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Studies on the Sulfur-containing Chelating Agents. XXXIV.[1] Determination of Stability Constant of Mercury Complex of Monothiodibenzoylmethane and Monothiothenoyltrifluoroacetone by Solvent Extraction Method

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Stability constants and extraction constants of mercury complexes of monothiodibenzoylmethane (SBB) and monothiothenoyltrifluoroacetone (STTA) were determined by the solvent extraction method in the presence of cyanide ion as the auxiliary complexing agent. Chloroform was used as the solvent. These values were compared with those of mercury dithizonate. Stability constant (log K) of mercury complexes decreases in the order, dithizone (42.5)$\approx$SBB (41.8)$>$STTA (33.0), whereas extraction constant (log K') of mercury complexes decreases in the order, dithizone (25.2)$>$STTA (19.6)$\approx$SBB (19.3). As far as the extractability is concerned, SBB and STTA may not be regarded as better reagents than dithizone. However, SBB is regarded as more advantageous reagent than dithizone and STTA, because of its stability in highly diluted solution.

The studies on monothio-β-diketones and their metal chelates have been mostly confined to their structural investigations, and the informations on their properties in solution and their reactivities have been insufficient. Attending to the high stability of mercury complex of monothiodibenzoylmethane (abbreviated as SBB hereafter), we established a radioisotope dilution method for the determination of trace amount of mercury, applying SBB as an extractant.[3] We attempted to study on the reaction of mercury with some monothio-β-diketones as a part of the study on the properties of monothio-β-diketones.

This paper deals with the determination of the stability constants and the extraction constants of mercury complexes of SBB and monothiothenoyltrifluoroacetone (abbreviated as STTA hereafter) and the comparison of the results with those in mercury dithizonate. The stability constants of several metal complexes of monothio-β-diketones have been determined by potentiometric method,[4–7] but those of the metal complexes with extremely high stability such as mercury complex have not been determined. We adopted the solvent extraction method to determine the stability constant of mercury complex considering that these monothio-β-diketones afford excellent properties as the reagent for the solvent extraction.[8–15] Since the stability constant of mercury complex is expected to be extremely high, the determination of the stability constant may be made possible by the use of suitable

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[1] Part XXXIII: Y. Sugiura, Y. Hojo and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **20** 1362 (1972).
[2] Location: *Yoshida, Shimoadachi-cho, Sakyo-ku, Kyoto.*
[3] H. Tanaka, N. Nakanishi, Y. Sugiura and A. Yokoyama, *Bunsekikagaku*, **17**, 1428 (1969).
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auxiliary complexing agent, which forms stable complex with mercury in aqueous phase and lowers the apparent extraction constant of mercury, as in the case of mercury dithizonate.[16)] Preliminary test for the selection of the auxiliary complexing agent revealed that cyanide ion is most favorable for this purpose among various anions tested such as chloride, bromide, iodide, thiocyanate and cyanide, which were chosen as the complexing agents forming water soluble and not extractable mercury complex with known stability constant.

Experimental

Materials——Reagent grade $Hg(OAc)_2$ was used to prepare approximately 1.0×10^{-3}M solution, which was standardized by EDTA titration. When this solution was diluted to proper concentration of mercury, trace amount of radioactive ^{203}Hg in the form of $Hg(OAc)_2$ was added. SBB and STTA were synthesized and purified by the method reported previously.[17)–19)] Reagent grade dithizone, obtained from Wako Pure Chemical Industries was used. Reagent solution (1.0×10^{-3}M) was prepared freshly at each experiment by dissolving the reagent in $CHCl_3$ and standardized and checked at regular time intervals by the measurement of absorbance at the wave-length of the absorption maximum. The absorption spectra of the reagents together with those of Hg complexes are shown in Fig. 1. Acetate buffer solution used as prepared by mixing suitable quantities of NaOAc and AcOH for the adjustment of the ionic strength of the solution (0.1). Solution of cyanide was prepared by reagent grade KCN. $CHCl_3$ was shaken with water, distilled and saturated with buffer solution before use. Water was purified by distillation and passing through an ion exchange column.

Apparatus——All solutions were prepared in 25 ml stoppered test tubes and shaken on Iwaki KM shaker, at 22±0.5°. Measurements of radioactivity were made with a Fujitsu well-type scintillation counter Model ATS-121 for a period of time necessary to obtain total count of at least 10000. Spectrophotometric measurements were carried out with a Hitachi EPS-2 spectrophotometer, and a Shimadzu QV-50 spectrophotometer. A Horiba Model F-5 type pH meter was used for pH measurements.

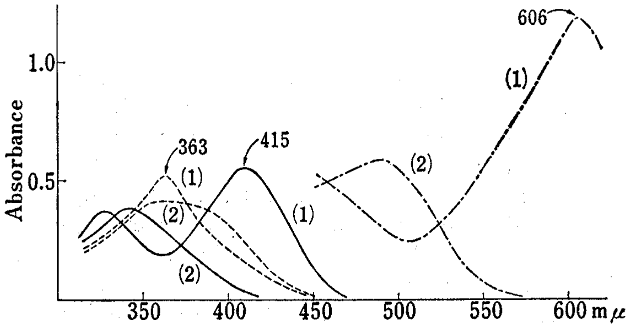

Fig. 1. Absorption Spectra of SBB, STTA, Dithizone and their Mercury Complexes

———: SBB, ----------: STTA, —-—-—: dithizone
(1): reagent (3.0×10^{-5}M in $CHCl_3$)
(2): mercury complex (1.5×10^{-5}M in $CHCl_3$)

Distribution of Reagent (D_r)——A buffer solution was shaken with equal volume of $CHCl_3$ solution of the reagent for 60 min, and allowed to stand for 10 min to ensure complete phase separation. The absorbance(A) of $CHCl_3$ phase was measured at λ_{max} shown in Fig. 1. The distribution ratio of reagent (D_r) was obtained by the following equation.

$$D_r = \frac{(A)_{final}}{(A)_{original} - (A)_{final}}$$

The pH of the aqueous phase was measured.

Distribution of Mercury (D_{Hg})——A 5 ml aliquot of a solution containing radioactive $Hg(OAc)_2$, KCN and buffer solution was shaken with equal volume of $CHCl_3$ solution of the reagent for 7 hr. After allowing to stand for 10 min, 2 ml aliquot of each phase was taken into a plastic tube for the counting of the radioactivity. The distribution ratio of mercury (D_{Hg}) was obtained by the following equation.

$$D_{Hg} = \frac{(\text{counts in } CHCl_3 \text{ phase})}{(\text{counts in aqueous phase})}$$

Under the experimental condition reported here, adsorption of mercury caused by the formation of radiocolloid was not observed.

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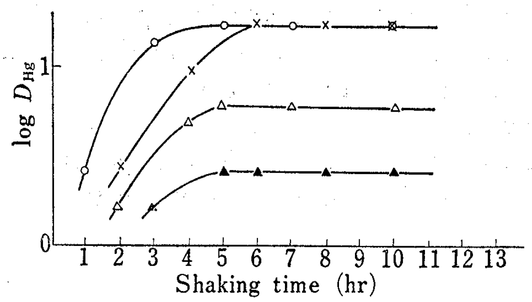

Fig. 2. Effect of Shaking Time on Extraction of Mercury

○: $[SBB]_o = 1.5 \times 10^{-4}$ M, $T_{Hg} = 7.5 \times 10^{-6}$ M, $T_{CN} = 1.0 \times 10^{-3}$ M, pH 4.94
×: $[SBB]_o = 1.5 \times 10^{-4}$ M, $T_{Hg} = 7.5 \times 10^{-6}$ M, $T_{CN} = 1.0 \times 10^{-3}$ M, pH 4.01
△: $[SBB]_o = 1.8 \times 10^{-4}$ M, $T_{Hg} = 1.5 \times 10^{-6}$ M, $T_{CN} = 2.0 \times 10^{-3}$ M, pH 4.54
▲: $[STTA]_o = 4.8 \times 10^{-5}$ M, $T_{Hg} = 1.5 \times 10^{-6}$ M. $T_{CN} = 1.0 \times 10^{-3}$ M, pH 4.20

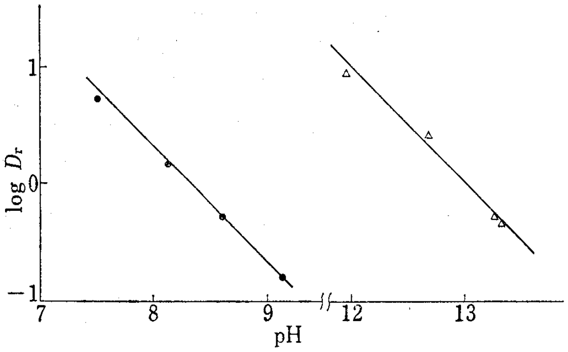

Fig. 3. Relationship between pH and Distribution of Reagent

△: $[SBB]_T = 5.0 \times 10^{-5}$ M in $CHCl_3$
●: $[STTA]_T = 5.0 \times 10^{-5}$ M in $CHCl_3$

For the selection of the experimental conditions, it was expected that attainment of extraction equilibrium may need considerably long time, since the concentration of free mercury ion in aqueous phase is decreased by the presence of the auxiliary complexing agent. The effect of the shaking time to the distribution ratio of mercury in the presence of CN^- shown in Fig. 2 indicates that for both reagents the extraction equilibrium was attained within 6 hr. We adopted 7 hr for the extraction time on the basis of this result.

Partition Coefficient of Mercury Complex (P_c)——One hundred ml of a solution containing Hg salt and buffer solution (pH 4) were prepared in 200 ml separatory funnel as aqueous phase, and shaken with 10 ml of $CHCl_3$ phase containing large excess molar quantity of reagent for 1 hr. After allowing to stand for 10 min, 2 ml aliquot of each phase was taken into a plastic tube for the counting of radioactivity. Then P_c was calculated after the correction of volume.

Calculations

Stability constants of mercury complexes were calculated in the following manner. In the presence of mercury ion (Hg^{2+}), the reagent (RSH) and cyanide ion (CN^-), the reactions are represented as equilibria (1)—(5), where $[\ ]_o$ and $[\ ]$ denote the organic phase and the aqueous phase, respectively.

$$\{Hg^{2+}\} + n\{CN^-\} \overset{\beta_n}{\rightleftarrows} \{Hg(CN)_n{}^{(2-n)+}\} \tag{1}$$

$$\{Hg^{2+}\} + 2\{RS^-\} \overset{K}{\rightleftarrows} \{Hg(RS)_2\} \tag{2}$$

$$\{RSH\} \overset{K_a}{\rightleftarrows} \{RS^-\} + \{H^+\} \tag{3}$$

$$\{RSH\}_o \overset{P_r}{\rightleftarrows} \{RSH\} \tag{4}$$

$$\{Hg(RS)_2\}_o \overset{P_c}{\rightleftarrows} \{Hg(RS)_2\} \tag{5}$$

β_n: formation constant of the mercury cyanide complexes

$$\beta_n = \frac{[Hg(CN)_n{}^{(2-n)+}]}{[Hg^{2+}][CN^-]^n} \tag{6}$$

K: stability constant of mercury complex of the reagent

$$K = \frac{[Hg(RS)_2]}{[Hg^{2+}][RS^-]^2} \tag{7}$$

K_a: acid dissociation constant of the reagent

$$K_a = \frac{[RS^-][H^+]}{[RSH]} \tag{8}$$

P_r: partition coefficient of the reagent

$$P_r = \frac{[\mathrm{RSH}]_o}{[\mathrm{RSH}]} \tag{9}$$

P_c: partition coefficient of mercury complex of the reagent

$$P_c = \frac{[\mathrm{Hg(RS)_2}]_o}{[\mathrm{Hg(RS)_2}]} \tag{10}$$

According to the treatment reported by Duncan, *et al.*,[16] equation (11) is derived with respect to the stability constant.

$$K = \frac{[\mathrm{Hg(RS)_2}]_o[\mathrm{H^+}]^2\{1+\sum_{n=1}^{N}\beta_n[\mathrm{CN^-}]^n\}P_r^2}{C_{\mathrm{Hg}}[\mathrm{RSH}]_o^2 P_c K_a^2} \tag{11}$$

where C_{Hg} is expressed by

$$C_{\mathrm{Hg}} = [\mathrm{Hg^{2+}}]\{1+\sum_{n=1}^{N}\beta_n[\mathrm{CN^-}]^n\} \tag{12}$$

These equations are valid under the condition where $[\mathrm{Hg(RS)_2}]$ can be neglected comparing with $[\mathrm{Hg(CN)}_n{}^{(2-n)+}]$ in aqueous phase.
The observed distribution ratio of the mercury (D_{Hg}) is represented as equation (13).

$$D_{\mathrm{Hg}} = \frac{[\mathrm{Hg(RS)_2}]_o}{C_{\mathrm{Hg}}} \tag{13}$$

Then K is expressed as equation (14).

$$K = \frac{D_{\mathrm{Hg}}[\mathrm{H^+}]^2\{1+\sum_{n=1}^{N}\beta_n[\mathrm{CN^-}]^n\}P_r^2}{[\mathrm{RSH}]_o^2 P_c K_a^2} \tag{14}$$

The extraction constant (K') which is defined as follows, is expressed as equation (15).

$$K' = \frac{[\mathrm{Hg(RS)_2}]_o[\mathrm{H^+}]^2}{[\mathrm{Hg^{2+}}][\mathrm{RSH}]_o^2}$$

$$K' = \frac{D_{\mathrm{Hg}}[\mathrm{H^+}]^2\{1+\sum_{n=1}^{N}\beta_n[\mathrm{CN^-}]^n\}}{[\mathrm{RSH}]_o^2} \tag{15}$$

Therefore when we obtain the values of K', P_c, P_r and K_a, the stability constant (K) can be calculated.

The value of P_r/K_a of the reagent was calculated in the following manner. From equations (8) and (9), equation (16) is derived.

$$D_r = \frac{[\mathrm{RSH}]_o}{[\mathrm{RSH}]+[\mathrm{RS^-}]} = \frac{P_r}{1+K_a/[\mathrm{H^+}]} \tag{16}$$

Under the experimental condition, in which pH of the buffer solution was chosen so as to have $K_a \gg [\mathrm{H^+}]$, equation (17) was obtained from equation (16).

$$\log D_r = -\mathrm{pH} + \log\frac{P_r}{K_a} \tag{17}$$

As shown in Fig. 3, the plots of log D_r *v.s.* pH gave a straight line with slope -1 in the pH range 12.0—13.5 and 7.5—9.2 for SBB and STTA, respectively. The values of P_r/K_a obtained by equation (17) are shown in Table I.

Result and Discussion

In the previous paper,[3] only 1:2 complex, $\mathrm{Hg(RS)_2}$, was approved to be as an extractable mercury complex into chloroform in the reaction of mercury with SBB. However in the presence of the auxiliary complexing agent, the existence of a mixed ligand complex may be expected in this system, similarly to the systems of dithizone-mercury-chloride[20] and xanthate-mercury-chloride.[21] The equilibria (18) and (19) should be added to the equilibria (1)—(5), the presence of the mixed complex being taken into account.

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[20] G.B. Briscoe and B.G. Cooksey, *J. Chem. Soc.* (*A*), **1969**, 205.

[21] K.G. Ashurst, N.P. Finkelstein and N.M. Rice, *J. Chem. Soc.* (*A*), **1970**, 2302.

$$\{Hg^{2+}\} + \{CN^-\} + \{RS^-\} \rightleftarrows \{Hg(RS)(CN)\} \qquad (18)$$

$$\{Hg(RS)(CN)\}_o \rightleftarrows \{Hg(RS)(CN)\} \qquad (19)$$

If the equilibria (18) and (19) are present, together with those (1)—(5), the Eq. (15) can not be approved. The plots of log D_{Hg} *v.s.* log $[RSH]_o$ are taken, where the experimental conditions are kept so as to get constant $[CN^-]$ and pH. As shown in Fig. 4, a linear relationship with slope 2 are observed between log D_{Hg} and log $[RSH]_o$. The Eq. (15) was satisfactorily approved in the region where the molar ratio of the reagents and cyanide ($[RSH]_o/T_{CN}$) are restricted within 2×10^{-2}—2×10^{-1}, 3×10^{-2}—2.5×10^{-1}, for SBB and STTA, respectively, where "T_{CN}" denotes total concentration of potassium cyanide. Accordingly, it was suggested that the presence of other mercury complexes except $Hg(RS)_2$ and mercury-cyanide complex are negligible. In the region where $[RSH]_o/T_{CN}$ is less than 2×10^{-2} for SBB and 3×10^{-2} for STTA, the plots of log D_{Hg} *v.s.* log $[RSH]_o$ deviated upwards slightly from the straight line with slope 2 as shown in Fig. 4. From this fact, the presence of the mixed ligand complex may be expected and the equilibria expressed by the equilibria (18) and (19) are considered to be involved in the extraction system.

The equilibrium between mercury and cyanide ions in aqueous phase was studied in the extraction. The concentration of free cyanide ion is shown as follows.

$$[CN^-] = \frac{K_{HCN}[HCN]}{[H^+]}$$

(K_{HCN}: acid dissociation constant of hydrogen cyanide)

Then Eq. (15) is expressed as Eq. (20).

$$K' = \frac{D_{Hg}[H^+]^2}{[RSH]_o^2}\left\{1+\sum_{n=1}^{N}\beta_n\frac{K_{HCN}{}^n[HCN]^n}{[H^+]^n}\right\} \qquad (20)$$

We used the following values from the reference[22] as the values of β_n and K_{HCN}; log β_1=18.00, log β_2=34.70, log β_3=38.53, log β_4=41.51, pK_{HCN}=9.14.

Under the experimental condition where large excess of concentration of potassium cyanide ($T_{CN}=1\times10^{-3}$—2×10^{-3}M) is present compared with the concentration of mercury ($T_{Hg}=1.5\times10^{-6}$M) in pH 4—6, the braced term in the Eq. (20) is expressed as $\beta_2 K_{HCN}{}^2 T_{CN}{}^2/[H^+]^2$ because other terms in Eq. (20) could be neglected and [HCN] is considered to be equal to T_{CN}.

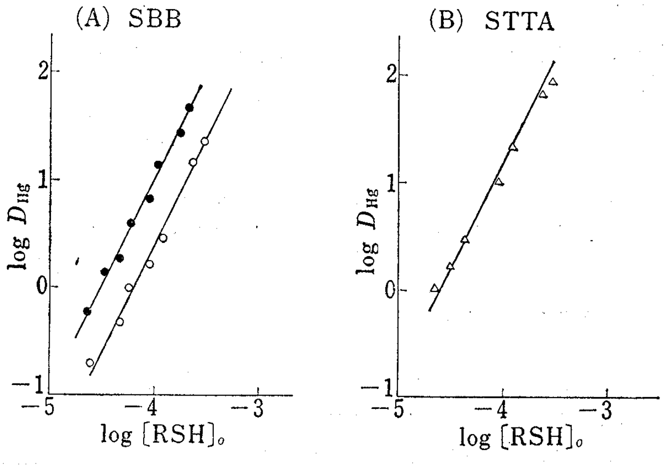

Fig. 4. Relationship between Distribution of Mercury and Concentration of Reagent

●: $T_{Hg}=1.5\times10^{-6}$M, $T_{CN}=1.0\times10^{-3}$M, pH 4.41
○: $T_{Hg}=1.5\times10^{-6}$M, $T_{CN}=2.0\times10^{-3}$M, pH 4.37
△: $T_{Hg}=1.5\times10^{-6}$M, $T_{CN}=1.0\times10^{-3}$M, pH 4.75

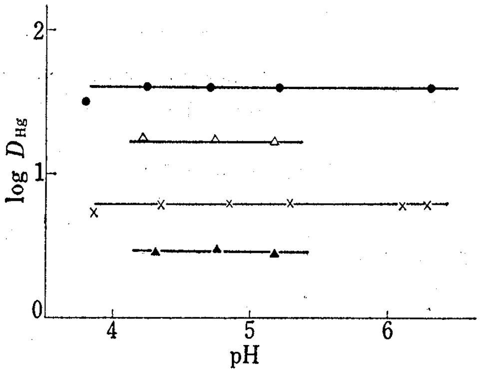

Fig. 5. Effect of pH on Extraction of Mercury

●: $[SBB]_o=6.0\times10^{-4}$M, $T_{Hg}=1.5\times10^{-6}$M, $T_{CN}=2.0\times10^{-3}$M
×: $[SBB]_o=1.8\times10^{-4}$M, $T_{Hg}=1.5\times10^{-6}$M, $T_{CN}=2.0\times10^{-3}$H
△: $[STTA]_o=1.2\times10^{-4}$H, $T_{Hg}=1.5\times10^{-6}$M, $T_{CN}=1.0\times10^{-3}$M
▲: $[STTA]_o=4.8\times10^{-5}$M, $T_{Hg}=1.5\times10^{-6}$M, $T_{CN}=1.0\times10^{-3}$M

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[22] G. Anderegg, *Helv. Chim. Acta*, **40**, 1022 (1957).

In addition, the concentration of mercury hydroxide and mercury acetate are negligibly small compared with the concentration of mercury cyanide complex under these experimental conditions. Then Eq. (20) is simplified as Eq. (21).

$$K' = \frac{D_{Hg}\beta_2 K_{HCN}{}^2 T_{CN}{}^2}{[RSH]_o{}^2} \qquad (21)$$

The Eq. (21) results the independence of D_{Hg} against pH, at constant $[RSH]_o$ and T_{CN}. The experimental results obtained under the above-mentioned conditions, where D_{Hg} was kept constant in the range of pH 3.5—6.0 as shown in Fig. 5, gave us the same conclusion as described above on the equilibrium of mercury cyanide complexes in this system.

According to the Eq. (21), K' was calculated. The results calculated from the data obtained from the range, where the linear relationship with slope 2 was approved, are shown in Table I. These values are the average values from at least five parallel experiments. In an attempt to compare these monothio-β-diketones with dithizone as the reagent for the solvent extraction, the stability constant of mercury dithizonate was measured by the similar procedures to those in the cases of SBB and STTA. The stability constant calculated by Eq. (21) is also shown in Table I, which agrees comparably with those reported previously.[16]

Table I. Extraction Constants and Stability Constants

Reagent	log K'	log (P_r/K_a)	log P_c	log K
SBB	19.3	13.0	3.4	41.8
STTA	19.6	8.3	3.3	33.0
Dithizone	25.2	10.5	3.8	42.5

In comparison on the properties among SBB, STTA and dithizone, the following characterizations as the reagent in the solvent extraction for these complexing agents may be derived, based on the results shown in Table I. The value of log K' is greater in dithizone than in SBB, although the stabilities of the complexes of these reagents are comparable each other. Whereas, the values of log K' are comparable each other in SBB and STTA, but the stability of mercury complex of STTA is lower than that of SBB. SBB and STTA may not be regarded as a better reagent for the solvent extraction than dithizone as far as the value of log K', which relates to the extractability of metal ion, is concerned. However, as far as the stability of the reagent is concerned, SBB is far more advantageous than dithizone, especially in highly diluted solution, as in the application towards the isotopic dilution method. Namely, it has been known that dithizone is considerably unstable in aqueous organic solvent although it is stable in pure organic solvent,[23] and dithizone has been used as zinc chelate in isotopic dilution method to avoid the decomposition in diluted solution.[24] In this case, decrease in the rate of the extraction of mercury is caused to some extent. Some of thio-β-diketones, including STTA, were found to be hydrolyzed in acid solution to form β-diketones.[6 25] However we found that SBB is fairly stable in acid medium,[25] moreover the fact that the great value of log (P_r/K_a) may be the reflection of the stability of this reagent on the solvent extraction treatment. Considering these discussions, it may be concluded that SBB is more advantageous reagent than dithizone and STTA.

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[24] G.B. Briscoe, B.G. Cooksey, J. Ruzicka and M. Williams, *Talanta*, **14**, 1457 (1967).

[25] A. Yokoyama, M. Chikuma, S. Harada and H. Tanaka, unpublished.