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Studies of Thio Acids. VIII.[1] The Reaction of Thiostearic Acid with Alcohols[*1]

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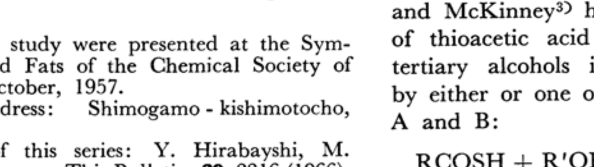
The products obtained by heating thiostearic acid in methanol, aqueous methanol, ethanol, or aqueous ethanol have been found to consist of hydrogen sulfide, distearoyl sulfide, methyl or ethyl stearate, thiostearic acid, and stearic acid, the last of which has been detected only in the case of aqueous alcohols. On the basis of the above results, the following scheme may be involved, at least in part, in the formation of carboxylic ester and hydrogen sulfide by heating the thio acid in alcohols:



$$2RCOSH \rightarrow RC(=O)-S-C(=O)R + H_2S$$

$$RC(=O)-S-C(=O)R + R'OH \rightarrow RCOOR' + RCOSH$$

Reid et al.[2] have reported that hydrogen sulfide and a normal ester (C_6H_5COOR) were formed by the reaction of thiobenzoic acid with a primary alcohol, while water and a thiol ester (C_6H_5COSR) were formed by the reaction of benzoic acid with a primary mercaptan. On the other hand, Stewart and McKinney[3] have reported that the reaction of thioacetic acid with primary, secondary, or tertiary alcohols in benzene solutions proceeds by either or one of the two ways shown by Eqs. A and B:

$$RCOSH + R'OH \rightarrow RCOOR' + H_2S \qquad (A)$$

$$RCOSH + R'OH \rightarrow RCOSR' + H_2O \qquad (B)$$

[*1] Parts of this study were presented at the Symposium of Oils and Fats of the Chemical Society of Japan, Nagoya, October, 1957.

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[1] Part VII of this series: Y. Hirabayshi, M. Mizuta and T. Mazume, This Bulletin, **39**, 2216 (1966).

[2] E. E. Reid, *Am. Chem. J.*, **43**, 489 (1910); L. S. Pratt and E. E. Reid, *J. Am. Chem. Soc.*, **37**, 1934 (1915); J. H. Sachs and E. E. Reid, ibid., **38**, 2746 (1916); J. W. Kimball and E. E. Reid, ibid., **38**, 2757 (1916); E. M. Faber and E. E. Reid, ibid., **39**, 1930 (1917).

[3] F. B. Stewart and P. V. McKinney, ibid., **53**, 1482 (1931).

The present paper relates to a study of the detection of additional products obtained on heating thiostearic acid in alcohol. This study suggests that the reaction of thiostearic acid with alcohol may also proceed by way of an intermediate (distearoyl sulfide), and that the production of hydrogen sulfide is not so simple as is shown in the reaction of Eq. A. Namely, when the thio acid is heated in an alcohol, diacyl sulfide is formed as an intermediate, together with hydrogen sulfide; the diacyl sulfide may then give carboxylic ester and thio acid in the reaction with the alcohol.[4] Accordingly, the formation of hydrogen sulfide and the carboxylic ester may not undergo the reaction of Eq. A alone. On the other hand, the formation of thiol ester (Eq. B) could not be verified in this study.

Experimental[*3] and Results

The Heating of Thiostearic Acid in Alcohols.— Experimental Method.—A mixture of thiostearic acid with absolute methanol, aqueous methanol, absolute ethanol, or with aqueous ethanol (in accordance with corresponding experiments) was placed in a round-bottomed flask (500 ml.) fitted with a reflux condenser with a calcium chloride tube; the mixture was then heated for 20 hr. on a water bath, with a gradual passing of dried nitrogen gas through the mixture (solution). Hydrogen sulfide was evolved during the heating in each experiment. After the heating had stopped, the alcohol or the water immediately distilled off under reduced pressure at below 60°C, and a reaction product was obtained (only when aqueous methanol was used, was the reaction product extracted with ether when the distillation had been nearly completed). The conditions of each experiment are shown in Table I.

TABLE I. THE EXPERIMENTAL CONDITIONS

Exp.	$C_{17}H_{35}COSH$[a)] g.	ROH, ml.	Heating-temp., °C
I	5.0	abs. CH_3OH, 340	65
II	3.0	88% CH_3OH, 553[b)]	
III	4.5	abs. C_2H_5OH, 450	78
IV	4.5	85% C_2H_5OH, 450	

a) The characteristics of thiostearic acid used in the experiments were as follows: m. p 39.8—40.3°C; neutralization value 185.4; sulfur content 10.55% (Kitamura's method).

b) A minimum quantity was used for the dissolution of thiostearic acid at the heating-temperature.

The Investigation of the Products.[*4]—*Exp. I.*—The characteristics of the reaction product I were as follows: m. p. 59—63°C, N. V. 121.7, $S(J)_{NV}$ 6.32%, S(K) 8.24%.

Its ultraviolet absorption spectrum is shown in Fig. 1, in which the intensity of the absorption maximum at 221 mμ is lower and the absorption in the region of 240—250 mμ is intensified as compared with the ultraviolet absorption spectrum of thiostearic acid.[5]

The reaction product I (2.6 g.) in an ether solution was separated into an acidic part (A) and a neutral part N by treating it with an aqueous solution of potassium carbonate. The characteristics of each part were as follows:

(A): Y 1.7 g., N. V. 162.4, $S(J)_{NV}$ 8.91%, S(K) 9.02%

(N): Y 0.9 g., N. V. 63.3, $S(J)_{NV}$ 2.94%.

The ultraviolet absorption spectrum of A was essentially identical with that of thiostearic acid, and that of N exhibited an absorption maximum at 238 mμ (Fig. 1). Therefore, each part was repeatedly recrystallized from benzene and hexane to give, eventually, the several fractions shown in Table II; their ultraviolet absorption spectra are given in Fig. 1.

The results of the above experiments, confirm that N-1 was distearoyl sulfide (no depression of melting point was observed when its further recrystallized product was admixed with a synthesized authentic sample; the two substances exhibited identical ultraviolet absorption spectra) and that A-2 was thiostearic acid (its characteristics and ultraviolet absorption spectrum were identical with those of thiostearic acid); A-3 was mostly thiostearic acid. It was found from the characteristics that N-3 consisted of an ester (about 85%), distearoyl sulfide, and thiostearic acid, which could not be separated by the above treatment. If the ester be methyl thiostearate ($C_{17}H_{35}COSCH_3$), a high-intensity absorption should appear in the neighborhood of 230 mμ,[6] but it was not actually shown in the absorption

TABLE II. THE CHARACTERISTICS OF THE FRACTIONS OBTAINED FROM THE PRODUCT I (2.6 g.)

F	Y, g.	M. p., °C	N. V.	$S(J)_{NV}$, %
N-1	0.2	79.5—80.5	104.1	5.49[a)]
N-2	0.4	76—79.5	—	—
N-3	0.2	34—35	28.9[b)]	2.12
A-1	0.05	55—60	115.0	0.91
A-2	0.8	39.5—40.5	184.8	10.37[c)]
A-3	0.6	35.5—37.0	161.1	9.04

a): S(K) 5.62%. b): S.V. 192.4. c): S(K) 10.53%

[*3] All melting points are uncorrected. The ultraviolet absorption spectra were measured by using a Shimadzu Quartz spectrophotometer, Model QB-50, and a silica cell (1 cm.).

[4] Y. Hirabayashi, M. Mizuta and T. Mazume, This Bulletin, **38**, 1099 (1965).

[*4] The following notations will be used hereafter; F: fraction; Y: yield; S. V.: saponification value: N. V.: neutralization value; S(J): sulfur content as determined by the iodine mehtod; $S(J)_{NV}$: sulfur content as determined by titrating the solution with an iodine solution after the N. V. has been determined; S(K): sulfur content as determined by Kitamura's method. (It was assumed for the purposes of calculation that stearic acid and sulfuric acid were produced by thiostearic acid in the case of mixtures; S(K) was determined by volumetric analysis, which was not always accurate.)

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

[6] Y. Hirabayashi and T. Mazume, This Bulletin, **38**, 171 (1965).

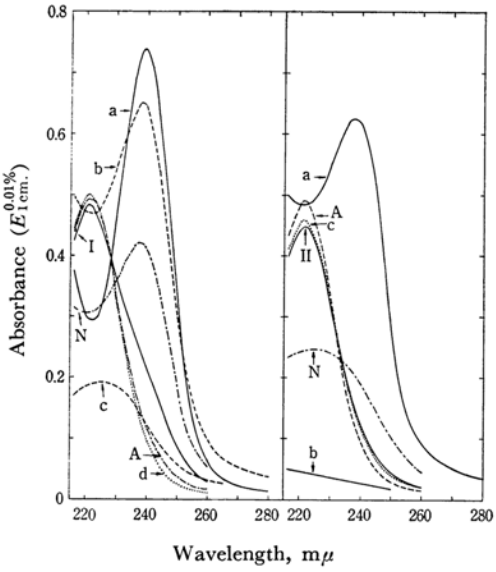


Fig. 1. Fig. 2.

Fig. 1. Ultraviolet absorption spectra of product I and its fractions (shown in Table II) in cyclohexane.

I; product I, A; acidic part A of I, N; neutral part N of I
a; fraction N-1, b; fraction N-2, c; fraction N-3, d; fraction A-3

Fig. 2. Ultraviolet absorption spectra of product II and its fractions (shown in Table III) in cyclohexane.

II; product II, A; acidic part A of II, N; neutral part N of II
a; fraction 1, b; fraction 2, c; fraction 6

curve. The ester was identified as methyl stearate on further recrystallization.

Exp. II.—The characteristics of the reaction product II were as follows:

m. p. 38—42°C, N. V. 137.0, $S(J)_{NV}$ 7.51%, S(K) 8.49%.

Its ultraviolet absorption spectrum is shown in Fig. 2, which is essentially identical with that of the reaction product I.

The reaction product II (2.5 g.) was then separated into an acidic part (A) and a neutral part (N) by the same treatment as was used in Exp. I. The ultraviolet absorption spectrum of A was essentially identical with that of thiostearic acid, while that of N did not exhibit a sharp absorption maximum at 238 mμ and so was different from that of the N of the reaction product I (Fig. 2). Since N was obtained in a small amount, it was again combined with A; the combination was repeatedly recrystallized from benzene and hexane to give, eventually, the several fractions shown in Table III. Their ultraviolet absorption spectra are shown in Fig. 2.

As a result of the above experiments, it was found that the main component of 1 was distearoyl sulfide; that of 2 was stearic acid, and that of 3, 4, 5, and especially 6 was thiostearic acid, containing an ester. This ester is assumed to be methyl stearate from its characteristics and from the ultraviolet absorption spectra of the fractions; the approximate contents of methyl stearate in 3, 4, 5, and 6 were 4, 14, 16, and 22% respectively.

Table III. The characteristics of the fractions obtained from the product II (2.5 g.)

F	Y, g.	M. p., °C	N. V.	$S(J)_{NV}$, %
1	0.2	76.5—78	—	—a)
2	0.15	68.5—69.5	196.5	0.21
3	1.1	38—40	177.2	9.71b)
4	0.4	38.5—39.5	158.9	9.32c)
5	0.3	37—38	155.2	8.99
6	0.2	34.5—35.5	144.1	7.37

S(K): a) 8.61; b) 10.14; c) 9.47%.

Exp. III.—The characteristics of the reaction product III were as follows:

m. p. 36—40°C, N. V. 129.7, $S(J)_{NV}$ 7.21%, S(K) 7.90%.

Its ultraviolet absorption spectrum is shown in Fig. 3, in which the intensity of the absorption maximum at 221 mμ is lower and that of the absorption in the 240—250 mμ region is higher than in the ultraviolet absorption spectrum of thiostearic acid.

The distearoyl sulfide present in I and II might be decomposed in the treatment with alkali.4) Hence, the separation of the product into neutral and acidic parts was omitted, and the reaction product III (3.8 g.) was repeatedly recrystallized from benzene and hexane to give, eventually, the several fractions shown in Table IV (cf. Fig. 3).

Table IV. The characteristics of the fractions obtained from the product III (3.8 g.)

F	Y, g.	M. p., °C	N. V.	$S(J)_{NV}$ %	S(K) %
1	0.45	80.5—81.5	—	—	6.01
2	0.2	76—78	—	—	7.67
3	0.3	60—70	165.5	5.53	7.69
4	0.9	38—40	173.5	10.24	10.42
5	0.3	32.5—34.5	—	—	—
6	1.5	30.5—31.5	106.5	5.77	6.14

As a result of the above experiments, it was found that 1 was distearoyl sulfide, 2 was distearoyl sulfide containing a small amount of thiostearic acid, 4 was thiostearic acid, and 5 and 6 were mixtures of thiostearic acid and an ester. The fraction 6 is assumed not to be a mixture of thiostearic acid and ethyl thiostearate, judging from its characteristics; it is reasonable to consider that the ester part consists of ethyl stearate similar to the methyl stearate in the reaction products I and II; the ethyl stearate content in 6 was about 43%.

Exp. IV.—The characteristics of the reaction product IV were as follows:

m. p. 55—60°C, N. V. 95.9, $S(J)_{NV}$ 3.59%, S(K) 4.51%.

Its ultraviolet absorption spectrum, shown in Fig. 4, is very different from those of the reaction products I, II, and III.

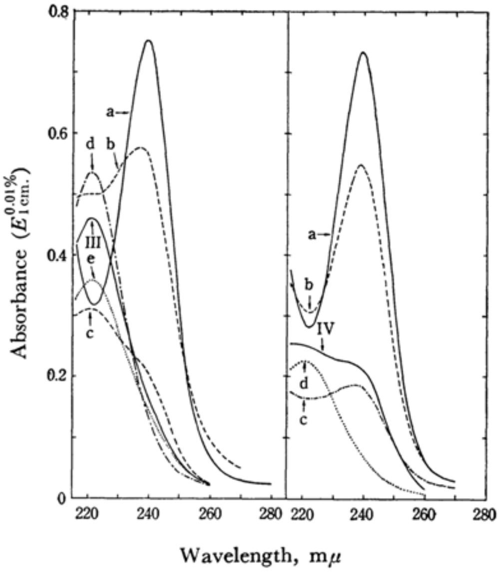


Fig. 3. Fig. 4.

Fig. 3. Ultraviolet absorption spectra of product III and its fractions (shown in Table IV) in cyclohexane.

III; product III, a; fraction 1, b; fraction 2, c; fraction 3, d; fraction 4, e; fraction 6

Fig. 4. Ultraviolet absorption spectra of product IV and its fractions (shown in Table V) in cyclohexane.

IV; product IV, a; fraction 1, b; fraction 2, c; fraction 3, d; fraction 5

The reaction product IV (3.8 g.) was repeatedly recrystallized from benzene and hexane to give, eventually, the several fractions shown in Table V. Their ultraviolet absorption spectra are shown in Fig. 4.

As a result of the above experiments, it was found that 1 was distearoyl sulfide, 2 was mostly distearoyl sulfide, 3 was stearic acid containing a small amount of distearoyl sulfide, and 5 was a mixture of ethyl stearate (about 65%), thiostearic acid, and distearoyl sulfide (a trace).

TABLE V. THE CHARACTERISTICS OF THE FRACTIONS OBTAINED FROM THE PRODUCT IV (3.8 g.)

F	Y g.	M. p. °C	N. V.	S(J)NV %	S(K) %
1	0.9	80.5—81.5	—	—	6.08
2	0.2	76—80	—	—	—
3	0.8	68—69	160.8	1.42	1.52
4	0.1	60—63	—	—	—
5	1.7	29.5—31	44.5—68.6	2.59—3.61	4.41

Discussion

When thiostearic acid was heated in methanol, ethanol, aqueous methanol, or aqueous ethanol, hydrogen sulfide was evolved, and the products consisted of distearoyl sulfide, methyl or ethyl stearate, thiostearic acid, and stearic acid (the last product was obtained only in the case of aqueous alcohols). These results are summarized in Table VI.

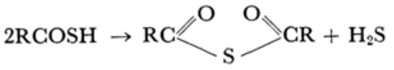
TABLE VI. THE COMPONENTS OF THE PRODUCTS OBTAINED BY HEATING THIOSTEARIC ACID IN ALCOHOLS

Alcohol	Component of product ($R=C_{17}H_{35}$-, $R'=CH_3$- or C_2H_5-)				
	RCOSOCR	RCOSH	RCOOR′	RCOOH	RCOSR′
abs. CH_3OH	○	○	○	×	×
aq. CH_3OH	○	○	○	○	×
abs. C_2H_5OH	○	○	○	×	×
aq. C_2H_5OH	○	○	○	○	×

The mark " ○ " means presence and " × " means absence.

On the basis of the above data, it may be concluded that the reaction consists of the following processes:

1. Distearoyl sulfide is formed according to Eq. 1.
2. Thiostearic acid is re-formed from the distearoyl sulfide and the alcohol according to Eq. 2, by which the stearic ester is also formed, whereas the formation of the thiolester according to Eq. 3 does not occur.
3. The re-formed thiostearic acid repeats the reaction of Eqs. 1 and then that of 2.
4. When aqueous alcohol is treated, thiostearic acid is re-formed, together with the stearic acid formed by partial reaction with water, as is shown in Eq. 4.



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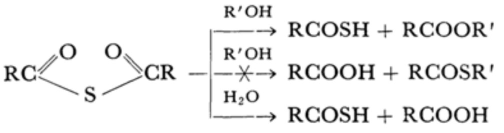

(2)
(3)
(4)

$$RCOSH + R'OH \longrightarrow RCOOR' + H_2S \qquad (5)$$

$$RCOSH + R'OH \longrightarrow RCOSR' + H_2O\ (?) \qquad (6)$$

As has been described in a previous paper,[4] the reaction of Eq. 2 has been confirmed by investigating the properties of distearoyl sulfide. Accordingly, it is not reasonable to say that hydrogen sulfide and the carboxylic ester are formed only in the reaction of thio acid with alcohol (Eq. 5); they may be formed by the two reaction processes, Eqs. 1 and 2, and 5.

The above reaction mechanisms are not confined to the reaction of thiostearic acid only, but could be applied equally well to that of other thio acids.

Stewart and McKinney[3] have reported that Eqs. 5 and/or 6 occurred when thioacetic acid was heated with methanol, ethanol, isopropanol, or triphenylcarbinol in benzene. Their experiments and discussion were based on the assumptions that hydrogen sulfide was produced according to Eq. 5 alone and that the acid (thioacetic acid) disappeared according to both Eqs. 5 and 6; if both reactions of Eqs. 5 and 6 took place simultaneously, the amount of hydrogen sulfide formed would be less than that of the acid disappearing.

However, the following facts have been confirmed in the reaction of thiostearic acid with alcohol: the evolution of hydrogen sulfide is due to the formation of an intermediate, diacyl sulfide, and/or to the reaction of Eq. 5; the thio acid and the carboxylic ester are formed by the reaction of the diacyl sulfide with an alcohol4); the thiol ester is not identified in the product. Stewart and McKinney assumed the occurrence of the reactions of Eqs. 5 and 6 by the estimation of hydrogen sulfide and residual acid without considering the formation and behavior (measurements for the estimate of residual acid) of the diacyl sulfide; they then discussed the mechanism of the esterification of the alcohol with the carboxylic acid, but it seems to be important to consider the presence of diacyl sulfide as an intermediate.