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A NMR Study of the Thioacetic Acid-Acetone Mixture

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It is well known that thiols add readily and reversibly to the carbonyl group of aldehydes and ketones to form hemimercaptals and hemimercaptols as intermediates to mercaptals and mercaptols respectively. Hemimercaptals and hemimercaptols have been isolated only for aldehydes and ketones which contain electron-withdrawing groups.[1] Although it was demonstrated that thioacetic acid adds to simple aldehydes to form vacuum-distillable hemimercaptals,[2] the isolation of hemimercaptol has never been reported.

In the present study, we measured the NMR spectra of mixtures of acetone and thioacetic acid (**1a**), α-chlorothioacetic acid (**1b**), or α-dichlorothioacetic acid (**1c**). These mixtures were considered to be in equilibrium, as is shown below:

$$\mathrm{RCOSH + CH_3COCH_3 \rightleftarrows (CH_3)_2C(OH)SCOR} \qquad (1)$$

$\mathbf{1}$a: $R=CH_3$ $\mathbf{2}$a: $R=CH_3$
b: $R=CH_2Cl$ b: $R=CH_2Cl$
c: $R=CHCl_2$ c: $R=CHCl_2$

Therefore, we can expect at the lower temperatures to detect the spectra of α-hydroxyisopropyl thioacetate (**2a**), α-chlorothioacetate (**2b**), and α-dichlorothioacetate (**2c**). We determined each equilibrium constant in a large excess of acetone-d_6. Such substituents as α-chloro- and α-dichlorothioacetate were chosen for the sake of the simplicity of the NMR spectra.

Experimental

Acetone was dried over anhydrous calcium sulfate and distilled. Thioacetic,[3] chlorothioacetic[4], and dichlorothioacetic acid[4] were prepared and purified by the method described in the literature. The NMR spectra were measured on a JNM 3H-60 spectrometer, with tetramethylsilane as the internal standard. The probe temperature was determined immediately after each spectral measurement, using a thermocouple in a sample tube containing 0.5 m*l* of acetone. The accuracy of the temperature thus obtained should be within 1°.

Measurements of Equilibrium Constants. The NMR spectra of thioacetic acid solutions (3—7%) in a large excess of acetone-d_6 were taken, and the areas of the resonances of the R-group protons of RCOSH (**1**) and $(CD_3)_2C(OH)SCOR$ (**2**) were measured at various temperatures. The equilibrium constants were determined from:

$$K = [\text{Area of } (\mathrm{CD_3})_2\mathrm{C(OH)SCO}\underline{\mathrm{R}}]/[\text{Area of } \underline{\mathrm{R}}\mathrm{COSH}]$$

In 6.8, 4.2, and 3.0% solutions of thioacetic acid, all the plots of log K against $1/T$ gave only a straight line, with a correlation coefficient of 0.993 (Fig. 2). Therefore, at concentrations below 7% the molar fraction of acetone can safely be anticipated to be 1. Each measurement was initiated about 10 min after the solution in an NMR tube and the NMR probe had been temperature-equilibrated.

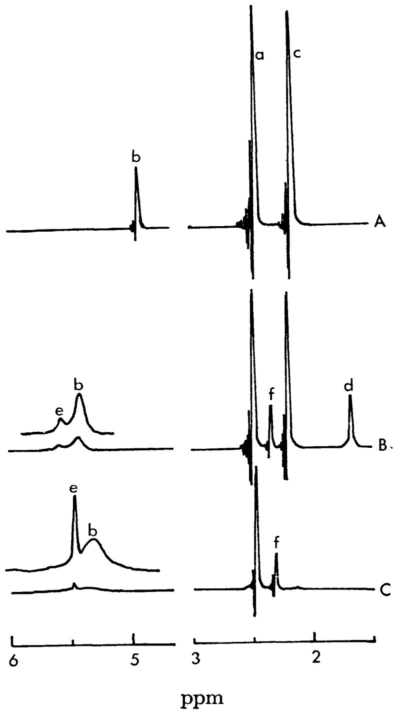

Fig. 1. The NMR spectra of thioacetic acid. A: 70 w/w% acetone solution at 25°C, B: at −56°C, C: 40 w/w% acetone-d_6 solution at −36°C.

$$\underset{a}{\mathrm{C\underline{H}_3}}\mathrm{COS}\underset{b}{\underline{\mathrm{H}}}+(\mathrm{C}\underset{c}{\underline{\mathrm{H}}_3})_2\mathrm{CO}$$
$$\Updownarrow$$
$$(\mathrm{C}\underset{d}{\underline{\mathrm{H}}_3})_2\mathrm{C(O}\underset{e}{\underline{\mathrm{H}}}\mathrm{)SCOC}\underset{f}{\underline{\mathrm{H}}_3}$$

Results and Discussion

The NMR spectrum of the mixture of acetone and thioacetic acid at room temperature showned only resonances of acetone and thioacetic acid (Fig. 1A). However, in the spectrum at a low temperature, two additional peaks appeared reversibly at $\delta=1.7$ (d) and $\delta=2.3$ (f) (Fig. 1B). The intensities of these spectra increased as the temperature was lowered, and integral ratios of these peaks were always 2 : 1. When acetone was replaced with acetone-d_6, only the peak of $\delta=2.3$ remained (Fig. 1C). Therefore, these peaks (d and f) may be considered to be responsible for the methyl groups of the 1 : 1 adduct of thioacetic acid and acetone, which was concluded to be hemimercaptol (**2a**). As another possible adduct of thioacetic acid and acetone,

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[1] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 2, Chemical Publishing Co., Inc., New York, N. Y. (1960), p. 205, and Vol. 3, p. 320; E. Campaigne, "Organic Sulfur Compounds," Vol. 1, ed. by N. Kharasch, Pergamon Press Inc., New York, N. Y. (1961), p. 134.

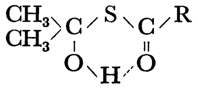
[2] H. Böhme, H. Bezzenberger, M. Clement, A. Dick, E. Nurnberg, and W. Schlephack, *Ann.*, **623**, 92 (1959).

[3] E. K. Ellingboe, "Organic Syntheses," Vol. 31, (1950), p. 105.

[4] J. I. Cunneen, *J. Chem. Soc.*, **1947**, 134.

we may consider α-hydroxyisopropyl thionacetate $(CH_3)_2C(OH)OCSCH_3$, which is produced by the addition of tautomeric thionacetic acid to acetone. This possibility could not be excluded experimentally.[5] However, thioacetic acid reacted with aldehyde to produce hemimercaptal,[6] and also no example has been reported of thionesters being prepared from thioacetic acid.[7] Therefore, the authors prefer the first conclusion. In the spectrum of the lower field, the sharp former peak of the hydroxy proton (e) of **2a** can be interpreted as partly overlapped on the broad peak of the sulfhydryl proton (b) of thioacetic acid by comparing their strengths.

Mercaptol (**2a**) is expected to have the following intra-molecular hydrogen bond.[8] The most striking



characteristic of an intra-molecular hydrogen bond is the absence of any shift upon dilution with an inert solvent.[9] Therefore, we tried to obtain the spectra in a dilute solution of an inert solvent. However, in a large excess of carbon disulfide Eq. (1) lies so far to the left, even at a low temperature, and the concentration of **2a** is so small that the peak of the hydroxyl proton can not be detected. Therefore, the following experiment was carried out. A mixture of **1a** (20 mg) and acetone (0.5 m*l*) in an NMR tube was cooled slowly to −78°C. Fortunately, we found that, at such a low temperature, the rates of both the formation and decomposition of **2** in Eq. (1) become very slow. (See the bending of the straight line at lower temperatures in Fig. 2.) The NMR tube maintained at this temperature was attached to a vaccum line; in this way the acetone was almost evaporated, whereupon about 0.5 m*l* of carbon disulfide was added. The NMR spectrum of this solution was measured at −78°C. The spectrum indicated the presence of a large amount of hemimercaptol (**2a**) ([**2a**]/[acetone]=1.5). The peaks of the sulfhydryl and hydroxyl protons were detected separately at $\delta=4.72$ and $\delta=5.38$ respectively in such an inert solvent. The chemical shift of the latter peak did not move when the solvent was changed from acetone to carbon disulfide. This fact supports the above chelating structure.

The proton resonances of the methylene and methine groups in **2b** and **2c** appeared at $\delta=4.68$ and at $\delta=6.84$ respectively at −35°C; they were in a field lower by 0.22 and 0.14 ppm than those of the corresponding thioacetic acids, **1b** and **1c**. However, the peak of the hydroxyl proton seemed to be superposed on, and was indistinguishable from, that of the sulfhydryl proton.

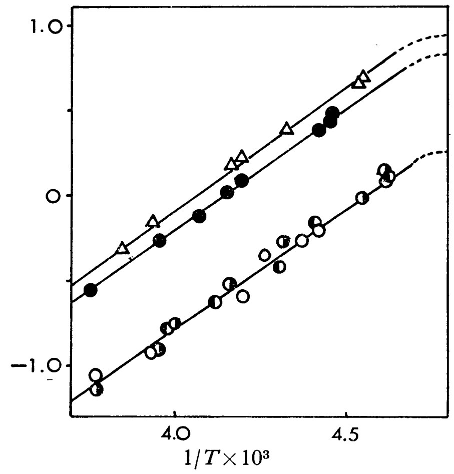


Fig. 2. Plots of log *K* *vs.* 1/*T* in acetone-d_6.
○: **2a** (3%), ◑: **2a** (4.2%), ◐: **2a** (6.8%), ●: **2b** (5.0 %), △: **2c** (6.8%).
Full lines were drawn by the method of least-squares and dashed lines indicated that experimental points were not on the full lines below *ca.* −60°C.

Table 1. Thermodynamic quantities for the formation of **2** in a large excess of acetone-d_6

Thioacetic acid	ΔH (kcal/mol)	ΔS (e.u.)	Correlation coefficient
CH_3COSH	-6.5 ± 0.2	-30 ± 1	0.993
$ClCH_2COSH$	-6.6 ± 0.1	-27.4 ± 0.6	0.999
$Cl_2CHCOSH$	-6.5 ± 0.1	-26 ± 0.5	0.999

The equilibrium constants were determined in the presence of a large excess of acetone-d_6 between −5 and −50°C. Figure 2 shows a plot of these data employed to determine the thermodynamic quantities (Table 1). The substitution of the electronegative group for the proton of thioacetic acid influences the entropy term more than enthalpy term in the equilibrium. Thus, the value of $-\Delta S$ in the formation of **2b** and **2c** is smaller than that of **2a**. These results can be explained by the view that the substitution of groups which weaken the six-membered chelation increases the degree of freedom of hemimercaptol.

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[5] In IR spectra, either C=O or C=S stretching absorption of the adduct could not be detected because of being concealed behind the very large absorptions of a large amount of acetone and thioacetic acid.

[6] We prepared the adducts of thioacetic acid and aldehyde, RCHO (R: H, CH_3, and CH_3CH_2), described in Ref. 2, and in IR spectra detected the C=O stretching absorptions, respectively in 1680, 1670, and 1675 cm⁻¹.

[7] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 4, Chemical Publishing Co., Onc., New York, N. Y. (1962), p. 12.

[8] Böhme claimed the presence of six-membered chelation of hemimercaptal in Ref. 2.

[9] "Jikken Kagaku Koza, Zoku," Vol. 12, ed. by K. Kotake, Maruzen Co., Tokyo, (1967), p. 371.