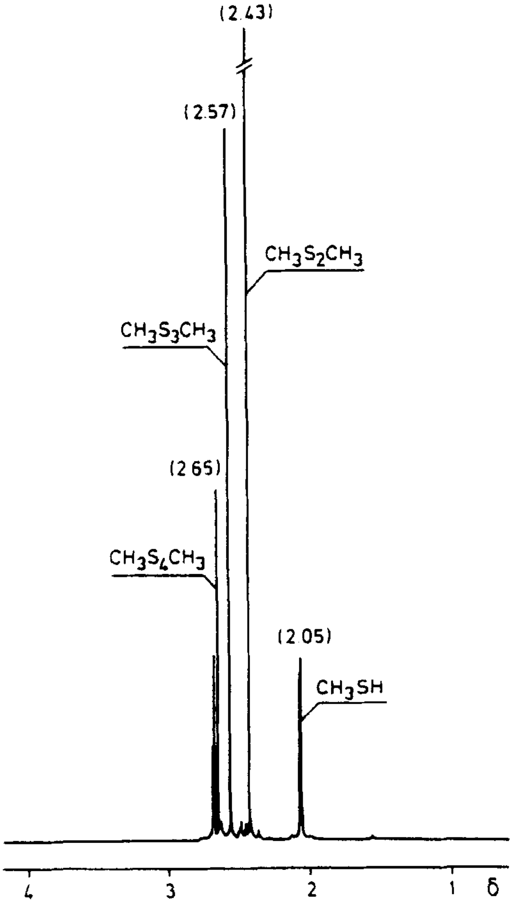


FIGURE 5. ^1H NMR spectrum of the $CDCl_3$-extractable compounds formed when methyl mercaptan is reacted with potassium tetrathionate.

The characteristic feature of the sulfur-sulfur bond is its ability to undergo ionic (heterolytic) scission in reactions with nucleophilic reagents. The kinetic evidence available indicates that the ionic scission is of the second order i.e. the displacements are of the S_N2 type[6]. According to Pryor[10], it is likely that many of the substitutions on sulfur by nucleophiles do not involve a simple one-step displacement reaction, but are due rather

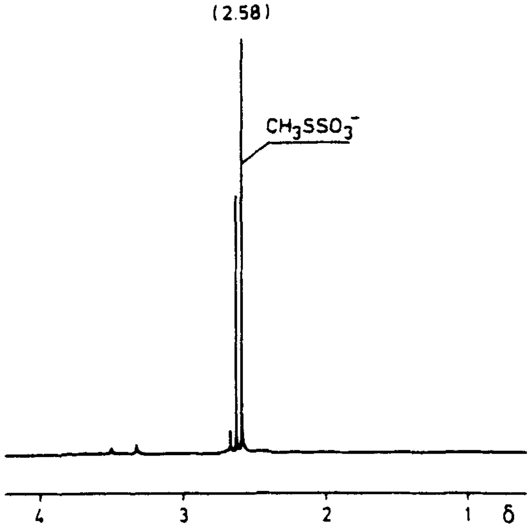


FIGURE 6. ^1H NMR spectrum of the remaining D_2O phase after $CDCl_3$-extraction. The main peak at $\delta = 2.58$ is assigned to $CH_3SSO_3^-$.

to an addition elimination sequence involving a metastable intermediate in which sulfur has expanded its coordination number and its electron octet. In general C-S-bonds are much more stable towards oxidation, reduction or hydrolysis than S-S-bonds[5].

Several investigations have been directed towards the reactions of polythio compounds with various nucleophiles. Pryor[11] has suggested that the relative nucleophilicities towards a sulfur of a S-S-bond decrease in the following order:

$(EtO)_3P > R^-$, $\underline{HS}^-$, $\underline{EtS}^- > PhS^- > Ph_3P > CN^- > \underline{SO_3}^{2-} >$
$\underline{HO}^- > 2,4\text{-}(NO_2)_2PhS^- > N_3^- > SCN^-$, I^-, $PhNH_2$

Thus the order of S-nucleophilicity is different from that of C-nucleophilicity.

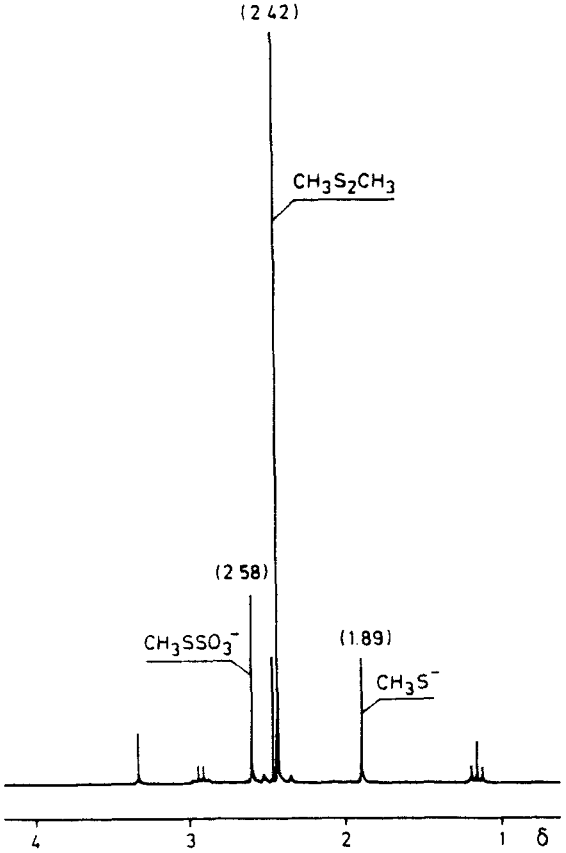


FIGURE 7. ^1H NMR spectrum after addition of sodium sulfite to a reference sample of CH_3SSCH_3 in D_2O.

The reactions between bivalent sulfur and nucleophiles (Nu^-) can schematically be written as shown in eq. 1. (X and Y represent alkyl, aryl or sulfur substituents or combinations thereof).

$$X\text{-}S\text{-}S\text{-}Y + Nu^- \rightleftharpoons X\text{-}S\text{-}Nu + Y\text{-}S^- \qquad 1$$

Applied to the present study the reactions can be formulated as a nucleophilic attack of a methyl mercaptide anion on a sulfur atom in a polysulfide(e.g. eq. 2) or polythionate (e.g. eq. 3) chain.

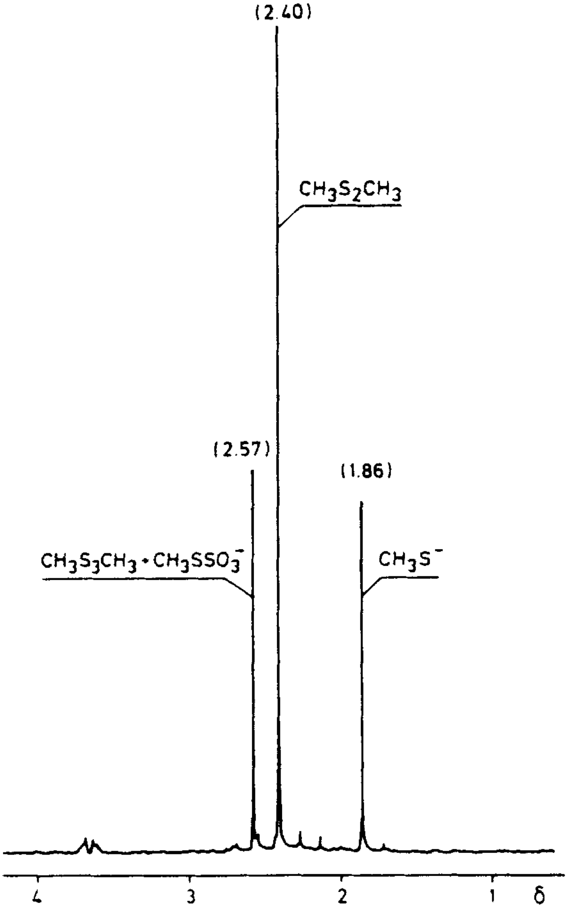


FIGURE 8. ^1H NMR spectrum after addition of sodium sulfite to a reference sample of CH_3SSSCH_3 in D_2O.

$$^-SSSS^- + CH_3S^- \rightleftharpoons CH_3SSS^- + ^-SS^- \qquad 2$$

$$^-O_3SSSSO_3^- + CH_3S^- \rightleftharpoons CH_3SSSO_3^- + ^-SSO_3^- \qquad 3$$

The compounds formed react in the same way with S-nucleophiles present in the solution leading to polythio compounds with different chain lengths (cf. Fig. 1,2,5,6). The reactions are very fast, reversible and complex, due to the coupled equilibria involved.

Excess of a strong nucleophile results in desulfuration[6] of the polythio compounds, e.g. eq. 4 and 5.

$$CH_3SSS^- + Nu^- \rightleftharpoons CH_3SNu + {}^-SS^- \qquad 4$$
$$CH_3SSSO_3^- + Nu^- \rightleftharpoons CH_3SNu + {}^-SSO_3^- \qquad 5$$

Consequently, an excess of methyl mercaptan (Nu = CH_3S) should ultimately yield CH_3SSCH_3. This was confirmed in the present experiments where a large excess of CH_3SH on polysulfide or polythionate resulted in the formation of emulsions of CH_3SSCH_3. By analogy, sodium sulfide or sodium sulfite give CH_3SS^- (Fig. 3,4) or $CH_3SSO_3^-$ (Fig. 7,8) respectively, when added to CH_3SSCH_3 or CH_3SSSCH_3. The formation of these ionic compounds implies a simultaneous release of methyl mercaptan.

By adding sulfite to a "normal" kraft black liquor (i.e. with no polysulfide added) it has been shown[3] that more than 50 per cent of the total amount of methyl mercaptan can exist in a bound (organopolysulfide[12]), less volatile form.

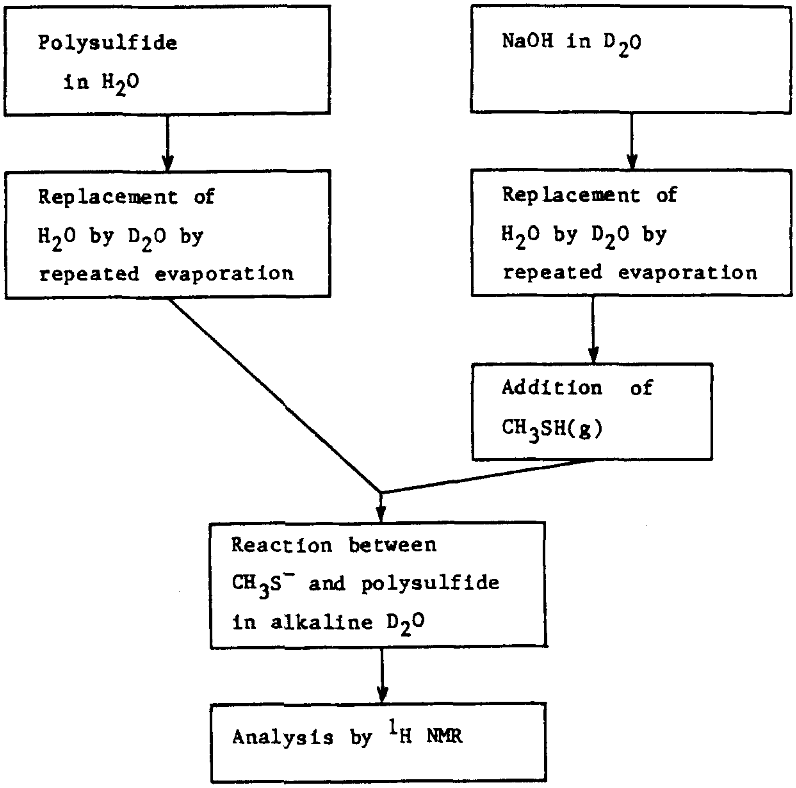
EXPERIMENTAL

A general description of the procedure including reaction conditions and the gas phase analysis technique used is given by Teder and Tormund[3].

The method applied to the NMR-studies in D_2O-solutions is outlined in Scheme 1. The water was removed by repeated evaporation with D_2O. The volumes used were 2-3 ml. In order to obtain sufficient amounts of products the experiments were carried out at considerably higher reactant concentrations (0.2 mol/l CH_3SH) than those previously used (0.2 mmol/l)[3].

SCHEME 1

Method used for the direct ^1H NMR-analysis of reaction products from reactions between methyl mercaptan and polysulfide.



The NMR spectra were recorded on a Bruker WP 200 (200 MHz) instrument using TMS (in $CDCl_3$) and sodium 3-(trimethylsilyl)-propane sulfonate (in D_2O) as internal standards.

Reagents: CH_3SH (AGA Specialgas AB, Sweden), CH_3SSCH_3, pro synth. (Merck, W. Germany), CH_3SSSCH_3 and $CH_3SSSSCH_3$, technical grade (Columbia Organic Chemicals Co Inc, USA),

$K_2S_4O_6$ (Merck, W. Germany). The polysulfide solution used was prepared and characterized according to Teder[13,14].

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