BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1971—1974 (1966)

Studies of Thio Acids. VI.[1] The Electrolysis of Thiostearic Acid[*1]

By Yoshio HIRABAYASHI and Tetsuro MAZUME[*2]
Faculty of Engineering, Gifu University, Kagamigahara-shi, Gifu

(Received December 25, 1965)

Potassium thiostearate was electrolyzed in methanol in the presence of an excess of thiostearic acid by the use of platinum electrodes and a direct current. The product obtained by this electrolysis was found to consist of distearoyl disulfide, methyl stearate, stearic acid, and thiostearic acid. The mechanism of the formation of the above components was discussed in contrast with that of the Kolbe reaction of fatty acids.

Many studies of the Kolbe reaction of fatty acids have been made, whereas the studies of the electrolysis of thio acid have been very scanty, Bunge[2] reported that thioacetic acid (CH_3COSH) yielded diacetyl disulfide ($CH_3COSSOCCH_3$) on electrolysis, the reaction of which was different from the Kolbe reaction of fatty acids. However, no study of the electrolysis of higher aliphatic thio acids has yet been reported.

The present investigation was undertaken to

---

[1] Part V of this series: Y. Hirabayashi, M. Mizuta and T. Mazume, This Bulletin, **38**, 1099 (1965).

[2] N. Bunge, *Ber.*, **3**, 295, 911 (1870).

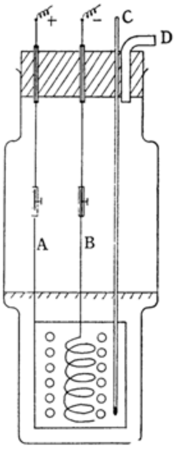
[*1] Parts of this study were presented at the Symposium of Oils and Fats of the Chemical Society of Japan, Nagoya, November, 1958.

[*2] Present address: Shimogamo-kishimotocho, Sakyo-ku, Kyoto.

obtain detailed knowledge of the electrolysis of thio acids. Potassium thiostearate was electrolyzed in methanol in the presence of an excess of thiostearic acid; then the reaction mechanism was discussed and the products investigated. The results will be described in this paper.

Experimental*[3] and Results

Experimental Methods and Conditions.—After a solution of thiostearic acid (6 g.)*[4] in absolute methanol (60 ml.) had been neutralized with ca. 1 N methanolic potassium hydroxide (21.75 ml.; concentration of methanol: 96 vol.%), thiostearic acid (5 g.) and methanol (40 ml.) were added; then the resulting solution was electrolyzed in an electrolytic cell, as is shown in Fig. 1, in which a platinum spiral wire was used as the cathode and a platinum cylinder with holes (4 cm. in diameter and 5 cm. high.) as the anode.



A : Anode
B : Cathode
C : Thermometer
D : Outlet tube of gas

Fig. 1. Electrolytic cell.

Conditions of electrolysis:
Direct current
Voltage: 11.0—11.5 V.
Current: 0.5 amp. (at the beginning)
Temperature of electrolyte: 50—55°C

A while after the electrolysis had started, a solid substance was gradually deposited on the anode; this substance disturbed the passage of the current through the solution, and the evolution of the gas (H_2) on the cathode was also gradually decreased. Then, after the electrolysis had occasionally been interrupted, the deposit on the anode was scraped off into the solution with a glass rod in order to expose the anode surface as much as possible and so facilitate continued electrolysis. A current of 0.5 amp. was again passed through the solution after the exposure of the anode surface. After 2 hr., thiostearic acid (5 g.) and methanol (10 ml.) were again added. Furthermore, after 3 hr., thiostearic acid (5 g.) and methanol (20 ml.) were again added in order to make the electrolysis continue for 5 more hours. The total period of the electrolysis was 10 hr.; the interruptions of electrolysis for the removal of the deposit mentioned above corresponded to one-third of the total period, although almost no interruption was required in the last 2 hr.

The Identification of the Products.—After the electrolysis had ended, the contents of the cell were diluted with warm water (600 ml.), acidified with dilute hydrochloric acid, and extracted with ether; then the ether layer was washed with water in order to remove the excess hydrochloric acid. The ether layer was dark yellow and turbid. The suspending ether-insoluble matter was filtered off; then the filtrate was dried over anhydrous sodium sulfate, and the ether was removed. The following parts were obtained: the

TABLE I. THE CHARACTERISTICS OF FRACTIONS OBTAINED FROM THE ETHER-INSOLUBLE PART (5.5 g.)

Fraction	Yield, g.	M. p., °C	S(K), %
(1)	1.0	83.5—84.5	10.0
(2)	3.1	83.0—84.0	10.4
(3)	0.4	81.5—82.5	10.8
(4)	0.7	79 —81	10.7

S(K): sulfur content determined by Kitamura's method (by volumetric analysis)

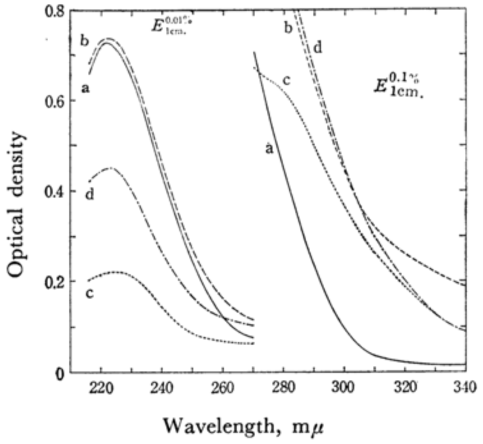


Fig. 2. Ultraviolet absorption spectra in cyclohexane.

a : Fraction 1, 2, or 3 in Table I
b : Fraction 4 in Table I
c : Fraction N-4 in Table II
d : Fraction A-3 in Table II

---

*[3] All the melting points are uncorrected. The ultraviolet absorption spectra were measured with a Shimadzu quartz-spectrophotometer, model QB-50, and a silica cell (1 cm.).

*[4] The characteristics of the thiostearic acid used in this experiments were as follows: m. p. 39.8—40.3°C; neutralization value, 185.8; sulfur content, 10.54 (iodine method), 10.62% (Kitamura's method).

ether-insoluble part, 5.5 g.; the ether-soluble part, 15.5 g.

The ether-insoluble part (5.5 g.) was repeatedly recrystallized from benzene to give, eventually, four fractions. Their characteristics and their absorption spectra are shown in Table I and Fig. 2.

The fractions, 1, 2, and 3, were identified as distearoyl disulfide by means of their characteristics and absorption spectra. Fraction 4 formed 3.3% of the total product. Its principal component was distearoyl disulfide, but it was supposed from its characteristics and absorption spectrum to contain a trace of an impurity. The saponification values of the above fractions were measured in order to determine whether or not hydrocarbons, formed by a reaction similar to the Kolbe reaction of fatty acids, were present. Their saponification values varied depending upon the heating time and the alkali concentration, but they were almost identical with the values determined by measuring an authentic distearoyl disulfide under the same conditions. Consequently, the presence of hydrocarbon in these fractions was unlikely.

The ether-soluble part (15.5 g.) was again dissolved in ether, washed thoroughly with a dilute solution of potassium hydroxide, and divided into neutral (N) and acidic (A) parts by the usual method. The contents of N and A in the total product were 64.8 and 9% respectively. Each part was repeatedly recrystallized from hexane and methanol, thus giving, eventually, four fractions (from N) or three fractions (from A). Their characteristics and ultraviolet absorption spectra are shown in Table II and Fig. 2.

TABLE II. THE CHARACTERISTICS OF FRACTIONS OBTAINED FROM THE ETHER-SOLUBLE PART (15.5 g.)

Fraction	Yield, g.	M. p., °C	A.V.	S(J)
(N-1)	0.8	82 —83	—	—
(N-2)	4.4	38.7—39.2	0.7a)	—
(N-3)	2.9	38.0—39.0	7.2	0
(N-4)	4.5	36 —37	4.8	0.1
(A-1)	0.6	69.5—70.5	197.2	—
(A-2)	0.2	69 —70	196.3	0.6
(A-3)	0.7	45 —50(60)	102.8	1.8b)

A.V.: acid value, S(J): sulfur content determined by the iodine method, a): saponification value 188.2, b): S(K) 6.9%

These fractions were identified as follows:

N-1 was distearoyl disulfide which could not be separated out by the ether-extraction.

N-2, N-3, and N-4 were methyl stearate, judging from their characteristics; above all, N-2 was identified by a mixed melting point determination with an authentic sample, while it was known by their ultraviolet absorption spectra that they contained a trace of an impurity; above all, its content was highest in N-4.

A-1 was stearic acid.

A-3 was thiostearic acid, containing 30—40% of an unidentified substance.

As a result of the above investigations, the components and composition of the product were found to be approximately as follows:

Distearoyl disulfide+	31%
Methyl stearate	37
The part in which methyl stearate is the principal component+	24
Stearic acid	4
The part in which thiostearic acid is the principal component+	4

(+: Supposed to contain traces of unidentified substances).

Discussion

The electrolysis of potassium thiostearate in methanol (above 96 vol.%) in the presence of an excess of thiostearic acid at 50—55°C gave a product consisting of large amounts of distearoyl disulfide and methyl stearate, small amounts of stearic acid and thiostearic acid, and a trace of an unidentified substance. However, since hydrocarbons were not present in the product, the reaction mechanism of electrolysis of thio acids is considered to be different from that of the Kolbe reaction of fatty acids. Accordingly, more consideration will now be given to this subject.

The mechanism of the Kolbe reaction of fatty acids has been established to be as follows3): in the initial step, acyloxy radicals are formed by the discharge of a carboxylate anion on an anode; they decompose into alkyl radicals and carbon dioxide, and then the alkyl radicals yield saturated hydrocarbons, olefin, alcohol, and ester.

On the contrary, in the electrolysis of the potassium salt of thio acid, it may be considered that the acylthio radical (RCOS·) is formed on an anode by the discharge of the carbothiolate anion ($RCOS^-$) formed from the potassium salt of thio acid; then the acylthio radical is dimerized to diacyl disulfide without being decomposed into alkyl radicals and carbon oxysulfide (Eq. 1). It is interesting that the electrolysis of thio acid is different from the Kolbe reaction of fatty acids in which various products are formed from acyloxy radicals. However, it is still unknown whether or not the difference between the two reactions is to be attributed to the difference in properties between RCOO· and RCOS·. It may be also considered that two dimers, $(RCO)_2O_2$ and $(RCO)_2S_2$, are formed from RCOO· and RCOS· in the respective cases; the different products formed by the two reactions may be attributed to

---

3) E.g., C. L. Wilson and W. T. Lippincott, *J. Am. Chem. Soc.*, **78**, 4290 (1956).

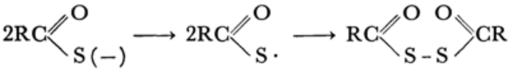
the difference in stability between the two dimers[*5]: i. e., $(RCO)_2O_2$ proceeds to decomposition and $(RCO)_2S_2$ remains. In this case, the mechanism of the Kolbe reaction should be reconsidered by considering the results of this study.

On the other hand, it may also be considered that the formation of distearoyl disulfide is caused by the oxidation with oxygen generated at the anode by a trace of mixed water (Eq. 2). However, since it has been recognized that electrolysis in absolute methanol (CH_3OH–$C_{17}H_{35}COSK$–$C_{17}H_{35}COSH$ system) also gives distearoyl disulfide under the same conditions,[*6] distearoyl disulfide is not formed by oxidation with the oxygen generated at the anode, but by the dimerization of the acylthio radicals, as has been mentioned above.

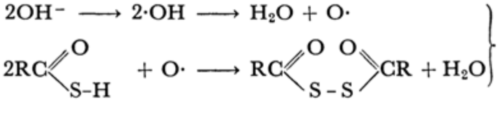
The reason for the formation of a large amount of methyl stearate is considered to be as follows: it has been recognized that distearoyl sulfide is formed by the elimination of hydrogen sulfide when thiostearic acid is heated in methanol at about 60°C; thiostearic acid and methyl stearate are then formed from the distearoyl sulfide and the methanol. Furthermore, the latter reaction is accelerated by the presence of a trace of alkali1) (Eq. 3). On the other hand, it is also considered that methyl stearate is also formed by the direct reaction of thiostearic acid and methanol (Eq. 4). Accordingly, it may be concluded that methyl stearate is formed by the above reactions during a long-continued electrolysis in methanol, and that the formation of methyl stearate has no direct relation with the electrolysis.

A small amount of stearic acid may be formed by the change of thiostearic acid to stearic acid in the presence of a trace of water and alkali (Eq. 5).

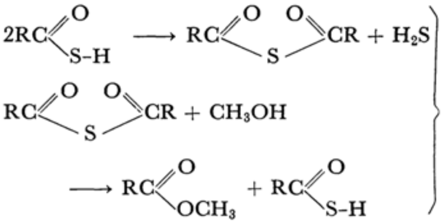
The formation mechanism of the principal components was to be concluded as has been described. However, since unidentified substances were found in some fractions of the product, though present only in traces, and since an equilibrium between thiolic and thionic forms of the potassium salt of thio acid may exist in the solution, reactions other than above-mentioned may possibly occur. This situation will be clarified under other conditions by more detailed investigations in the near future.



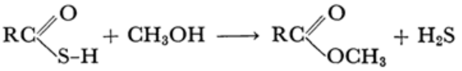
$$2RC(=O)S^{(-)} \longrightarrow 2RC(=O)S\cdot \longrightarrow RC(=O){-}S{-}S{-}C(=O)R \qquad (1)$$



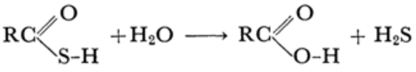
$$\left.\begin{array}{l} 2OH^- \longrightarrow 2{\cdot}OH \longrightarrow H_2O + O\cdot \\ 2RC(=O)S{-}H + O\cdot \longrightarrow RC(=O){-}S{-}S{-}C(=O)R + H_2O \end{array}\right\} \qquad (2)$$



$$\left.\begin{array}{l} 2RC(=O)S{-}H \longrightarrow RC(=O){-}S{-}C(=O)R + H_2S \\ RC(=O){-}S{-}C(=O)R + CH_3OH \\ \qquad \longrightarrow RC(=O)OCH_3 + RC(=O)S{-}H \end{array}\right\} \qquad (3)$$



$$RC(=O)S{-}H + CH_3OH \longrightarrow RC(=O)OCH_3 + H_2S \qquad (4)$$



$$RC(=O)S{-}H + H_2O \longrightarrow RC(=O)O{-}H + H_2S \qquad (5)$$

[*5] In a study of the mechanism of the electrolysis of potassium caproate, Fichter et al. have stated that the decomposition of the primary electrolysis product, $(C_5H_{11}CO_2)_2$, is due to the evolution of heat at the cathode. (F. Fichter and R. Zumbrunn, *Helv. Chim. Acta*, **10**, 869 (1927).)

The good parallel between the products of Kolbe reactions and the decomposition of the corresponding diacyl peroxides suggests that the two processes have common paths or that peroxides are intermediates in the former. (S. Goldschmidt and M. Minsinger, *Chem. Ber.*, **87**, 956 (1954).)

[*6] Not yet published.