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I hereby recommend that the thesis prepared under my supervision by Jack B. Callaway

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be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

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THE INTERACTION OF MERCURIC OXIDE WITH SIMPLE ESTERS IN CARBON BISULFIDE SOLUTION

A Dissertation Submitted

to the

GRADUATE SCHOOL

of the

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by

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INTRODUCTION

Since primary amines have been shown, in this laboratory (1), to react readily with carbon bisulfide, iodine and pyridine to form thiocarbanilides in conformity with the following reaction mechanism scheme:

$$2RNH_2 + CS_2 \longrightarrow (RNH)_2CS + H_2S \qquad (a)$$

$$H_2S + I_2 \longrightarrow 2HI + S \qquad (b)$$

$$2HI + 2C_5H_5N \longrightarrow 2C_5H_5N.HI \qquad (c)$$

$$\Big\{ (a), (b), (c).\quad 2RNH_2 + CS_2 + I_2 + 2C_5H_5N \longrightarrow (RNH)_2CS + S + 2C_5H_5N.HI \qquad (A)$$

the idea occurred that a simple aliphatic ester such as ethyl formate might display similar behavior to form thiocarbonic acid esters thus:

$$2HCOOC_2H_5 + CS_2 \longrightarrow (COOC_2H_5)_2S + H_2S \qquad (a)$$

$$H_2S + I_2 \longrightarrow 2HI + S \qquad (b)$$

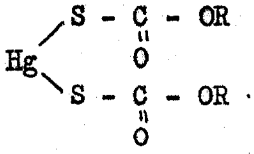
$$2HI + 2C_5H_5N \longrightarrow 2C_5H_5N.HI \qquad (c)$$

$$\Big\{ (a), (b), (c),\quad 2HCOOC_2H_5 + CS_2 + I_2 + 2C_5H_5N \longrightarrow (COOC_2H_5)_2CS + S + 2C_5H_5N.HI \qquad (B)$$

When ethyl formate in carbon bisulfide solution with molecular quantities of iodine and pyridine, as noted in the above equation (B) were heated together for several hours, a reaction occurred with copious evolution of hydrogen sulfide, but no organic sulfur compound was found when the reaction mixture was evaporated to dryness.

It was then decided to substitute mercuric oxide for the pyridine. This modification, it was hoped, would also eliminate hydrogen sulfide formed in the course of the reaction by the formation of mercuric sulfide. Trials were made using ethyl formate in carbon bisulfide. Mercuric sulfide was precipitated and from the reaction mixtures upon evaporation white crystalline compounds containing mercury and sulfur were obtained.

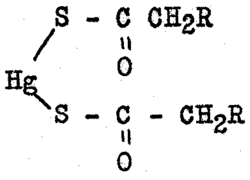
The analyses and properties of the white compounds obtained from methyl and ethyl formates gave evidence that they were mercury alkyl thiocarbonates of the general formula



$$\mathrm{Hg}\begin{cases}\mathrm{S}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{OR}\\ \mathrm{S}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{OR}\end{cases}$$

R represents a methyl or ethyl group.

Similar investigations of the reaction of methyl and ethyl acetates also gave white crystalline products. The structure tentatively given for the products from the reactions of the simple acetates may be represented by the formula, mercury salts of thioacids.



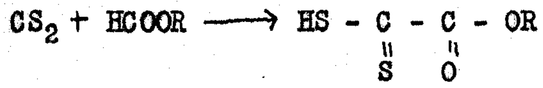
$$\mathrm{Hg}\begin{cases}\mathrm{S}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\ \mathrm{CH_2R}\\ \mathrm{S}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{CH_2R}\end{cases}$$

The present study deals first with original methods for the preparation of mercury salts of thioacids herewith obtained by the interaction of four esters - methyl and ethyl formates, methyl and ethyl acetates - with mercuric oxide in carbon bisulfide solution, and second, with investigations essential to establishing the structural formulas of the compounds so formed. This study also embodies accounts of the improved methods developed for the quantitative estimation of mercury in carbon compounds.

THEORETICAL

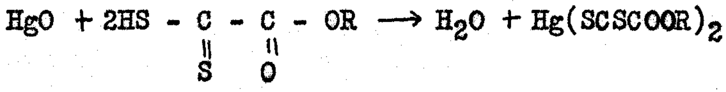
The preliminary experiments noted in the introduction indicated that methyl and ethyl formates on interaction in carbon bisulfide solution with mercuric oxide gave mercury alkyl thiocarbonates of the general formula $Hg(SCOOR)_2$. Before recording the experimental procedure of preparation, analyses and determination of structural formulas of these compounds, the following reaction mechanism scheme is proposed to explain their syntheses.

It is assumed that the first reaction occurring is the combination of carbon bisulfide with the ester according to equation (a):



$$CS_2 + HCOOR \longrightarrow HS - \underset{\displaystyle S}{\overset{}{\underset{\|}{C}}} - \underset{\displaystyle O}{\underset{\|}{C}} - OR \qquad (a)$$

The basic mercuric oxide then reacts with the acidic addition compound, a hydrosulfide, according to equation (b):



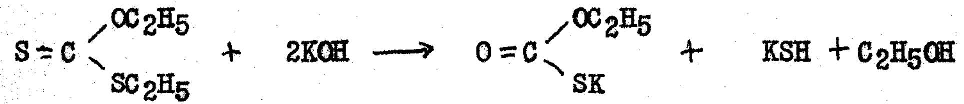
$$HgO + 2HS - \underset{\displaystyle S}{\underset{\|}{C}} - \underset{\displaystyle O}{\underset{\|}{C}} - OR \longrightarrow H_2O + Hg(SCSCOOR)_2 \qquad (b)$$

During the course of the reaction the red mercuric oxide rapidly turns black due to formation of mercuric sulfide. This would presumably entail the substitution of oxygen for sulfur in the compound formed in equation (b), according to the following equation (c):

$$Hg(S\text{-}CS\text{-}COOR)_2 + 2HgO \longrightarrow Hg(S\text{-}CO\text{-}COOR)_2 + 2HgS \qquad (c)$$

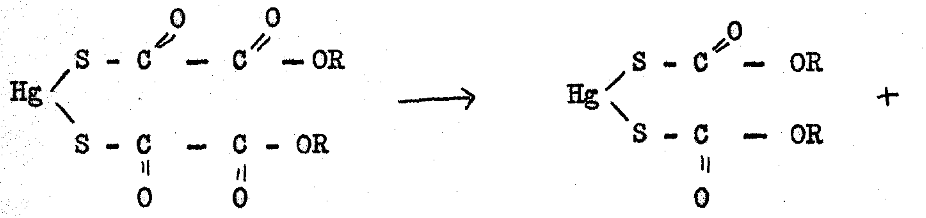
It may be parenthetically noted that this substitution of oxygen for sulfur is quite conceivable in view of the parallel substitution reported by Debus (2), ~~(Ann. 75, 121 (1850)~~, between ethyl xanthate and alcoholic potassium hydroxide wherein the radicals =C=S becomes

=C=O with the formation of KHS thus:



$$S{=}C\begin{matrix}\diagup OC_2H_5\\ \diagdown SC_2H_5\end{matrix} + 2KOH \longrightarrow O{=}C\begin{matrix}\diagup OC_2H_5\\ \diagdown SK\end{matrix} + KSH + C_2H_5OH$$

Furthermore, during the course of the reaction carbon monoxide was evolved. (Its identification is subsequently described in the experimental part). The liberation of carbon monoxide may be represented by the decomposition of the compound noted in equation (c), assumed to be the following equation, (d).



$$Hg\begin{matrix}\diagup S-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OR\\ \diagdown S-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-OR\end{matrix} \longrightarrow Hg\begin{matrix}\diagup S-\overset{O}{\overset{\|}{C}}-OR\\ \diagdown S-\underset{O}{\underset{\|}{C}}-OR\end{matrix} + 2CO \qquad (d)$$

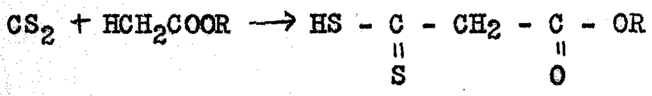
which completes the synthesis of the mercury alkyl thiocarbonates.

The summation of the above equations (a), (b), (c), and (d) gives the following final equation:

$$\Sigma\ (a), (b), (c), (d). \quad 2HCOOR + 2CS_2 + 3HgO \longrightarrow Hg(SCOOR)_2 + 2CO + 2HgS + H_2O$$

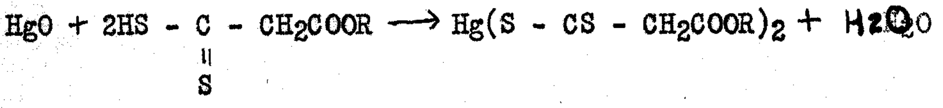
A reaction mechanism scheme similar to the above for the reactions of the esters of formic acid is proposed for the reactions of esters of acetic acid. It is tentatively assumed that the compounds formed from the interaction of mercuric oxide with ethyl and methyl acetates in carbon bisulfide solution are also mercury salts of thioacids synthesized in accordance with the following reaction mechanism scheme.

It is assumed that the first reaction occurring is the combination of the ester with carbon bisulfide according to the analagous equation (a'):



$$CS_2 + HCH_2COOR \longrightarrow HS-\underset{\underset{S}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OR \tag{a'}$$

The basic mercuric oxide then reacts with the acidic addition compound according to equation (b'):

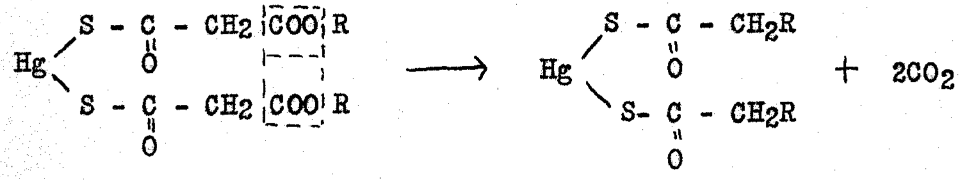


$$HgO + 2HS-\underset{\underset{S}{\|}}{C}-CH_2COOR \longrightarrow Hg(S-CS-CH_2COOR)_2 + H_2O \tag{b'}$$

As in the formate reactions, the mercuric oxide rapidly blackens due to the formation of mercuric sulfide as noted in equation (c'):

$$Hg(S-CS-CH_2COOR)_2 + 2HgO \longrightarrow Hg(S-CO-CH_2COOR)_2 + 2HgS \tag{c'}$$

Differing from the reactions of the formates which evolved carbon monoxide (equation d), the acetates liberated carbon dioxide. This reaction may be represented by the decomposition of the product noted in equation (c') in conformity with equation (d'):



$$Hg\left\langle\begin{array}{l} S-\underset{\underset{O}{\|}}{C}-CH_2\boxed{COO}R \\ S-\underset{\underset{O}{\|}}{C}-CH_2\boxed{COO}R\end{array}\right. \longrightarrow Hg\left\langle\begin{array}{l} S-\underset{\underset{O}{\|}}{C}-CH_2R \\ S-\underset{\underset{O}{\|}}{C}-CH_2R\end{array}\right. + 2CO_2 \tag{d'}$$

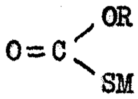
Which completes the synthesis of the mercury thioacid salt.

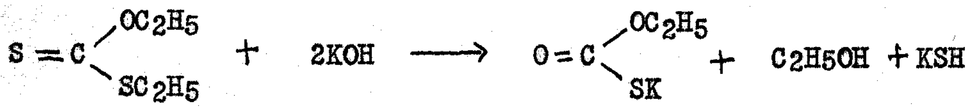
The summation of the equations (a'), (b'), (c') and (d') gives the following final equation:

(a'), (b'), (c'), (d'). $2CH_3COOR + 2CS_2 + 3HgO \longrightarrow Hg(SCOCH_2R)_2 + 2HgS + 2CO_2 + H_2O.$

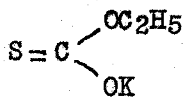
HISTORICAL

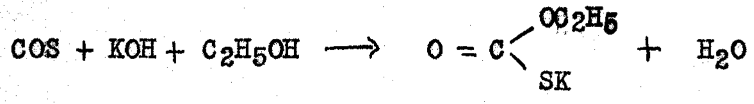
Precisely the same type of investigation as the present one has not been recorded in the classical literature. Compounds analogous to mercury alkyl thiocarbonate and mercury thioacid salts have been reported. This section will be devoted to a review of the methods used in preparing these analogs.

Debus (2) was the first to report the preparation of metal alkyl thiocarbonates of the type  $\mathrm{O{=}C}\begin{matrix}\diagup \mathrm{OR}\\ \diagdown \mathrm{SM}\end{matrix}$ where R represents an alkyl radical and M a metal. He prepared the potassium derivative by treatment of ethyl xanthate with alcoholic potassium hydroxide as noted in equation (a):



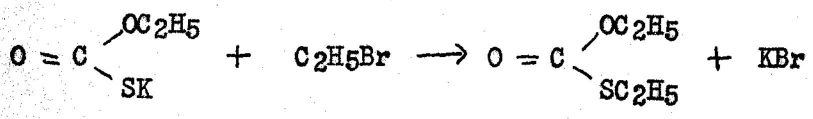
$$\mathrm{S{=}C}\begin{matrix}\diagup \mathrm{OC_2H_5}\\ \diagdown \mathrm{SC_2H_5}\end{matrix} + 2KOH \longrightarrow \mathrm{O{=}C}\begin{matrix}\diagup \mathrm{OC_2H_5}\\ \diagdown \mathrm{SK}\end{matrix} + C_2H_5OH + KSH \qquad (a)$$

That the thiolcarbonate was the product formed and not its isomer, the thionocarbonate,  $\mathrm{S{=}C}\begin{matrix}\diagup \mathrm{OC_2H_5}\\ \diagdown \mathrm{OK}\end{matrix}$, was confirmed by Bender (3), who prepared the same compound by the interaction of carbonyl sulfide with alcoholic potassium hydroxide according to equation (b):



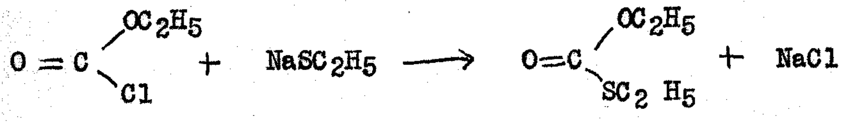
$$COS + KOH + C_2H_5OH \longrightarrow \mathrm{O = C}\begin{matrix}\diagup \mathrm{OC_2H_5}\\ \diagdown \mathrm{SK}\end{matrix} + H_2O \qquad (b)$$

The product noted in equation (b) will interact with ethyl bromide to form the ethyl derivative according to equation (c):



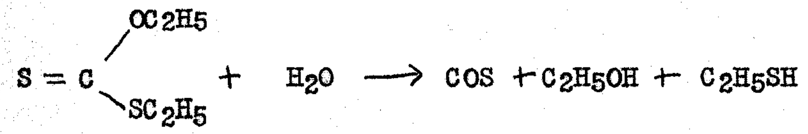
$$\mathrm{O = C}\begin{matrix}\diagup \mathrm{OC_2H_5}\\ \diagdown \mathrm{SK}\end{matrix} + C_2H_5Br \longrightarrow \mathrm{O = C}\begin{matrix}\diagup \mathrm{OC_2H_5}\\ \diagdown \mathrm{SC_2H_5}\end{matrix} + KBr \qquad (c)$$

Solomon (4) produced the compound noted in equation (c) by interacting sodium mercaptide with ethyl chlorcarbonate according to equation (d):



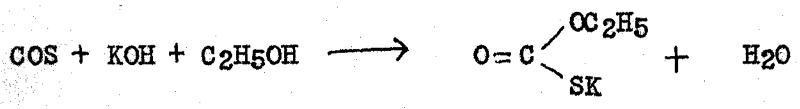
$$O=C\begin{matrix}\diagup OC_2H_5\\ \diagdown Cl\end{matrix} + NaSC_2H_5 \longrightarrow O=C\begin{matrix}\diagup OC_2H_5\\ \diagdown SC_2H_5\end{matrix} + NaCl \qquad (d)$$

It may be noted that the essential reaction in equation (a) is an exchange of a carbonyl sulfur atom for a carbonyl oxygen atom by a metallic hydroxide. Two mechanisms have been suggested for this exchange of sulfur for oxygen. Solomon (5) postulates first a hydrolysis of the xanthate according to equation (e):



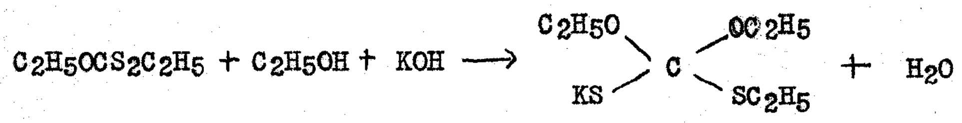
$$S=C\begin{matrix}\diagup OC_2H_5\\ \diagdown SC_2H_5\end{matrix} + H_2O \longrightarrow COS + C_2H_5OH + C_2H_5SH \qquad (e)$$

A reaction then occurs with the alcoholic potassium hydroxide as in the following equation (f):

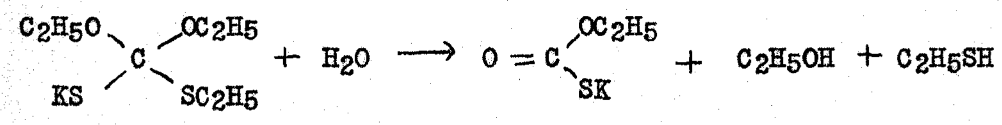


$$COS + KOH + C_2H_5OH \longrightarrow O=C\begin{matrix}\diagup OC_2H_5\\ \diagdown SK\end{matrix} + H_2O \qquad (f)$$

Wallach (6) explains the exchange of sulfur for oxygen by the formation of an addition product followed by hydrolysis according to the following equations:



$$C_2H_5OCS_2C_2H_5 + C_2H_5OH + KOH \longrightarrow \begin{matrix}C_2H_5O\diagdown\\ KS\diagup\end{matrix}C\begin{matrix}\diagup OC_2H_5\\ \diagdown SC_2H_5\end{matrix} + H_2O \qquad (g)$$



$$\begin{matrix}C_2H_5O\diagdown\\ KS\diagup\end{matrix}C\begin{matrix}\diagup OC_2H_5\\ \diagdown SC_2H_5\end{matrix} + H_2O \longrightarrow O=C\begin{matrix}\diagup OC_2H_5\\ \diagdown SK\end{matrix} + C_2H_5OH + C_2H_5SH \qquad (h)$$

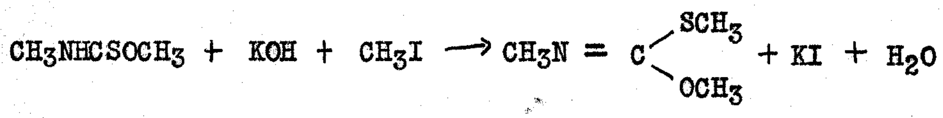
Debus (2) in attempting to prepare the mercury derivative of the ethyl thiocarbonate treated the potassium salt with an aqueous mercuric chloride solution noting the formation of a white precipitate which dissolved in an excess of mercuric chloride. Bender (3) repeated this experiment and noted only that the white precipitate acquired a superficial yellow coating upon standing. No other properties were reported.

The corresponding compound prepared in the present investigation is soluble in a mercuric chloride solution and likewise acquires the yellow color after a few minutes exposure to air.

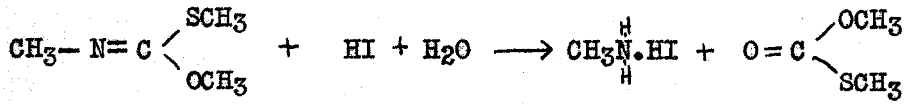
Bender (3) prepared the copper, zinc, lead and silver salts of thiocarbonic acids by treating the potassium ethyl thiocarbonate with the metallic acetates.

Delépine (7) prepared the corresponding methyl esters through the interaction of mustard oils with alcohols according to the following equations:

$$CH_3NCS + CH_3OH \longrightarrow CH_3NHCSOCH_3$$

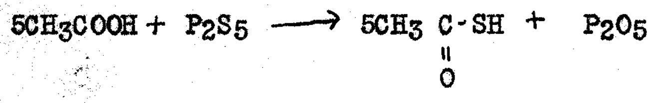


$$CH_3NHCSOCH_3 + KOH + CH_3I \longrightarrow CH_3N = C\begin{matrix} \diagup SCH_3 \\ \diagdown OCH_3 \end{matrix} + KI + H_2O \qquad (a)$$



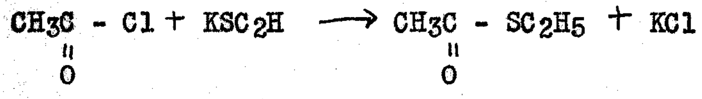
$$CH_3{-}N{=}C\begin{matrix} \diagup SCH_3 \\ \diagdown OCH_3 \end{matrix} + HI + H_2O \longrightarrow CH_3\overset{H}{\underset{H}{N}}.HI + O{=}C\begin{matrix} \diagup OCH_3 \\ \diagdown SCH_3 \end{matrix} \qquad (b)$$

Turning now to a consideration of the thio fatty acids, it may be noted that Kekulé (8) was the first to prepare a thioacid by the interaction of acetic acid with phosphorus pentasulfide:



$$5CH_3COOH + P_2S_5 \longrightarrow 5CH_3\underset{\underset{O}{\|}}{C}\text{-}SH + P_2O_5$$

Vasselmann and Jaquemin (9) prepared the ethyl ester by interacting acetyl chloride and potassium mercaptide:



$$CH_3\underset{\underset{O}{\|}}{C} - Cl + KSC_2H \longrightarrow CH_3\underset{\underset{O}{\|}}{C} - SC_2H_5 + KCl$$

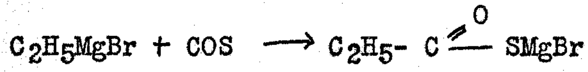
The only mercury salt reported is that of thioacetic acid, prepared by Ulrich (10). This salt was obtained by treating the potassium thioacetate with mercuric chloride.

$$2CH_3C\ O\ S\ K + HgCl_2 \longrightarrow (CH_3COS)_2Hg + 2KCl$$

The mercury salt forms as a white precipitate which soon darkens due to the formation of mercuric sulfide.

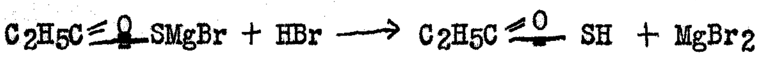
Roscoe and Schorlemmer (11) state that the copper and silver salts have not been prepared in a pure state. No later reference was found for these last named salts.

Weigert (12) prepared thiopropionic acid by the interaction of the Grignard reagent with carbon oxysulfide according to the following equations:



$$C_2H_5MgBr + COS \longrightarrow C_2H_5\text{-}\ C\overset{O}{\lessgtr}SMgBr$$

The free acid was obtained by treatment of the product with dilute acid as shown in the following equation:



$$C_2H_5C\overset{O}{\lessgtr}SMgBr + HBr \longrightarrow C_2H_5C\overset{O}{\lessgtr}SH + MgBr_2$$

The methods of preparation and the properties of the metal salts were not found in the literature.

EXPERIMENTAL PROCEDURE

The apparatus used in investigating the interactions of methyl and ethyl esters with carbon bisulfide and mercuric oxide may be classified under two divisions: (a) equipment for stirring, and (b) equipment for adsorption of gases evolved during the course of the reactions. Part(b) will be described under the individual runs, which called for variations.

Throughout the entire course of the work the same type of reaction vessel and stirring device were utilized. A one liter round bottom three neck flask served adequately as a reaction vessel. A glass stirring rod activated by a 1/64 H.P. motor extended through a mercury seal into the middle neck of the flask. A spiral reflux condenser was fitted to the second neck by a rubber stopper. In order to sweep out the system with nitrogen, the third neck was fitted with a rubber stopper through which extended a short piece of glass tubing equipped with a stopcock. All stoppers were sealed with de Khotinsky cement and connections between glass tubing were made with thick-walled gum rubber tubing.

Identical systems were always set up in duplicate.

A. ETHYL FORMATE

(a) Experimental procedure.

Inasmuch as the ethyl formate reaction was intensively studied first and since experience gained from its investigation conditioned the nature of the subsequent setups, work with this ester will now be considered.

Twelve duplicate runs were made with the ester with the purpose first to increase yields of the mercury ethyl thiocarbonate and second to find an efficient method for the estimation of carbon monoxide evolved during the course of the reaction.

Eastman's ethyl formate was fractionated by means of a four bulb Glinsky column. Only the fraction boiling between 53.5 degrees to 54.5 degrees C was used in the experimental runs. Mallinckrodt's carbon bisulfide was likewise distilled, the fraction boiling between 46 degrees to 47 degrees C being used. Kahlbaum's reprecipitated mercuric oxide was used for a microscopic examination of same revealed homogeneity and uniform particle size.

Two moles of the ester and 200 c.c. (3.3 moles) of carbon bisulfide was measured into the reaction flask and the stirrer activated. One half mole of mercuric oxide was slowly poured through the third neck of the flask which was then closed by the stopper and stopcock. A flame under the water bath was regulated to give a fairly vigorous but constant rate of refluxing. Whenever it was necessary to interrupt the stirring and refluxing, the system was swept out by a stream of nitrogen for fifteen minutes. The total time for refluxing and stirring varied from ten to fifty-six hours.

At first the course of the reaction could be followed by a gradual darkening as black mercuric sulfide formed. This darkening usually appeared after a quarter of an hour, and in two to three hours the solid phase was completely black. Small portions of the solid were removed from time to time, crushed and microscopically examined for the red mercuric oxide.

At the conclusion of a run as determined by no further evolution of gas, the contents of the reaction flasks were filtered through two sheets of fine filter paper on a Büchner funnel and the black residue on the filter was thoroughly washed with carbon bisulfide. The filtrates were yellow and had a somewhat fluorescent hue. The filtrate and washings were again filtered into a 500 cc. distilling flask, evaporated down to approximately 100 c.c., then poured into a crystallizing dish, which was placed in a dessicator, and the remainder of the liquid evaporated at room temperature under reduced pressure. Yellowish white crystalline plates formed.

The crystalline product was then dissolved in 95% ethyl alcohol, the solution filtered and poured into a liter of cold water with stirring. Glistening white plates, insoluble in water, were immediately precipitated. They were filtered on a Büchner, washed with water without delay and dried in a desiccator over calcium chloride. Exposure to moist air for even a short time caused the crystals to show a dark superficial layer of what is probably mercuric sulfide. The crystalling compound was readily soluble in methyl and ethyl alcohols, ether, chloroform, and carbon bisulfide.

Melting points were determined with calibrated short stem thermometers, using a concentrated sulfuric acid bath in a Thiele melting point tube. The compound obtained by the ethyl formate reaction melted after repeated crystallizations at 64.5 degrees to 65 degrees.

(b) Quantitative estimation of mercury in the mercury ethyl thiocarbonate

Qualitative analyses showed the presence of mercury and sulfur in the crystalline compound, assumed to be mercury ethyl thiocarbonate formed according to the reactions proposed in the theoretical part.

The first difficulty was in effecting complete solution of the samples for analysis. Modifications of a composite of standard methods, hereinafter noted, were found to be necessary. The usual procedures for effecting solution of organic mercury compounds involving the use of concentrated acids and oxidizing agents, left a gummy layer on the surface of the solution, and hence were abandoned.

It was however found that 6 N sodium hydroxide solution decomposed the sample for analysis with the precipation of red mercuric sulfide. Then the addition of freshly prepared ammonium sulfide dissolved the residual mercuric sulfide completely according to the following equation (14)

$$HgS + Na_2S \longrightarrow Hg(SNa)_2$$

This method of solution was adopted in all analyses for the estimation of mercury in the mercury thiocarbonates.

The subsequent procedure, following the complete solution of the sample as described above, necessitates the complete precipitation and weighing of mercury as mercuric sulfide. The precipitation may be accomplished by the addition of ammonium nitrate as described by Treadwell and Hall (14) ~~(V.2, 169)~~ and Whitmore (15), involving the reaction:

$$Hg(SNa)_2 + 2NH_4NO_3 \longrightarrow HgS + (NH_4)_2S + 2NaNO_3$$

Approximately 0.2 gram samples for analysis were accurately weighed into 400 c.c. beakers and dissolved by the addition of 10 to 15 c.c. of freshly prepared 6 N sodium hydroxide solution followed by 15 to 20 c.c. of freshly prepared ammonium sulfide solution. The contents of the beakers were heated and stirred until solution was complete. The solutions were then diluted to 200 c.c. with water and 5 grams of ammonium nitrate for each 0.1 gram of sample were added. Mercuric sulfide precipitated at once. To insure complete precipitation and to facilitate subsequent filtration, the contents of the beakers were held at a temperature just under boiling for at least 8 hours. Water was added as needed to maintain a volume of 200 c.c. As suggested by Whitmore (loc.cit.) the beakers were then allowed to remain undisturbed for at least 12 hours prior to filtration through a weighed Gooch crucible which contained a heavy mat of asbestos. The precipitates were washed repeatedly with hot water to which had been added 1 c.c. of 6 N nitric acid per 100 c.c. of water. The precipitate then did not run through the asbestos mat. After a final washing with cold water and ethyl alcohol, the crucibles were first dried by suction and then in an oven at 110 degrees C. From the weight of mercuric sulfide found, the percentage of mercury in the thiocarbonic ester was calculated.

It may be noted that Whitmore (15) by use of a Carius tube for dissolving the sample then neutralizing the resulting acid solution with sodium bicarbonate and precipitating mercuric sulfide by one precipitation with ammonium sulfide reports "almost no free sulfur." Other authors (14,16) report the frequent occurrence of the contaminating sulfur, and suggest its removal by extraction with boiling carbon bisulfide.

It is significant that free sulfur was not present when the method described above was used. This was evident when the mercuric sulfide was dissolved by hydriodic acid solution and the crucible reweighed according to the latest method of Coley and Burford (17). No free sulfur was found in the crucible.

(c) Quantitative determination of sulfur in the mercury ethyl thiocarbonate

The use of the Parr peroxide bomb for this determination proved to be the most convenient method. A search of the literature upon this determination provided a wealth of data (18, 19, 20). The following method was adopted as most suitable.

Approximately 0.5 gram samples were weighed into the bomb, followed by the addition of 12 grams of sodium peroxide. After vigorous shaking of the mixture the bomb was fired in the usual manner, cooled, the contents removed by washing thoroughly with water, and then acidified with hydrochloric acid. Iron from the bomb was reduced by the addition of aluminum powder as suggested by Allen and Bishop (21) and mercury was thereby displaced from solution at the same time. The contents of the beaker were then filtered into a one liter beaker, diluted to 800 c.c. and barium sulfate precipitated by the drop-wise addition of a 5% barium chloride solution. Filtration was not attempted until the beaker and contents had stood at least 12 hours. Filtration, drying and weighing of the barium sulfate were carried out in the usual manner and the percentage of sulfur in the mercury ethyl thiocarbonate calculated from the weight of barium sulfate found.

(d) Quantitative determination of mercury in the mercuric sulfide-mercuric oxide reaction residue.

The method of the estimation of the mercury in the black reaction residues which were apparently mixtures of mercuric sulfide and oxide necessitated a different procedure for effecting solution of the samples for analysis. Approximately 0.5 gram samples were accurately weighed into beakers and 10 c.c. of concentrated nitric acid followed by 5 c.c. of concentrated hydrochloric acid were added. The contents of the beakers were heated and stirred until reaction had ceased. Then 1 to 2 c.c. of bromine were added. The samples dissolved rapidly and completely. The solutions were then gently heated until the excess bromine had evaporated and water was added to increase the volumes to 200 c.c. The solutions were gently boiled until colorless, then almost neutralized with sodium carbonate. Addition of ammonium sulfide precipitated mercuric sulfide which was filtered and weighed in Gooch crucibles. The percentages of mercury in the reaction residues were then calculated from the weight of mercuric sulfide found.

(e) Quantitative determination of sulfur in the reaction residues

The samples for analyses were dissolved exactly as described under the mercury estimation. The acid solution was then carefully neutralized with sodium carbonate and again made acid with hydrochloric acid. Barium sulfate was precipitated as described in the determination of sulfur in the thiocarbonate and the percentage of sulfur in the reaction residue calculated from the weight of barium sulfate found.

(f) Estimation of carbon monoxide evolved in ethyl formate reactions

It was deemed advisable, if possible, to estimate quantitatively the carbon monoxide evolved during the course of the reaction of ethyl formate with mercuric oxide and carbon bisulfide. The checking of such determinations would serve to measure the extent of the occurrence of the reaction proposed for the formation of the mercury thiocarbonic esters represented by the proposed equation:

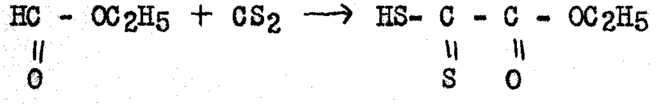
$$2CS_2 + 2HCOOC_2H_5 + 3HgO \longrightarrow Hg(SCOOC_2H_5)_2 + 2HgS + 2CO + H_2O$$

The method of Nicloux (22) was used. The procedure, in essence, consists in the reduction of iodine pentoxide by carbon monoxide at 120 degrees to 150 degrees C as noted in the following equation:

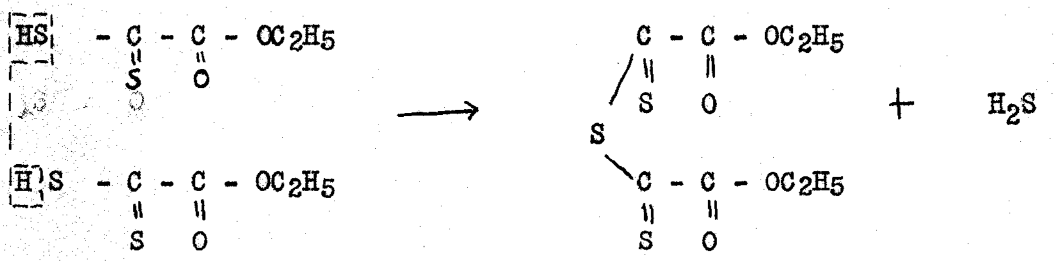
$$5CO + I_2O_5 \longrightarrow 5CO_2 + I_2$$

The standard determination involves the estimation of the iodine liberated. In this work, however, the loss in weight of the iodine pentoxide was used to measure the quantity of carbon monoxide formed.

The removal of interfering vapors of carbon bisulfide, ethyl formate and the gas, hydrogen sulfide, which was also liberated, constituted a serious problem. The formation of hydrogen sulfide may be due to some assumed secondary reaction, probably involving the following changes:



$$\underset{\overset{\|}{O}}{HC} - OC_2H_5 + CS_2 \longrightarrow HS-\underset{\overset{\|}{S}}{C} - \underset{\overset{\|}{O}}{C} - OC_2H_5 \qquad (a)$$



(b)

(a),(b). $2HCOOC_2H_5 + 2CS_2 \longrightarrow H_2S + (CSCOOC_2H_5)_2S$

That the reaction probably does occur and that the compound noted in (b) is unstable, is indicated by the formation of hydrogen sulfide when pyridine was used instead of mercuric oxide but no other compound was found as noted in the introductory section.

The most satisfactory method for eliminating reducing gases other than carbon monoxide has been developed by C. R. Hoover (23) who passed a mixture of gases through activated cocoanut charcoal. All reducing gases except carbon monoxide were absorbed.

In this investigation, cocoanut charcoal in lumps the size of peas was reactivated by heating in a flask while suction was applied.

The method of adsorption of the gases finally decided upon was as follows: the gases were conducted from the top of the reflux condenser through a 10 centimeter U tube filled with calcium chloride, then through charcoal in two 25 centimeter U tubes and finally through iodine pentoxide mixed with glass wool in 10 centimeter U tubes suspended in an oil bath maintained at a temperature of 140 degrees to 150 degrees C. Blank runs using all reagents except mercuric oxide and emulating the same conditions of refluxing and stirring gave no indication of liberated iodine.

The tubes containing the iodine pentoxide were fitted with glass stoppers which were sealed with Plaster of Paris and sodium silicate. The tubes were weighed before and after a reaction, the decrease in weight representing the amount of iodine pentoxide decomposed by carbon monoxide liberated in the reaction. At the end of a run the iodine was swept out by a stream of nitrogen, the tubes then removed and wiped free of oil. The weight of the carbon monoxide was then calculated from the equation:

$$I_2O_5 + 5CO \longrightarrow 5CO_2 + I_2$$

The bearing of the carbon monoxide determination on the reaction is discussed in a later section.

(G) Molecular weight determination: mercury ethyl thiocarbonate

As a check on the proposed constitution of the product it was decided to cryoscopically determine the molecular weight. Benzene, in which the compound is very soluble, was used as the solvent.

Approximately 0.5 gram samples were dissolved in 13 to 16 grams of benzene and the lowering of the freezing point noted as outlined in the standard procedure of Daniels, Mathews and Williams (24). The molecular weight of mercury ethyl thiocarbonate was then calculated. The data and calculations are embodied in the following table.

TABLE I

Mercury ethyl thiocarbonate g.	Benzene g.	Freezing Point Lowering Degrees C	Molecular weight found	Molecular weight calculated
0.4988	17.300	.367	402.3	410.7
0.6068	16.665	.446	418.0	410.7
0.7104	16.099	.543	416.1	410.7
			412.1 Av.	

The molecular weight of mercury ethyl thiocarbonate is 410.7. The average of the molecular weight determinations made is 412.1, an acceptable experimental error of less than 1% deviation from the theoretical.

The following summary of the analytical data upon the mercury and sulfur determinations establishes the empirical composition of the mercury ethyl thiocarbonate.

TABLE II

Mercury: mercury ethyl thiocarbonate

Mercury ethyl thiocarbonate g.	HgS found g.	Hg found %	Hg theory %
0.3104	0.1735	48.18	48.88
0.2547	0.1420	48.08	48.88
0.1844	0.1036	48.45	48.88
0.1627	0.0925	49.04	48.88
		48.44 Av.	

TABLE III

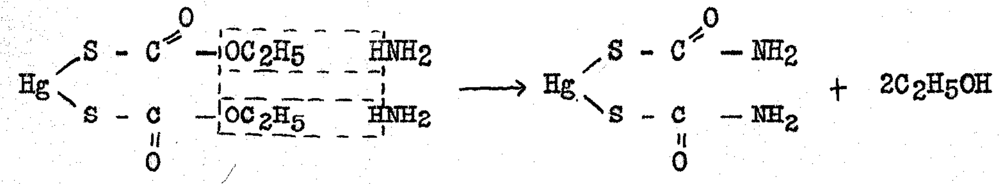
Sulfur: mercury ethyl thiocarbonate

Mercury ethyl thiocarbonate g.	$BaSO_4$ found g.	S found %	S theory %
0.8713	0.9814	15.45	15.59
0.3167	0.3614	15.63	15.59
0.4212	0.4744	15.44	15.59
0.8102	0.9183	15.53	15.59
		15.51 Av.	

The percentages of mercury and sulfur found are practically identical with the calculated percentages of mercury and sulfur in mercury ethyl thiocarbonate and accordingly confirm the formula for same as developed through the equations in the reaction mechanism scheme proposed for its synthesis.

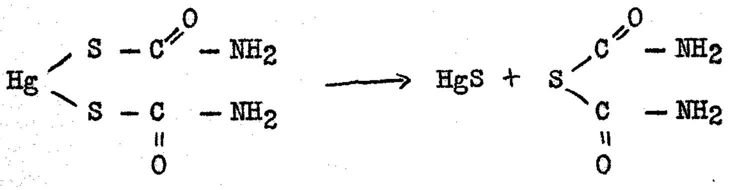
(h) Reaction of mercury ethyl thiocarbonate with ammonia

Granting the compound to be an ethyl ester, its reaction with ammonia would be expected to yield an amide in conformity with the following equation (a):



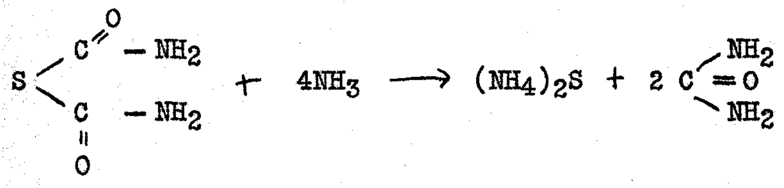
(a)

Since treatment of this compound with ammonia gave an abundant precipitation of mercuric sulfide, its formation may be represented by equation (b) in which a thioamide is also formed.



(b)

Further reaction of the thioamide compound with ammonia would yield ammonium sulfide and urea according to equation (c):



(c)

The summation of equations (a), (b), and (c) follows:

$$\left\{ \text{(a), (b), (c).} \quad Hg(SCOOC_2H_5)_2 + 6NH_3 \longrightarrow 2C_2H_5OH + HgS + 2CO(NH_2)_2 + (NH_4)_2S \right. \qquad \text{(C)}$$

The experimental confirmation of the reaction as reported in the above derived summation equation was accomplished as follows.

Two samples of the thiocarbonate were suspended in water saturated with ammonia. The container was stoppered and vigorously shaken. The suspension turned yellow after a few minutes, then black after a few hours. After standing for several days with occasional shaking, brilliant red crystals had formed and the supernatant liquid had become perfectly clear. The crystalline product was filtered off and weighed. Part of the filtrate was evaporated to dryness leaving a white product which was recrystallized from alcohol. A subsequent melting point and biuret test on the product indicated urea. The red crystals, upon analysis, proved to be the red modification of mercuric sulfide. Ethyl alcohol was detected in the filtrate by the iodoform test. When another portion of the filtrate was boiled, hydrogen sulfide, evidently due to the decomposition of ammonium sulfide, was detected.

The data obtained is summarized in the following table.

TABLE IV

Mercuric sulfide: interaction of mercury ethyl thiocarbonate with ammonia

Mercury ethyl thiocarbonate g.	HgS found g.	HgS theory g.
1.4899	0.8477	0.8439
1.7790	1.0163	1.0080

The weights of the mercuric sulfide obtained agree closely with the weights calculated and, in conjunction with the qualitative detection of urea, ethyl alcohol and ammonium sulfide confirm the reaction mechanism scheme as summarized in equation C. Furthermore this reaction substantiated the structure of the compound as developed in the reaction mechanism scheme proposed for the synthesis of mercury ethyl thiocarbonate.

(i) Observations upon the formation of carbon monoxide

Unfortunately the quantity of carbon monoxide calculated from the weight of iodine pentoxide decomposed as previously described did not check the weight of mercury ethyl thiocarbonate obtained in the same reaction as based upon the proposed equation

$$2HCOOC_2H_5 + 2CS_2 + 3HgO \longrightarrow Hg(SCOOC_2H_5)_2 + 2CO + 2HgS + H_2O$$

which requires that the mercury ethyl thiocarbonate and the carbon monoxide formed should be in the ratio of 1:2 respectively. It is possible that the charcoal used to absorb hydrogen sulfide, carbon bisulfide and ethyl formate present in the gas stream, also absorbed some carbon monoxide thus giving rise to low results. Alcohol-water solutions and aniline, substituted for the charcoal, proved ineffective as absorbing agents.

The theoretical quantity of mercury ethyl thiocarbonate formed in the course of the reaction was calculated from the weight of carbon monoxide equivalent to the iodine pentoxide decomposed. The following table summarizes the data obtained.

TABLE V

Carbon monoxide: mercury ethyl thiocarbonate

Weight I_2O_5 decomposed g.	CO calculated g.	$Hg(SCOOC_2H_5)_2$ found g.	$Hg(SCOOC_2H_5)_2$ calculated CO g.
0.386	0.213	5.3	1.56
0.323	0.178	4.7	1.31
0.256	0.141	2.3	1.03
0.218	0.120	2.0	0.88

Since the yields of mercury ethyl thiocarbonate are much in excess of the yields of carbon monoxide, in terms of the proposed reaction, it is evident that the quantity of carbon monoxide found is not sufficient to confirm the occurrence of the proposed reaction quantitatively. The detection of carbon monoxide evolved during the course of the reaction verifies only qualitatively the reaction mechanism scheme proposed for the synthesis of mercury ethyl thiocarbonate.

B. Methyl Formate

(a) Experimental procedure:

The study of the interaction of methyl formate with mercuric oxide and carbon bisulfide followed exactly the procedure described in Part A. Two moles of Eastman's methyl formate (boiling point 31.5 to 32 degrees C) were refluxed and stirred with 0.5 mole of mercuric oxide and 200 c.c. (3.3 moles) of carbon bisulfide. Darkening of the mercuric oxide, due to the formation of black mercuric sulfide, was noted after 4 hours, and after 25 hours the solid phase was completely black — no particles of mercuric oxide being revealed by microscopic examination.

Upon completion of a run, as determined by no further evolution of gas, the mixture was filtered and the filtrate evaporated to 100 c.c. Yellow white crystals were thus obtained which, after repeated crystallizations, formed white glistening plates melting at 93 to 93.5 degrees C. The crystalline compound, like the ethyl homolog, was readily soluble in methyl and ethyl alcohols, ether, chloroform, and carbon bisulfide. Exposure to moist air caused the crystals to show a dark superficial layer, apparently mercuric sulfide.

Four duplicate runs were made with the purpose first to estimate carbon monoxide formed in the course of the reaction and second to increase yields of the mercury methyl thiocarbonate.

(b) Summary of analytical data upon mercury methyl thiocarbonate: mercury and sulfur.

The following summary of the analytical data upon mercury and sulfur determinations obtained in the same manner as described in

Part A, establishes the empirical composition of the mercury methyl thiocarbonate.

TABLE VI

Mercury: mercury methyl thiocarbonate

Mercury methyl thiocarbonate g.	HgS found g.	Hg found %	Hg theory %
0.3186	0.1938	52.47	52.46
0.1959	0.1195	52.61	52.46
		52.54 Av.	

TABLE VII

Sulfur: mercury methyl thiocarbonate

Mercury methyl thiocarbonate g.	$BaSO_4$ found g.	S found %	S theory %
0.2629	0.3212	16.75	16.74
0.2667	0.3254	16.73	16.74
		16.74 Av.	

The percentages of mercury and sulfur found are practically identical with the calculated percentages of mercury and sulfur in mercury methyl thiocarbonate and accordingly confirm the formula for same as developed through the equations in the reaction mechanism scheme proposed for its synthesis.

(c) Reaction of mercury methyl thiocarbonate with ammonia.

The same procedure was followed in the study of the interaction of mercury methyl carbonate with ammonia as described in experimental part A. Weighed samples ofthe compound were suspended in water saturated with ammonia. After three days the red mercuric sulfide which had precipitated was filtered off and weighed. Methyl alcohol, urea and ammonium sulfide were detected in the filtrate.

The reaction is represented by the following equation:

$$Hg(SCOOCH_3)_2 + 6NH_3 \longrightarrow 2CH_3OH + HgS + 2(NH_2)_2CO + (NH_4)_2S$$

The data obtained is summarized in the following table.

TABLE VIII

Mercuric sulfide: interaction of mercury methyl thiocarbonate with ammonia.

Mercury methyl thiocarbonate g.	HgS found g.	HgS theory g.
1.0188	0.6188	0.6179
0.6676	0.4051	0.4050

The weights of mercuric sulfide obtained are practically identical with the weights calculated and, in conjunction with the qualitative detection of urea, methyl alcohol and ammonium sulfide confirm the reaction as summarized in the above equation. Furthermore this reaction substantiates the structure of the compound as developed in the reaction mechanism scheme proposed for the synthesis of mercury methyl thiocarbonate.

(d) Observations upon the formation of carbon monoxide.

An attempt to quantitatively determine carbon monoxide formed during the course of the reaction of methyl formate with mercuric oxide and carbon bisulfide gave anomalous results similar to those noted in part A with ethyl formate. The theoretical quantity of mercury methyl thiocarbonate formed in the course of the reaction was calculated from the weight of the carbon monoxide formed in accordance with the following equation.

$$2HCOOCH_3 + 2CS_2 + 3HgO \longrightarrow Hg(SCOOCH_3)_2 + 2CO + 2HgS + H_2O$$

The following table summarizes the data obtained.

TABLE IX

Weight I_2O_5 decomposed g.	CO calculated g.	$Hg(SCOOCH_3)_2$ found g.	$Hg(SCOOCH_3)_2$ calculated CO g.
.700	0.386	2.5	2.64
.328	0.181	2.0	1.24

The yields of mercury methyl thiocarbonate do not agree closely enough with the yields of carbon monoxide in terms of the proposed reaction to confirm the occurrence of the reaction quantitatively. They approach the theoretical values, however, and thus they qualitatively check the reaction and verify the reaction mechanism scheme proposed for the synthesis of mercury methyl thiocarbonate.

C. Ethyl Acetate

(a) Experimental Procedure

The study of the interaction of ethyl acetate with mercuric oxide and carbon bisulfide followed essentially the procedure described in part A except that a gas absorbing train for the purpose of collecting carbon dioxide formed in the course of the reaction was included in the set-up. Two moles of Eastman's ethyl acetate (boiling point 76 to 77 degrees C) were refluxed and stirred with 0.5 mole of mercuric oxide and 200 c.c. (3.3 moles) of carbon bisulfide. Darkening of the mercuric oxide was noted after four hours and after 30 hours no particles of mercuric oxide were revealed by microscopic examination.

Upon completion of a run the black reaction residue was filtered off and the filtrate evaporated to 100 c.c. A finely divided brown solid and a yellow oil appeared when the filtrate was further evaporated at room temperature. After standing for several hours the oil partly crystallized forming light brown leaflets and a considerable quantity of an oily gum. The crystals were dissolved by the addition of alcohol and separated from the gum by filtration. Addition of water to the filtrate reprecipitated the brown white crystals which, after several crystallizations, were found to melt at 61.1 - 61.4 degrees C.

(b) Quantitative estimation of mercury and sulfur

Extremely low yields of the product, tentatively assumed to be mercury thiobutyrate in accordance with the reaction mechanism scheme proposed in the theoretical section, limited the number of analyses in the procedure for the quantitative estimation of mercury and sulfur. A summary of the data obtained in the same manner as described in part A is embodied in the following tables.

TABLE X

Mercury: mercury thiobutyrate

Mercury thiobutyrate g.	HgS found g.	Hg found g.	Hg theory g.
0.2009	0.1150	49.38	49.32
0.2033	0.1159	49.17	49.32
		49.28 Av.	

TABLE XI

Mercury thiobutyrate	$BaSO_4$ found	S found	S theory
0.2815	0.2998	14.60	15.73
0.2283	0.2446	14.69	15.73
		14.65 Av.	

The percentages of mercury found are practically identical with the percentages of mercury in mercury thiobutyrate. The percentages of sulfur found, however, do not check closely enough the percentage of sulfur in mercury thiobutyrate. Due to low yields of the product and the lack of time to determine the conditions necessary to increase the yields, further analyses were not made.

(c) Observations upon the formation of carbon dioxide

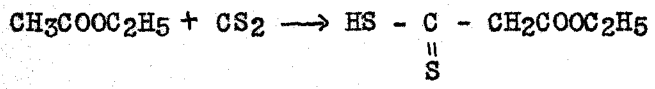
Since carbon dioxide was formed in the course of the reaction it was deemed advisable to quantitatively determine if possible the amount of this gas produced. Checking of these determinations would serve to measure the occurrence of the reaction proposed for the formation of mercury thiobutyrate as represented by the proposed equation:

$$2CS_2 + 2CH_3COOC_2H_5 + 3HgO \longrightarrow Hg(SCOC_3H_7)_2 + 2HgS + 2CO_2 + H_2O.$$

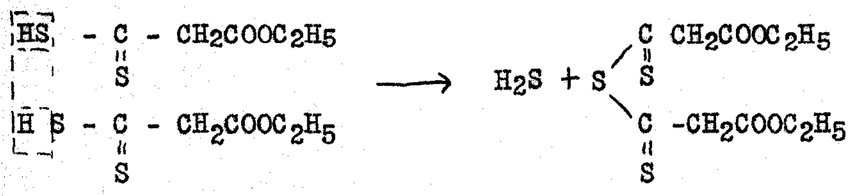
The following procedure was followed.

Vapors of carbon bisulfide and ethyl acetate were first removed by conducting the gas stream through a Milliken gas washing bottle containing 200 cc. of a 60% by volume alcohol in water solution. It was experimentally determined that this solution dissolved 30 c.c. of carbon bisulfide and 20 c.c. of ethyl formate. Carbon dioxide is reported to be much less soluble in an aqueous alcohol solution than in either pure alcohol of water. (25)

Hydrogen sulfide formed in the course of the reaction may be accounted for by some assumed secondary reaction possibly involving the following changes:



$$CH_3COOC_2H_5 + CS_2 \longrightarrow HS - \underset{\overset{\|}{S}}{C} - CH_2COOC_2H_5 \qquad (a)$$



(b)

$$\left\{ (a),(b). \quad 2CH_3COOC_2H_5 + 2CS_2 \longrightarrow H_2S + S(CSCH_2COOC_2H_5)_2 \right.$$

The second product in equation (b) above is probably unstable as was discussed in the introductory section.

The hydrogen sulfide was removed by passing the gas mixture through an aqueous solution of silver nitrate (50 grams of $AgNO_3$ per liter) acidified with nitric acid, according to the method of Perillon (26). The gas was then passed through calcium chloride saturated with carbon dioxide and finally through Linter bottles filled with Ascarite which absorbed the carbon dioxide. The Ascarite bottles were weighed before and after reaction, the difference in weights representing the amount of carbon dioxide absorbed.

The theoretical quantity of mercury thiobutyrate formed in the course of the reaction was calculated from the weight of carbon dioxide produced in accordance with the equation proposed for their syntheses.

The following table summarizes the data obtained.

TABLE XII

Carbon dioxide found g.	Mercury thiobutyrate found g.	Mercury thiobutyrate calculated carbon dioxide g.
0.156	1.2	0.72
0.153	1.2	0.71
0.177	2.8	0.82
0.166	2.5	0.77

The actual yields of the product tentatively assumed to be mercury thiobutyrate, do not check the yields of carbon dioxide in terms of the proposed reaction. The qualitative detection of carbon dioxide however indicates the plausibility of the assumption but further investigations must be made to confirm the proposed reaction mechanism scheme for the synthesis of mercury thiobutyrate.

D. Methyl Acetate

(a) Experimental Procedure

In every respect the study of the interaction of methyl acetate with mercuric oxide and carbon bisulfide followed the procedure described in part C. Two moles of methyl acetate (boiling point 56 to 57 degrees C) were refluxed and stirred with 0.5 mole of mercuric oxide and 200 c.c. (3.3 mole) of carbon bisulfide. Darkening of the mercuric oxide was noted in less than 1 hour and after 17 hours the reaction residue had formed a hard brown cake which was broken up before stirring was resumed. The residue soon hardened again and it was deemed advisable to stop the reaction and filter off the residue. The cloudy brown filtrate upon evaporation yielded a brown oil which was partly soluble in alcohol. The residue dissolved in chloroform but did not crystallize upon evaporation of the solvent. White crystals were obtained when the alcoholic solution was diluted with water.

The yield was less than 1 gram. After a second crystallization the product was found to melt at 89 to 90 degrees C. Time was available for only one other run and the yields obtained were also very small.

(b) Quantitative estimation of mercury and sulfur

The quantitative estimations of mercury and sulfur in the product, tentatively assumed to be mercury thiopropionate formed in accordance with the reaction mechanism scheme proposed for its synthesis in the theoretical section, were carried out as described in part A. The data obtained is summarized in the following tables.

TABLE XIII

Mercury thiopropionate g.	HgS found g.	Hg found %	Hg theory %
0.1241	0.0757	52.60	52.97
0.1442	0.0870	52.02	52.97
		52.31 Av.	

TABLE XIV

Mercury thiopropionate g.	$BaSO_4$ found g.	S found %	S theory %
0.0627	0.0765	16.73	16.90
0.0913	0.1090	16.36	16.90
		16.55 Av.	

The percentages of mercury and sulfur found are in close agreement with the theoretical percentages of these elements in mercury thiopropionate. Low yields of the product made it imperative to use small samples for the analyses and this may account for the slightly lower results obtained.

(c) Observations upon the formation of carbon dioxide

The procedure described in part C for the collection of carbon dioxide was followed in an attempt to obtain quantitative confirmation of the proposed reaction mechanism scheme for the formation of mercury thiopropionate as represented by the following equation:

$$2CS_2 + 2CH_3COOCH_3 + 3HgO \longrightarrow Hg(SCOC_2H_5)_2 + 2HgS + 2CO_2 + H_2O$$

The theoretical quantity of mercury thiopropionate was calculated from the weight of carbon dioxide produced in accordance with the above equation. The following table embodies the data obtained.

TABLE XV

Carbon dioxide found g.	Mercury thiopropionate found g.	Mercury thiopropionate calculated carbon dioxide g.
.302	0.37	1.29
.168	0.22	0.73

The actual yields of the product, tentatively assumed to be mercury thiopropionate, do not quantitatively check the amounts of carbon dioxide found. The qualitative detection of carbon dioxide, however, does indicate the possibility of the occurrence of the proposed reaction mechanism scheme for the synthesis of mercury thiopropionate. The low yields of mercury thiopropionate signifies the occurrence of other reactions, the nature of which call for further extended study.

SUMMARY OF YIELDS

A. Mercury ethyl thiocarbonate

Yield found g.	Theory %
15	22
16	23
12	18
17	25
11	16
13	18

B. Mercury methyl thiocarbonate

3.2	5.0
2.1	3.2
4.0	6.3
4.3	6.8

C. Mercury thiobutyrate

1.5	2.4
2.0	3.2
2.8	4.1
2.3	3.4

D. Mercury thiopropionate

0.4	0.6
0.2	0.3
1.2	1.9
1.2	1.9

GENERAL SUMMARY AND CONCLUSIONS

1. The interaction of mercuric oxide with methyl and ethyl formates in carbon bisulfide solution have led to original syntheses of two compounds: mercury ethyl thiocarbonate and mercury methyl thiocarbonate. The former has been prepared previously by an entirely different method. The latter is not recorded in the literature.

2. A reaction mechanism scheme has been proposed to account for the formation of these compounds.

3. Study of the reactions of each of these compounds with aqueous ammonia has given products which (a) permit the writing of an equation involved for the reaction with ammonia, (b) afford proof for the structural formula proposed for these compounds and, (c) confirm quantitatively the equation for the interaction with ammonia.

4. The interaction of mercuric oxide with methyl and ethyl acetates in carbon bisulfide solution gave low yields of compounds quite analogous in composition to the mercury thiocarbonates noted in (1), their formation being accounted for by parallel equations for the reactions involved.

5. Modifications of and marked improvements on the quantitative estimation of mercury in organic compounds have been developed and applied.

6. Extents of the occurrence of the proposed reactions were in no case sufficient to establish complete stoichiometrical ratios between the interacting substances and the yields of the products formed.

7. It has been found that mercury thiocarbonates are apparently formed when mercuric acetate reacts with these simple esters in carbon bisulfide solution. This observation suggests further researches pertinent to the character of these reactions.

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