fied with inactive inosite, has never been spoken of as "a bios." It is one of the constituents into which Lucas separated Wildiers' bios; by itself it has little if any effect on the yeast crop; but if the other constituent, namely, "Bios II," be present in the culture medium, addition of inosite much increases the crop. As to the inosite from tea, Miss Eastcott's paper, J. Phys. Chem., 32, 1094 (1928), states that it was recrystallized from methyl alcohol and water and obtained in two "clear white" crystalline forms, anhydrous and the dihydrate, both of which were analyzed; also that it made no difference in the yeast crops obtained with various preparations of Bios II whether Kahlbaum's inosite was employed or that from tea. Her laboratory note-books show that the last six recrystallizations had no effect on the "activity" of the latter.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

## INTERACTION OF ALKYL SULFIDES AND SALTS OF MERCURY

By W. F. FARAGHER, J. C. MORRELL AND S. COMAY Received January 10, 1929 Published September 5, 1929

The property of organic sulfides of forming compounds with certain heavy metal salts was discovered by Loir.<sup>1</sup> He prepared compounds of methyl and ethyl sulfides with mercuric chloride, mercuric iodide and platinum chloride.

Some of the results reported by Loir were criticized by subsequent investigators. Blomstrand<sup>2</sup> found the properties of the product formed by the interaction of ethyl sulfide and platinic chloride to be different from those reported by Loir: the melting point was 70° higher. Abel,<sup>8</sup> who discovered ethyl sulfide in dog's urine, contested the originally reported melting point of the compound of ethyl sulfide and mercuric chloride.

Phillips<sup>4</sup> disputed the formula assigned by Loir to the reaction product of methyl sulfide and mercuric chloride. He found that the compound was  $3HgCl_2 \cdot 2(CH_3)_2S$  and not  $(CH_3)_2S \cdot HgCl_2$ , as stated by Loir. The reason for the conflict between reports is presented in this paper.

The compounds of alkyl sulfides and salts of platinum were quite extensively investigated by Blomstrand,<sup>2</sup> Blomstrand and his co-workers,<sup>5</sup> Klason<sup>6</sup> and Rây.<sup>7</sup>

On the other hand, the literature contains little information about the compounds of alkyl sulfides and salts of mercury. Smiles<sup>8</sup> reported the preparation of five addition compounds of alkyl sulfides and mercuric iodide:  $(CH_3)_2S \cdot HgI_2$ ,  $(CH_3SC_2H_5) \cdot HgI_2$ ,  $(C_2H_5)_2S \cdot HgI_2$ ,  $(C_5H_{11})_2S \cdot HgI_2$  and  $(C_6H_5CH_2)_2S \cdot HgI_2$ .

- <sup>1</sup> Loir, Ann., 87, 369 (1853).
- <sup>2</sup> Blomstrand, J. prakt. Chem. [2] 27, 190 (1883).
- <sup>3</sup> Abel, Z. physiol. Chem. (Hoppe-Seyler) 20, 269 (1895).
- <sup>4</sup> Phillips, This Journal, 23, 254 (1901).
- <sup>5</sup> Blomstrand and others, J. prakt. Chem., [2] 38, 353 (1888).
- <sup>6</sup> Klason, Ber., 28, 1493 (1895).
- <sup>7</sup> Rây, Quart. J. Indian Chem. Soc., 2, 178 (1925).
- <sup>8</sup> Smiles, J. Chem. Soc., 77, 163 (1900).

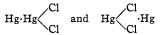
Faragher, Morrell and Monroe<sup>9</sup> found that alkyl and aromatic sulfides react quantitatively with powdered "normal" mercurous nitrate,  $Hg_2$ - $(NO_8)_2 \cdot 2H_2O$ . No analysis of the products or description of the reaction was given by them since this problem was outside the scope of their work.

It was first observed in the present work that metallic mercury is formed when an alkyl sulfide reacts with a mercurous salt, *e. g.*, mercurous nitrate. The reaction is shown by the equation

 $2R_2S + Hg_2(NO_3)_2 \longrightarrow (R_2S)_2 Hg(NO_3)_2 + Hg + heat$ 

The behavior of ethyl sulfide and other organic sulfides toward the mercurous salts used was found to be analogous to the behavior of pyridine toward mercurous salts. Lang<sup>10</sup> found that metallic mercury is precipitated at once when mercurous nitrate is treated with pyridine. The mercuric nitrate formed reacts with the pyridine to give the compound  $(C_{b}H_{5}N)_{2}$ ·Hg $(NO_{3})_{2}$ . No quantitative results were reported. François<sup>11</sup> investigated quantitatively the action of aniline, phenol and alcohol on mercurous iodide at an elevated temperature and found that the decomposition of mercurous iodide was in each case limited. Lang explains the mechanism of the change by the assumption, "A state of equilibrium exists in the solution of the mercurous salt dissociated partially into mercury and mercuric salt, the number of molecules decomposing and reforming in unit time being equal; but if the equilibrium is destroyed by the removal of the mercuric salt by pyridine, etc., metallic mercury separates."

Werner<sup>12</sup> in discussing the constitution of the mercurous salts considers that Lang's discovery that pyridine rapidly decomposes mercurous chloride into mercury and mercuric chloride is not in accord with the formula for mercurous chloride, Cl-Hg-Hg-Cl. He says: "This behavior of mercurous chloride seems to indicate that it is an addition product of mercury and mercuric chloride, and mercury, like water, is capable of forming addition compounds; the amalgams correspond to the hydrates as was shown in such an excellent way by Förster." Accordingly, Werner proposed either of the following two formulas for mercurous chloride



Although pyridine reacts rapidly with solid mercurous chloride, ethyl sulfide does not react, and methyl sulfide causes the formation of metallic mercury from mercurous chloride only in the presence of water. It will be shown that it cannot be predicted that because a substance reacts readily with a mercuric salt it will react with the corresponding mercurous salt; the specific reactivity of each of the reacting substances cannot be ignored.

<sup>&</sup>lt;sup>9</sup> Faragher, Morrell and Monroe, J. Ind. Eng. Chem., 19, 1283 (1927).

<sup>&</sup>lt;sup>10</sup> Lang, Ber., 21, 1587 (1888).

<sup>&</sup>lt;sup>11</sup> François, Compt. rend., 121, 253, 700, 880 (1895).

<sup>&</sup>lt;sup>12</sup> Werner, Z. anorg. Chem., 15, 5 (1897).

Usually some members in the series of alkyl sulfides are more reactive than others toward a particular mercurous salt. In some cases the solvent is an important factor. Methyl sulfide, as previously stated, does not react with mercurous chloride unless water is present; but it reacts with mercurous acetate in the absence of water. Ethyl sulfide and the other alkyl sulfides used in this investigation caused mercury to separate from mercurous acetate only in the presence of water. Thiophene does not react with powdered "normal" mercurous nitrate, but if water is added, mercury is precipitated. Methyl sulfide, ethyl sulfide and iso-amyl sulfide separate mercury immediately from mercurous sulfate in the absence of water. Although in some of the instances mentioned solubility may be the reason for the fact that the reaction proceeds only in the presence of water, nevertheless in the case of methyl sulfide and mercurous chloride, the compound formed is practically insoluble in water. Therefore, it is apparent that the mechanism of the reaction requires further investigation, especially when one recalls that pyridine separates mercury from solid mercurous chloride immediately and also that the sulfides separate mercury from mercurous iodide in the absence of water.

## Experimental

Action of Alkyl Sulfides on Mercurous Salts. Ethyl Sulfide and  $Hg_2(NO_3)_2 \cdot 2H_2O$ .—Analysis of the products of the interaction of ethyl sulfide and mercurous nitrate showed that the reaction is represented by  $2Et_2S + Hg_2(NO_3)_2 \longrightarrow (Et_2S)_2 \cdot Hg(NO_3)_2 + Hg$ 

This was shown as follows: 180 cc. of an 8% aqueous solution of mercurous nitrate (0.5% of nitric acid was added to keep the salt in solution) was treated with 2.27 g. of ethyl sulfide. The metallic mercury that separated weighed 2.51 g. or 99.6% of the theoretical weight.

When ethyl sulfide and powdered normal mercurous nitrate were used in molecular proportions, the amount of mercury weighed was 97 to 98% of the theoretical amount.

The compound,  $(Et_2S)_2 Hg(NO_3)_2$ , was isolated as follows. The sulfide was dissolved in hexane and treated with normal mercurous nitrate by shaking for five minutes. After standing for a few hours the hexane and the liquid reaction product were decanted from the mercury and the liquid product separated from the hexane. The sirupy reaction product was filtered twice to remove all traces of metallic mercury. The filtrate was placed under a vacuum of two cm. of mercury and after a few hours long white needles appeared. The needles were removed and kept under vacuum again for fifteen hours. They melted to a clear liquid at 63°. The crystals are very hygroscopic and if kept even for a short time in the open they absorb moisture from the air and become pasty.

Analysis of the dry crystals for mercury was made by treating them with a solution of sodium thiosulfate, using in excess of four moles to one mole of mercuric nitrate. The method of analysis was as follows. The weighed sample was added to 15 cc. of an 18% thiosulfate solution and allowed to boil for five to ten minutes. As soon as the addition compound is added even in the cold it dissociates into the organic and Sept., 1929

inorganic components; the odor of the sulfide is very pronounced. A concentrated solution of sodium sulfide was then added until an almost clear solution was obtained. If red or black mercuric sulfide was still left undissolved, the mixture was boiled until a complete solution was obtained. About 150 cc. of water and some solid ammonium nitrate crystals were added. The mixture was boiled for fifteen minutes and the precipitate collected in a Gooch crucible, washed and dried at  $120^{\circ}$  in the usual manner. This procedure was found to give accurate results when mercuric chloride was treated with sodium thiosulfate solution.

The reaction between solid sodium thiosulfate and mercuric chloride was investigated by Allen and Crenshaw. $^{13}$ 

The accuracy of the procedure adopted in this work can be seen from the following results: for 0.5000 g. of mercuric chloride, theory requires 0.4283 g. of mercuric sulfide. Found: 0.4270 and 4275 g.

When the black precipitate first formed on boiling 0.5000 g. of mercuric chloride with 1.828 g. of the thiosulfate in 15 cc. of water was weighed after washing and drying, the amounts of mercuric sulfide obtained were 0.3885 and 0.3883 g., respectively, approximately only 90% of the theoretical.

The crystals of the addition compound,  $(Et_2S)_2 Hg(NO_3)_2$ , were analyzed for mercury by the procedure just described and the percentage of mercury corresponded within experimental error to that required by the formula given.

Anal. Calcd.: Hg, 39.75. Found: Hg, 39.58, 39.45.

**Reaction** between Alkyl Sulfides and Mercurous Salts.—The following alkyl sulfides were tested qualitatively for their behavior toward various mercurous salts: methyl sulfide, ethyl sulfide, *n*-propyl sulfide, *n*-butyl sulfide, *iso*butyl sulfide and *iso*-amyl sulfide. The results obtained are given briefly.

(1) All alkyl sulfides precipitate mercury from powdered mercurous nitrate,  $Hg_2(NO_3)_2 \cdot 2H_2O$ , or aqueous solution of mercurous nitrate.

(2) Only methyl sulfide precipitates mercury from mercurous chloride and it does so only in the presence of water. The other alkyl sulfides seem to have no action on this mercurous salt even in the presence of water.

(3) Methyl sulfide precipitates mercury from mercurous acetate even when water is absent. The other sulfides react likewise but only in the presence of water.

(4) All the alkyl sulfides used react with mercurous sulfate even in the absence of water.

(5) All the sulfides precipitate mercury from mercurous iodide. Methyl, ethyl and *n*-propyl sulfides when used in excess give solutions and metallic mercury. The other sulfides give grayish precipitates which dissolve in benzene with the separation of mercury.

Alkyl Sulfides and Mercuric Salts.—Generally speaking, the addition compounds of alkyl sulfides with salts of oxy-acids are water-soluble compounds. This phenomenon is in agreement with the analogous finding of Blomstrand<sup>2</sup> that the compounds of ethyl sulfide and the platinum salts of oxy-acids (except the nitrite) are water soluble.

<sup>13</sup> Allen and Crenshaw, Am. J. Sci., [4] 34, 369 (1912).

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Interaction of Alkyl Sulfides and Mercuric Chloride.—Only the first two members in the series of the aliphatic sulfides had been investigated previously. The alkyl sulfides and mercuric chloride were found to give under different conditions two types of addition compounds for each sulfide, the types varying with the sulfide used. It was also found that Types 2 and 3 are in some cases easily converted into each other.

TABLE I PREPARATION, PROPERTIES AND ANALYTICAL DATA OF ADDITION COMPOUNDS OF ALKYL

Sulfides with Mercuric Chloride							
No.	Soln. of HgCl: in	Alkyl sulfide		Cryst. solvent		М. р., 9	°C.
1	Alcohol	Ethyl sulfide		Alcohol		76.5-77	
2	Alcohol	Ethyl sulfide		Bz or acetone		119 - 119.5	
3	Alcohol	n-Propyl sulfide		Alcohol		87.5-88	
4	Alcohol	n-Propyl sulfide		Benzene		121 - 122	
5	Alcohol	Isobutyl sulfide		Alcohol		116	
6	Alcohol	Isobutyl sulfide		Benzene		131	
7	Alc. or water	<i>n</i> -Butyl sulfide		Benzene		112-113	
8	Water	n-Butyl sulfide				Liquid	
9	Alc. or water	Iso-amyl sulfide		Benzene		• • • • • •	
10	Water	Iso-amyl sulf	ide			Liquid	
				——Analyse	s		
No.	Compound formed	Calcd. Hg	., % s	——Analyse E	Fou Ig	und,%	s
No. 1	Compound formed $(C_2H_5)_2S \cdot HgCl_2^a$	Calcd. Hg 55.47	<sup>., %</sup> s 9.19	н	Fou	-770	s 9.11
	•	_		н	Fou Ig 55.09	-770	
1	$(C_2H_5)_2S \cdot HgCl_2^a$	55.47	9.19	1 54.94 63.03	Fou Ig 55.09	8.99	9.11
1 2	$(C_2H_5)_2S \cdot HgCl_2^a$ $(C_2H_5)_2S \cdot 2HgCl_2^b$	55.47 $63.37$	9.19 5.05	1 54.94 63.03	Fou 1g 55.09 63.46 50.65	8.99 5.07 7.79	9.11
1 2 3	$(C_{2}H_{5})_{2}S \cdot HgCl_{2}^{a}$ $(C_{2}H_{5})_{2}S \cdot 2HgCl_{2}^{b}$ $(n-C_{3}H_{7})_{2}S \cdot HgCl_{2}^{c}$	$55.47 \\ 63.37 \\ 51.48$	$9.19 \\ 5.05 \\ 8.22$	154.94 63.03 50.42	Fou 1g 55.09 63.46 50.65	8.99 5.07 7.79	9.11 5.23 4.85
1 2 3 4	$\begin{array}{c} (C_{2}H_{\delta})_{2}S\cdot HgCl_{2}{}^{a} \\ (C_{2}H_{\delta})_{2}S\cdot 2HgCl_{2}{}^{b} \\ (n-C_{3}H_{7})_{2}S\cdot HgCl_{2}{}^{c} \\ (n-C_{3}H_{7})_{2}S\cdot 2HgCl_{2}{}^{d} \end{array}$	55.47 63.37 51.48 60.68	$9.19 \\ 5.05 \\ 8.22 \\ 4.84$	154.94 63.03 50.42 60.41	Fou Ig 55.09 63.46 50.65 60.91	8.99 5.07 7.79 4.80	9.11 5.23 4.85
1 2 3 4 5	$\begin{array}{l} (C_{2}H_{5})_{2}S\cdot HgCl_{2}{}^{a} \\ (C_{2}H_{5})_{2}S\cdot 2HgCl_{2}{}^{b} \\ (n-C_{3}H_{7})_{2}S\cdot HgCl_{2}{}^{c} \\ (n-C_{3}H_{7})_{2}S\cdot 2HgCl_{2}{}^{d} \\ (iso-C_{4}H_{9})_{2}S\cdot HgCl_{2}{}^{d} \end{array}$	55.47 63.37 51.48 60.68 48.04	9.19 5.05 8.22 4.84	14 54.94 63.03 50.42 60.41 47.81	Fou Ig 55.09 63.46 50.65 60.91 47.89	8.99 5.07 7.79 4.80	9.11 5.23 4.85
1 2 3 4 5 6	$\begin{array}{l} (C_{2}H_{5})_{2}S\cdot HgCl_{2}{}^{a} \\ (C_{2}H_{5})_{2}S\cdot 2HgCl_{2}{}^{b} \\ (n-C_{3}H_{7})_{2}S\cdot HgCl_{2}{}^{o} \\ (n-C_{3}H_{7})_{2}S\cdot 2HgCl_{2}{}^{d} \\ (iso-C_{4}H_{9})_{2}S\cdot HgCl_{2}{}^{d} \\ (iso-C_{4}H_{9})_{2}S\cdot 2HgCl_{2}{}^{f} \end{array}$	$55.47 \\ 63.37 \\ 51.48 \\ 60.68 \\ 48.04 \\ 58.21$	9.19 5.05 8.22 4.84 	$\begin{array}{c} 1 \\ 54.94 \\ 63.03 \\ 50.42 \\ 60.41 \\ 47.81 \\ 58.03 \end{array}$	Fou Ig 55.09 63.46 50.65 60.91 47.89 58.29	8.99 5.07 7.79 4.80	9.11 5.23 4.85
1 2 3 4 5 6 7	$\begin{array}{l} (C_{2}H_{5})_{2}S\cdot HgCl_{2}^{a} \\ (C_{2}H_{5})_{2}S\cdot 2HgCl_{2}^{b} \\ (n-C_{3}H_{7})_{2}S\cdot HgCl_{2}^{c} \\ (n-C_{4}H_{7})_{2}S\cdot 2HgCl_{2}^{d} \\ (iso-C_{4}H_{7})_{2}S\cdot 2HgCl_{2}^{d} \\ (iso-C_{4}H_{9})_{2}S\cdot 2HgCl_{2}^{f} \\ (n-C_{4}H_{9})_{2}S\cdot 2HgCl_{2}^{f} \\ (n-C_{4}H_{9})_{2}S\cdot 2HgCl_{2}^{g} \end{array}$	$55.47 \\ 63.37 \\ 51.48 \\ 60.68 \\ 48.04 \\ 58.21 \\ 58.21 \\ 35.37$	9.19 5.05 8.22 4.84  	$\begin{array}{c} & \\ 54.94 \\ 63.03 \\ 50.42 \\ 60.41 \\ 47.81 \\ 58.03 \\ 58.11 \end{array}$	Fou 1g 55.09 63.46 50.65 60.91 47.89 58.29 57.92	8.99 5.07 7.79 4.80	9.11 5.23 4.85

<sup>a</sup> White needles. If a large excess of  $HgCl_2$  is used or if the product is recrystallized several times from alcohol, the higher compound,  $(C_2H_5)_2S\cdot2HgCl_2$ , is formed. <sup>b</sup> White plates. When the product is recrystallized from alcohol it does not change. <sup>c</sup> Long white needles. Solvent of crystallization is important, while an excess of either of the reactants is of no moment. <sup>d</sup> White plates. When recrystallized from alcohol, the lower compound,  $(n-C_3H_7)_2S\cdotHgCl_2$ , is formed. <sup>e</sup> Same as for 3. <sup>f</sup> Same as for 4. <sup>g</sup> White plates. When alcohol is used as the solvent, a large excess of HgCl<sub>2</sub> is required in order to get precipitation. In water, molecular proportion of the reactants is sufficient. A clear oily liquid containing compounds 7 and 8 is formed. Addition of ether precipitates the solid. <sup>k</sup> Same as for 7.

Ethyl Sulfide and Mercuric Chloride.—The addition compound obtained by the interaction of ethyl sulfide and mercuric chloride was formerly considered to be an equimolecular compound of the two reacting substances. Abel<sup>3</sup> in disagreeing with the discoverer about the melting point of the reaction product said that Loir did not make a pure compound. Abel found that the melting point of his purified compound, which was recrystallized from alcohol and ether, was 119°. Loir had reported a melting point of 90° for his product. Abel assumed that the compound melting at 119° was the same as that made by Loir. No analysis was reported by Abel, although he obtained under some conditions a product melting at 80°.

During the present investigation many experiments were made to find the reason for these discrepancies. As will be shown later, the reason was discovered to be the existence of two compounds of ethyl sulfide and mercuric chloride,  $Et_2S$ ·HgCl<sub>2</sub> and  $Et_2S$ ·2HgCl<sub>2</sub>. The two compounds have widely different melting points. They are obtained in a pure state when the proper conditions of formation as well as of recrystallization are used.

(a)  $Et_2S$ ·HgCl<sub>2</sub>.—This compound is obtained when ethyl sulfide and mercuric chloride are used in an equimolecular proportion and the product is recrystallized either from absolute alcohol or from acetone containing a small quantity of ethyl sulfide.

When this crystalline compound was recrystallized from ether, a compound melting at 112–119° was obtained. This compound is a mixture of the two addition compounds. This fact explains why Abel obtained the higher-melting product, since he purified his product by recrystallization from ether.

(b)  $Et_2S:2HgCl_2$ .—This compound may be obtained pure if an excess of mercuric chloride solution is used and the product of the reaction is recrystallized once or twice from acetone or from benzene.

An acetone solution of the crude product obtained as described in section (a) was left partially covered overnight. Both types of crystals were formed. They were separated by hand-picking and were found to melt at 77° and 119.5°, respectively. Crystals of  $Et_2S$ ·HgCl<sub>2</sub> when recrystallized several times from either acetone or benzene are converted into  $Et_2S$ ·2HgCl<sub>2</sub>. The crystals thus obtained were recrystallized several times from absolute alcohol. No conversion was effected; the compound melted at 119.5°.

*n*-Propyl Sulfide and Mercuric Chloride. (a) n-Pr<sub>2</sub>S·HgCl<sub>2</sub>—When alcohol is the medium of the reaction, the crude reaction product melts invariably at 85°, even though an excess of the sulfide or of the mercuric salt is used. Also, in both cases the compounds recrystallized from absolute alcohol consist of long white needles melting at 87.5–88°.

(b) n-Pr<sub>2</sub>S·2HgCl<sub>2</sub>.—This compound is obtained by recrystallizing n-Pr<sub>2</sub>S·HgCl<sub>2</sub> (a) twice from benzene.

When this compound is recrystallized from alcohol, long needles of  $n-Pr_2S\cdot HgCl_2$ , melting at 87.5–88°, are invariably obtained. Thus the two compounds are convertible into each other.

Isobutyl Sulfide and Mercuric Chloride. (a) iso-Bu<sub>2</sub>S·HgCl<sub>2</sub>.—The compound was obtained by the action of *iso*butyl sulfide on an alcoholic solution of the mercuric salt. The precipitate was very voluminous. Recrystallized from absolute alcohol, the crystals melted at 116° after sintering.

(b)  $iso-Bu_2S-2HgCl_2$ .—The compound was obtained by recrystallizing  $iso-Bu_2S-HgCl_2$  (a) twice from benzene.

Some of the crystals melting at  $131^{\circ}$  were recrystallized again from alcohol. The new crystals melted at  $116^{\circ}$ . Analysis gave Hg, 47.79, instead of the theoretical value of 48.04 for *iso*-Bu<sub>2</sub>S·HgCl<sub>2</sub>.

Thus isobutyl sulfide behaves like ethyl sulfide and n-propyl sulfide by forming with

mercuric chloride two addition compounds; it is like n-propyl sulfide with respect to the easy conversion of one compound into the other by using different solvents for recrystallization.

*n*-Butyl Sulfide and Mercuric Chloride.—The interaction of *n*-butyl sulfide and mercuric chloride yielded two types of addition compounds, one of which had not been made with ethyl, *n*-propyl and *iso*butyl sulfides. The compound, *n*-Bu<sub>2</sub>S·HgCl<sub>2</sub>, seems to be non-existent. When the sulfide and the mercuric salt are used in the molecular proportion of 1:1 in alcohol, no precipitate is formed; but when the reacting substances are taken in the molecular proportion of 2:1, a heavy precipitation of white crystals occurs. However, if water is used as the solvent, a liquid separates when the reacting substances are taken in the molecular proportion of 1:1.<sup>14</sup> This liquid product when treated with a small quantity of ether yields a heavy mass of white crystals which on analysis were found to be the addition compound, *n*-Bu<sub>2</sub>S·2HgCl<sub>2</sub>. The ether solution, when evaporated, leaves an oily residue which by analysis was found to be the addition compound, (*n*-Bu<sub>2</sub>S)<sub>2</sub>·HgCl<sub>2</sub>.

The reactions involved may be explained as follows

$$3 n-Bu_2S + 3HgCl_2 = 2 n-Bu_2S \cdot 1HgCl_2 + n-Bu_2S \cdot 2HgCl_2$$
(1)  
Solution

 $2 n-Bu_2S\cdot 1HgCl_2 + n-Bu_2S\cdot 2HgCl_2 \xrightarrow{+ \text{ ether}} n-Bu_2S\cdot 2HgCl_2 + (n-Bu_2S)\cdot HgCl_2 \quad (2)$ (Soln.) (In ether soln.)

The compound  $n-Bu_2S\cdot 2HgCl_2$  is only slightly soluble in ether, while the compound  $(n-Bu_2S)_2\cdot HgCl_2$  is very soluble in this solvent.

(a) n-Bu<sub>2</sub>S·2HgCl<sub>2</sub>.—This compound was also obtained from 8.5 g. of mercuric chloride and 1.5 g. of *n*-butyl sulfide, *i. e.*, weights in the proportion of 3 moles of the salt to 1 mole of the sulfide. When only once recrystallized from benzene, the percentage of mercury found was 55.5, but when the product was crystallized again from the same solvent, almost the theoretical value for mercury was found.

(b)  $(n-Bu_2S)_2 \cdot HgCl_2$ .—This compound was obtained as previously described. Since Compound (a) is soluble in Compound (b), one would expect to find Compound (a) in Compound (b) as an impurity. On standing for a few days, a white precipitate was observed on the bottom of the test-tube. This change indicates the solubility of (a) in (b) as the cause of the high percentage of mercury.

Iso-amyl Sulfide and Mercuric Chloride.—The addition products obtained by the interaction of *iso*-amyl sulfide and mercuric chloride are similar in their constitution to those obtained from n-butyl sulfide and the mercuric salt. The method of preparation is also the same.

(a) iso-Am<sub>2</sub>S·2HgCl<sub>2</sub>.—The compound may be obtained either by using an excess of mercuric chloride in alcoholic solution or by using the reacting substances in the molecular proportion of 1:1 in an aqueous medium and then treating the product with ether. The results of analysis of the compound obtained by the latter method are given here.

(b)  $(iso-Am_2S)_2$ ·HgCl<sub>2</sub>.—This compound was obtained by using the sulfide and the mercuric salt in equimolecular proportion with water as the solvent; the product was then treated with ether. The high percentage of mercury may be explained by the solubility of Compound (a) in Compound (b).

Methyl Sulfide and Mercuric Chloride.-Loir<sup>1</sup> assigned to the reaction product of

 $<sup>^{14}</sup>$  *n*-Propyl sulfide and mercuric chloride in equimolecular proportions in water as solvent yield white crystals. This behavior shows that the reaction is different for *n*-butyl sulfide and *iso*-amyl sulfide.

methyl sulfide and mercuric chloride the formula  $(CH_3)_2S HgCl_2$ . Phillips<sup>4</sup> reinvestigated the compound and in accordance with the results of his analysis for mercury, sulfur and chlorine, gave to it the formula  $2(CH_3)_2S 3HgCl_2$ . The compound has no definite melting point. By heating rapidly, a clear liquid is obtained at 151°. The compound is only sparingly soluble in benzene and practically insoluble in the other ordinary organic solvents. The product obtained from alcoholic mercuric chloride and an equimolecular proportion of methyl sulfide was dissolved in an excess of boiling benzene. The crystals that separated were analyzed for mercury and sulfur.

Anal. Calcd. for 2(CH<sub>3</sub>)<sub>2</sub>S·3HgCl<sub>2</sub>: Hg, 64.63; S, 6.42. Found: Hg, 63.28, 62.83; S, 6.78, 6.73.

There is a possibility that the product is a "molecular" compound made up of equimolecular proportions of Me<sub>2</sub>S·HgCl<sub>2</sub> and Me<sub>2</sub>S·2HgCl<sub>2</sub>, the two types of addition compounds that were obtained from ethyl, *n*-propyl and *iso*butyl sulfide with mercuric chloride. Were it possible to find a favorable solvent, the two types might be separated. An analogous situation was found by Råy<sup>7</sup> for the compound (Et<sub>2</sub>S)<sub>2</sub>·PtCl<sub>3</sub>. On recrystallization from boiling alcohol, he succeeded in obtaining the compounds (Et<sub>2</sub>S)<sub>2</sub>·PtCl<sub>4</sub> from 2(Et<sub>2</sub>S)<sub>2</sub>·PtCl<sub>3</sub>.

## Summary

1. The action of alkyl sulfides on mercurous salts was investigated. The reaction was found to be a conversion of the mercurous salt into metallic mercury and the corresponding mercuric salt, and the formation of an addition compound of the alkyl sulfides with the mercuric salt.

2. In some cases the reaction takes place only in the presence of water.

3. Except for methyl sulfide, the alkyl sulfides have no action on mercurous chloride.

4. The addition compounds of alkyl sulfides and mercuric salts of most oxyacids are water soluble.

5. The products of reaction of alkyl sulfides and mercuric chloride were investigated. Three types of addition compounds were found. These types are  $(R_2S)_2$ ·HgCl<sub>2</sub>,  $R_2S$ ·HgCl<sub>2</sub> and  $R_2S$ ·2HgCl<sub>2</sub>. Each of the alkyl sulfides formed two of the types, depending on the solvent used.

6. *n*-Propyl sulfide and *iso*butyl sulfide form with mercuric chloride two types of compounds that are easily converted into each other by recrystallization from proper solvents.

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