Studies of Thio Acids. III.[1] The Ultraviolet Absorption Spectra of Thiostearic Acid and Related Compounds[*1]

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The ultraviolet absorption spectrum of thioacetic acid has been studied by Hantzsch,[2] Cunneen[3] and Koch.[4] However, no studies of the ultraviolet absorption spectra of higher aliphatic thio acids have yet been published.

The present authors have, therefore, investigated the ultraviolet absorption spectra of thiostearic acid,[5] its derivatives, and thioacetic acid. An absorption maximum of thiostearic acid appears at 221 mμ in a cyclohexane solution, while a low-intensity absorption appears at 260—290 mμ. The latter is assumed to be an R-band due to the C=O group. Similar phenomena have been observed with thioacetic acid and methyl thiostearate. An absorption maximum of thiostearic acid appears at 223 mμ in an ethanol solution, and in lower concentrations another absorption maximum

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[1] Part II of this series: Y. Hirabayashi, M. Mizuta and T. Mazume, This Bulletin, **38**, 320 (1965).

[*1] Most of this study was presented at the Symposium of Oils and Fats of the Chemical Society of Japan, Nagoya, November, 1956.

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[2] A. Hantzsch and E. Scharf, *Ber.*, **45**, 3570 (1913).

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

[4] H. P. Koch, ibid., **1949**, 387.

[5] Y. Hirabayashi, M. Mizuta and T. Mazume, This Bulletin, **37**, 1002 (1964).

appears at 250 mμ, which is probably due to the mesomeric anion produced by the dissociation. Similar phenomena have been observed with thioacetic acid and potassium thiostearate in ethanol.

Results and Discussion

The Spectra of the Solution in Cyclohexane. —*Thiostearic Acid and Thioacetic Acid.*—The ultraviolet absorption spectrum of thiostearic acid in cyclohexane shows a band with its maximum at 221 mμ (ε, 1800).[5)] The shape of the absorption curve is in good accord with that of thioacetic acid measured in cyclohexane by Cunneen.[3)] However, at higher concentrations, an inflection was observed in the region 260—290 mμ (see Fig. 1). The ε value at 275 mμ is nearly 40. This low-intensity absorption band in the region 260—290 mμ is not due to impurities, as is proved by the following observations. The thiostearic acid used for the measurement has a purity of more than 99%; the impurities which could not be separated by recrystallization are stearic acid and distearoyl disulfide.[5)] Distearoyl disulfide has an absorption in the region 260—290 mμ; λ_{max}=224 mμ, ε=4260 in cyclohexane (cf. Fig. 2). Distearoyl disulfide (10%) was added to the sample of thiostearic acid, and the ultraviolet absorption spectrum of the mixture in cyclohexane was measured (Fig. 1). The absorption band slightly shifts toward a longer wavelength and is intensified, but the inflection in the region 260—290 mμ is not intensified.

The ultraviolet absorption spectrum of thioacetic acid reported by Cunneen[3)] indicated no absorption at 260—290 mμ. However, according to the present authors' measurements, in the ultraviolet absorption spectrum of thioacetic acid in cyclohexane as well (Fig. 2, λ_{max}=220 mμ, ε=1660), an inflection was observed in the region 260—290 mμ at higher concentrations (ε=24 at 270 mμ).

Koch[4)] explained that the absorption band at 220 mμ is undoubtedly associated with the sulfur-carbonyl conjugation (between the non-bonding (3 p²) electron pair of the sulfur atom and the π electrons of the carbonyl group), involving contributions from the polar canonical structure*3 I in the excited state. As to the assignment of this band, the authors agree with Koch's opinion. However, the low-intensity absorption (inflection) at a longer wavelength measured by the present authors has never been discussed. The authors suppose that this absorption is an R-band due to the C=O group.

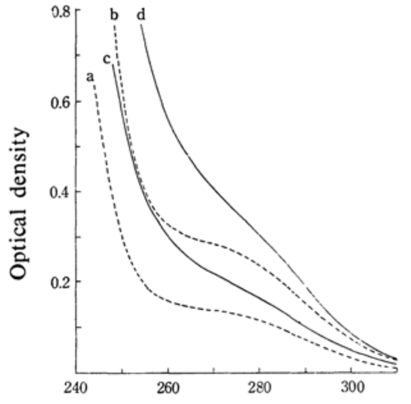


Fig. 1. Ultraviolet absorption spectra in cyclohexane.
Thiostearic acid (- - -): a, 1.0; b, 2.0 g./l. solution.
Thiostearic acid containing distearoyl disulfide (10%) (——): c, 1.0; d, 2.0 g./l. solution

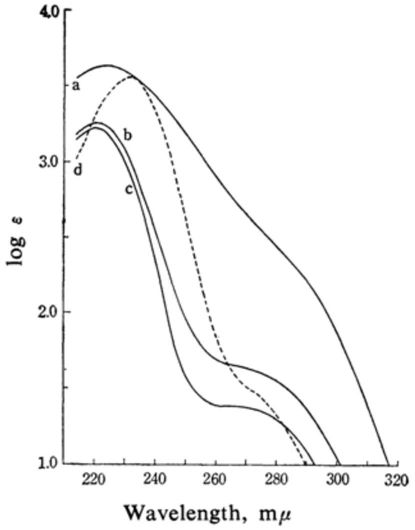
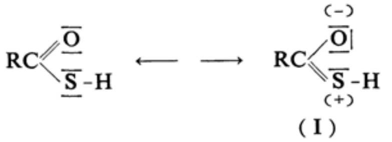


Fig. 2. Ultraviolet absorption spectra in cyclohexane.
a : Distearoyl disulfide
b : Thiostearic acid
c : Thioacetic acid
d : Methyl thiostearate



(I)

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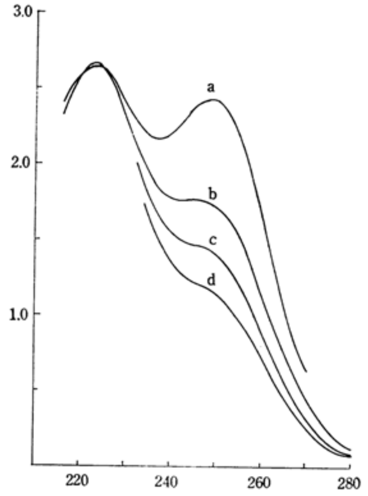
*3 Electron-diffraction bond-length measurements by Gordy suggest that I makes only a very slight contribution to the ground state of thioacetic acid (W. Gordy, *J. Chem. Phys.*, **14**, 560 (1946)).

Methyl Thiostearate.—The ultraviolet absorption spectrum of methyl thiostearate in cyclohexane is shown in Fig. 2 ($\lambda_{max}=231$ mμ, $\varepsilon=3560$). The absorption band at 231 mμ is undoubtedly associated with the sulfur-carbonyl conjugation. Probably the low-intensity absorption (inflection) at 265—290 mμ is an R-band due to the C=O group.

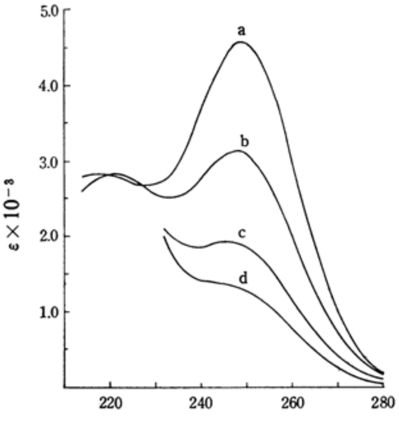
The Spectra of the Solution in Ethanol.—*Thiostearic Acid and Thioacetic Acid.* — The ultraviolet absorption spectrum of thiostearic acid in ethanol (98 wt.%) is shown in Fig. 3. At lower concentrations, the position and intensity of the absorption band at 223 mμ remain almost unchanged and a large inflection appears near 250 mμ. In further dilutions, the second absorption maximum (248 mμ) appears; its intensity varies, depending on the concentration (see Table I).



Wavelength, mμ

Fig. 3. Ultraviolet absorption spectra of thiostearic acid in ethanol.

Concn.: a : 0.83×10^{-4} mol./l.
b : 1.67×10^{-4} mol./l.
c : 3.33×10^{-4} mol./l.
d : 6.67×10^{-4} mol./l.



Wavelength, mμ

Fig. 4. Ultraviolet absorption spectra of thioacetic acid in ethanol.

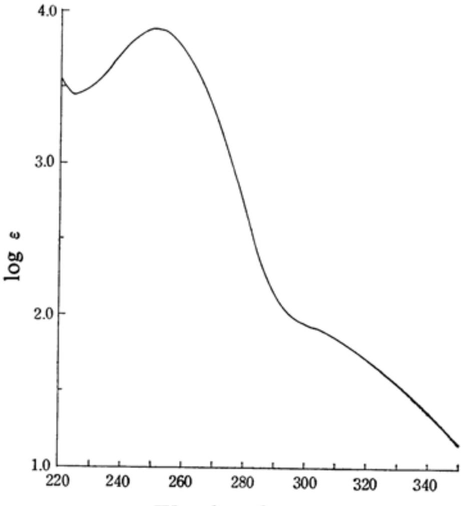
Concn.: a : 0.82×10^{-4} mol./l.
b : 1.64×10^{-4} mol./l.
c : 3.29×10^{-4} mol./l.
d : 6.58×10^{-4} mol./l.

These phenomena were found not only in such higher thio acids as thiostearic acid, but also in thioacetic acid. The ultraviolet absorption spectrum of thioacetic acid in ethanol is shown in Fig. 4. Absorption maxima appear in the regions 218—222 and 248—249 mμ as is shown in Table I.

Table I. Data of ultraviolet absorption spectra of thiostearic acid and thioacetic acid in ethanol

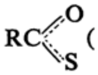
Concentration 10^{-4} mol./l.	1st absorption		2nd absorption	
	λ_{max}, mμ	ε	λ_{max}, mμ	ε
Thiostearic acid				
1.67	223	2650	247	1760
0.83	223	2640	248	2440
Thioacetic acid				
1.64	221	2830	248	3140
0.82	218	2820	249	4560

Potassium Thiostearate. — The ultraviolet absorption spectrum of potassium thiostearate in ethanol is shown in Fig. 5. At lower concentrations, only one absorption maximum appears, at 251 mμ ($c=9.30\times10^{-5}$ mol./l., $\varepsilon=7610$). At higher concentrations, another maximum appears in the region 290—350 mμ.

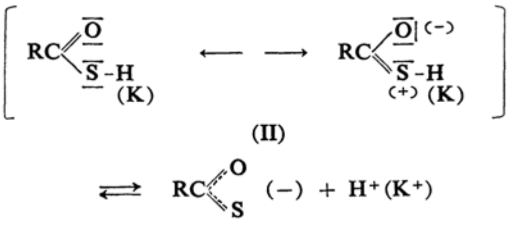


Wavelength, mμ

Fig. 5. Ultraviolet absorption spectrum of potassium thiostearate in ethanol.
Concn.: 220—280 mμ, 9.30×10^{-5} mol./l.
280—350 mμ, 3.72×10^{-3} mol./l.

The results obtained above show that in the spectra of thio acids or its salts, which are dissociable to  $RC\begin{smallmatrix}O\\S\end{smallmatrix}(-)$ and H^+ or K^+, an absorption maximum appears at 250 mμ in ethanol. Furthermore, in the spectra of thiostearic acid and thioacetic acid, the absorption at 250 mμ does not obey Beer's law, but increases in intensity in higher dilutions. In view of thess facts, it may be concluded that, in ethanol, thio acids are partly dissociated to produce the mesomeric anion III, which in turn causes the absorption at 250 mμ. The water content in ethanol probably has a great effect on the dissociation. On the other hand, the absorption at 223 mμ due to undissociated acid (II) obeys Beer's law approximately within the range of measuring concentrations. This behavior of the absorption at 223 mμ would appear to be apparently inconsistent with the above conclusion. This apparent discrepancy can be satisfactorily explained by considering the following two reasons together: first, the degree of the disociation of thio acid in ethanol is very low, so that the decrease in undissociated acid caused by the increasing dilution is very small; secondly, the absorption band at 223 mμ is partially superposed by that of the mesomeric anion, which has a high-intensity absorption at 250 mμ.

Potassium thiostearate is more ionized in ethanol. The anomaly at 290—300 mμ in a higher concentration observed in the spectrum of potassium thiostearate is probably related to the thionic acid form reported by Hantzsch.²⁾ This problem will be discussed in the future.



(II)

(III)

Experimental

Ultraviolet Absorption Spectra. — A Shimadzu quartz spectrophotometer, model QB-50, and a silica cell (1 cm.) were used (measuring temperature 26±1°C).

Methyl Thiostearate. — Thiostearic acid (3.5 g.) in absolute ethanol (350 ml.) was neutralized with ethanolic potassium hydroxide. Methyl iodide (15 g.) was added to the above solution, and the mixture was refluxed for 6 hr. and extracted with ether after the ethanol had been distilled off. The ether layer was washed with a diluted potassium carbonate solution and water succesively and dried over anhydrous sodium sulfate, and the ether was distilled off. The residue (yield 3.2 g.) was recrystallized from methanol to give colorless needles (m. p. 50.3—50.8°C) (yield 1.5 g.), which corresponded with the product obtained by Ralston in another way.⁶⁾
(Found: S, 10.14. Calcd. for $C_{19}H_{38}OS$: S, 10.19%).

Thioacetic Acid. — Prepared from phosphorus pentasulfide and glacial acetic acid and purified by Kitamura's⁷⁾ method (b. p. 88.0—88.5°C).
(Found: S, 41.80 (Kitamura's method). Calcd. for C_2H_4OS: S, 42.13%).

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6) A. W. Ralston, E. W. Segebreckt and S. T. Bauer, *J. Org. Chem.*, **4**, 502 (1939).

7) R. Kitamura, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **57**, 31 (1937).