196. Convenient Preparation and Spectroscopic Characterization of Methyl Hydrodisulfide and Methyl Deuterodisulfide

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Dedicated to Prof. Dr. *Tino Gäumann* on the occasion of his 60th birthday

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Methyl hydrodisulfide and methyl deuterodisulfide have been prepared in a four-step synthesis. These compounds have been characterized spectroscopically including microwave spectra.

Introduction. – The preparation of methyl hydrodisulfide **4** was described originally by *Böhme* and *Zinner* [1]. Since their account of the synthetic work omits essential details for a successful preparation of **4**, we report a convenient method for its synthesis. Methyl deuterodisulfide **5** was obtained by replacing CH_3OH and HCl with CH_3OD and DCl in the last reaction step. Adequate spectroscopic data of **3**–**5** are given for their characterization for the first time. The microwave spectra of **4** and **5** unequivocally prove the equilibrium structure of **4**. The analysis of the microwave spectra will be reported elsewhere [2].

The synthetic procedure started with the commercially available thioacetic acid and acetyl chloride. They were reacted to form diacetyl sulfide **1** [3].

$$CH_3COSH + CH_3COCl \rightarrow \underset{\mathbf{1}}{CH_3COSCOCH_3}$$

As an alternative, acetic anhydride and H_2S also yield **1** [4].

$$CH_3COOCOCH_3 + H_2S \rightarrow \underset{\mathbf{1}}{CH_3COSCOCH_3}$$

Acetylsulfur chloride **2** was prepared by reacting **1** with SO_2Cl_2 [4]. SO_2Cl_2 can be replaced by Cl_2 [5].

$$CH_3COSCOCH_3 + SO_2Cl_2 \rightarrow \underset{\mathbf{2}}{CH_3COSCl}$$

CH_3SH was combined with **2** to form the unstable acetyl methyl disulfide **3** [1].

$$CH_3COSCl + CH_3SH \rightarrow \underset{\mathbf{3}}{CH_3COSSCH_3}$$

To prevent decomposition **3** was stored in liquid N_2 immediately after preparation. Solvolysis of **3** with HCl in CH_3OH produced **4** [1].

$$CH_3COSSCH_3 + CH_3OH + HCl \rightarrow \underset{\mathbf{4}}{CH_3SSH}$$

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In this last step CH_3OH and HCl were replaced by CH_3OD and DCl to obtain **5**.

$$\underset{}{CH_3COSSCH_3} + CH_3OD + DCl \rightarrow \underset{\mathbf{5}}{CH_3SSD}$$

It was difficult to obtain very pure samples of **3**, **4**, and **5**, because they decomposed noticeably at 20°. They were stored always in liquid N_2. Despite this precaution they contained traces of polysulfides $CH_3COS_xCH_3$ and $CH_3S_xCH_3$ ($x = 3–6$) and some residual H_2O as shown by the mass spectra.

Spectroscopic Characterization of 4 and 5. *IR Spectrum.* The Ar matrix-isolated IR spectrum of **4** was recorded in the range of 4000–200 cm^{-1} at a resolution of better than 1 cm^{-1}. The premixed gases of 4 Torr of **4** and 760 Torr of Ar were deposited at a rate of 150 µm/h up to a final thickness of 0.9 mm on a CsI window in a liquid He cryostat. A low M:A ratio and a thick matrix were needed for sufficient absorption, since the IR spectrum of **4** was in general very weak. *Table 1* lists the observed frequencies of **4** together with the estimated relative intensities. The IR spectrum is compared to that of the related compounds CH_3SH [6] and CH_3SSCH_3 [7]. There exist 15 normal vibrations of **4** which are all IR active since the molecule has no symmetry in its equilibrium conformation [2]. Most of them were observed except one of the CH_3 rocking modes and two torsional modes below the spectral range covered. Their tentative assignment was derived from comparison with CH_3SH and CH_3SSCH_3. The frequencies of **4** attributed to the CH_3 group have mostly values between those of the corresponding ones in the test molecules. The SH, CS, and SS stretching frequencies compare favorably to those of the examples given. Furthermore, our assignment is consistent with the results reported for the SH

Table 1. *Vibrational Frequencies* [cm^{-1}] *of* CH_3SSH, CH_3SH, *and* CH_3SSCH_3

CH_3SSH (**4**)[a]			CH_3SH[b]		CH_3SSCH_3[c]	
Freq.	Int.[d]	Description	Freq.	Description	Freq.	Description
3007.0	*w*	CH_3 stretch	3011.0	CH_3 asym. stretch A′		
2995.0	br. *w*	CH_3 stretch	3007.0	CH_3 asym. stretch A″	2985	CH_3 asym. stretch
2930.0	*s*	CH_3 stretch	2948.1	CH_3 sym. stretch A′	2914	CH_3 sym. stretch
2535.0	br. *w*	SH stretch	2603.2	SH stretch A′		
1437.0	*s*	CH_3 deform.	1445.4	CH_3 asym. deform. A′	1432	CH_3 asym. bend
1419.2	*s*	CH_3 deform.	1435.3	CH_3 asym. deform. A″	1410	CH_3 asym. bend
1312.9	*m*	CH_3 deform.	1326.0	CH_3 sym. deform. A′	1298	CH_3 sym. bend
			1067.9	CH_3 rock. A′		
958.8 956.0	*m* *m*	CH_3 rock.	954.8	CH_3 rock. A″	950	CH_3 rock.
874.4	*mw*	SSH bend				
847.8	*w*	?	799.8	CSH in-pl. bend A′		
697.1	*mw*	CS stretch	704.0	CS stretch A′	690	CS stretch
512.0	*w*	SS stretch			517	SS stretch
314.1	*vs*	CSS bend			272	CSS bend
					240	CSS bend
					116	SS torsion

[a]) From the Ar matrix spectrum, this work.

[b]) From the Ar matrix spectrum [6].

[c]) From the IR and RE spectra of the liquid [7].

[d]) Estimated relative intensities.

Table 2. *Rotational Constants* [MHz] *of* CH_3SSH *and* CH_3SSD (standard deviations in parentheses)

	CH_3SSH	CH_3SSD
A	16865.3758(71)	15953.531(22)
B	4442.1185(18)	4298.021(11)
C	3680.3640(16)	3617.873(7)

stretching (2556.5, 2559.5 cm^{-1}) and SSH bending (882, 883 cm^{-1}) vibrations of H_2S_2 [8]. The doubling of the CH_3 rocking mode is considered to be caused by a site splitting in the Ar matrix.

MW Spectra. Rotational spectra of **4** and **5** were recorded over the range of 18–40 GHz with *Stark*-modulated spectrometers of our own design [2]. Rotational constants listed in *Table 2* were determined from the accurately measured transition frequencies. The molecular equilibrium structure compatible with these rotational constants exhibits a dihedral angle CSSH of 88.9° [2].

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Experimental Part

General. IR spectra of reasonably stable compounds were recorded as 5% solns. in CCl_4 with a 0.1-mm KBr cell on a *Perkin-Elmer 983* spectrophotometer. Those of unstable compounds were obtained in an Ar matrix at 4 K with M:A = 1:190 on a *Perkin-Elmer 325* spectrophotometer. ^{1}H-NMR spectra were taken on a *Bruker WM-300* (300 MHz), ^{13}C-NMR on a *Varian CFT-20* instrument. $CDCl_3$ was used as a solvent. Chemical shifts δ [ppm] refer to TMS as internal standard. Mass spectra were measured on a *Hitachi-Perkin-Elmer RMU-6M* instrument.

Acetyl Methyl Disulfide (**3**). Freshly distilled CH_3COCl (88 g, 1.12 mol) was added dropwise to 42.5 g (0.56 mol) of CH_3COSH over 15 min. The mixture was refluxed for 4 h and then fractionated at 54–56°/15 Torr: 43 g (0.36 mol, 65%) of **1** were obtained as a yellow liquid (content 92% by GLC). SO_2Cl_2 (49.1 g, 0.37 mol) was added dropwise to 43 g (0.36 mol) of **1** at – 30° over 30 min. The pressure was slowly reduced down to 11 Torr over 30 min and the mixture was then gradually heated to 30° within the next hour. Compound **2** (14.6 g, 132 mmol, 37%) remained as a dark yellow liquid. It was dissolved in 50 ml of Et_2O and added dropwise to a soln. of 9.2 g (190 mmol) of CH_3SH at – 20°. The mixture was stirred at – 10° for 30 min. The volatile parts were distilled off at 40°/14 Torr. The residue was fractionated at 80°/2–3 Torr yielding 4.5 g (37 mmol, 28%) of **3** which was collected in liquid N_2. IR (solution): 2921*m*, 1731*s*, 1430*m*, 1415*m*, 1351*m*, 1111*s*, 940*s*. ^{1}H-NMR: 2.45(*s*); 2.42(*s*). ^{13}C-NMR: 156.7(*s*); 28.6(*s*); 22.7(*s*). MS: 192(17), 158(13), 126(16), 122(46), 80(29), 79(52), 64(100), 47(34), 46(23), 45(56), 44(18), 43(97), 42(21), 34(11), 32(17), 28(11), 18(16), 15(46).

Methyl Hydrodisulfide (**4**). Compound **3** (1.0 g, 8.2 mmol) was mixed with a soln. of 1.0 g (27.4 mmol) of gaseous HCl in 4.0 g (125 mmol) of CH_3OH at 0° and stirred for 60 min at 0° and for 90 min without cooling. Finally, 10 ml H_2O was added and stirred for 5 min. A yellow oil (400 mg) was separated as the lower layer from the emulsion by centrifugation. The oil was shaken with 3 ml of H_2O and centrifuged. The crude product (340 mg) was transferred under vacuum to an ampoule and traces of CH_3COOCH_3 were pumped off yielding 230 mg (2.9 mmol, 34%) of **4** as a light yellow, slightly viscous liquid. IR (Ar matrix): *cf. Table 1.* ^{1}H-NMR: 3.20(*s*, SH): 2.46(*s*, Me). MS: 158(18), 128(14), 126(100), 111(17), 94(18), 80(65), 79(67), 64(59), 48(45), 47(86), 46(30), 45(71), 34(16), 32(13), 28(17), 18(18).

Methyl Deuterodisulfide (**5**). Compound **3** (1.0 g, 8.2 mmol) was reacted with a soln. of 1.0 g (26.7 mmol) of gaseous DCl in 4.0 g (121 mmol) of CH_3OD at 0° as described for the preparation of **4**. After workup with D_2O and trap-to-trap distillation in a vacuum line **5** (200 mg, 2.5 mmol, 30%) was obtained. It was characterized by its microwave spectrum *(cf. Table 2).*

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