It has been demonstrated that no nuclear condensation accompanied the formation of esters of benzoic, *o*-chlorobenzoic, *p*-nitrobenzoic and phenylacetic acids.

A method for the preparation of normal esters by the condensation of cyclopropane with acids has been described.

The preparation of normal and isopropyl sulfate has been described.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA*]

The Transition of the Mercuric Sulfides in Anhydrous Hydrogen Sulfide in Ammonia[1]

BY G. B. HEISIG

No information is available to show the behavior of the black and red modifications of mercuric sulfide when suspended in anhydrous ammonia, hydrogen sulfide or mixtures of the two. The transition point is 386 ± 2° and the change from the black to the red form is exothermal (382 cal.). Quam[2] found that the red modification is formed on suspending mercuric chloride in liquid hydrogen sulfide. The formation of the stable red modification is not in agreement with Ostwald's rule[3] although the change may be so rapid that the formation of the black modification has not been recorded.

By analogy to the behavior of water, liquid ammonia should not catalyze the transition of the modifications but a solution of ammonium sulfide in liquid ammonia should hasten the change from the red to the black form. This would be expected from a statement by Franklin[4] that a black precipitate is formed on adding ammonium sulfide (in liquid ammonia) to a mercury salt, and that the composition is doubtless that of the familiar sulfide of mercury.

Apparatus.—The all glass apparatus in which experiments were conducted is shown in Fig. 1. The ammonia was obtained from commercial tanks. The hydrogen sulfide was obtained from tanks or prepared by the action by dilute sulfuric acid on ferrous sulfide. The gases were dried by passing through drierite (G and H). Some reaction occurred between the drying agent and ammonia. In some runs the ammonia was dried by passing over ribbon sodium. The amount of liquid ammonia and liquid hydrogen sulfide was measured in the graduated tubes E and F at the temperature of dry ice. The volume of the portion of the system between the stopcocks A and B as well as the cross section of the manometer tubes was known, making it possible to add known quantities of these substances in the gaseous state. There was practically no non-condensable gas in the tank ammonia or hydrogen sulfide. The measured gases were condensed in tubes like C, containing the samples of mercuric sulfide at the temperature of liquid oxygen. Non-condensable gases were removed with an oil pump protected by the trap I immersed in liquid air and the tubes were sealed off. Before opening, the tubes containing the samples were cooled in liquid oxygen. After being opened, some were sealed to a high vacuum system maintained at 10^{-5} mm. and the volatile material condensed in a liquid air trap. The contents of other tubes were brought onto filter paper in a vacuum jacketed funnel and washed thoroughly with liquid ammonia.

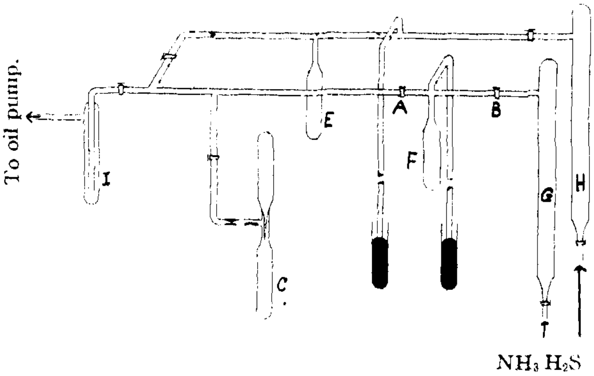

Fig. 1.

Materials.—The samples of black mercuric sulfide were commercial products containing 92.8% of mercuric sulfide (P_B) and 92.1% (M_B). Also samples were prepared by saturating a 0.3 *N* hydrochloric acid solution of mercuric chloride with hydrogen sulfide (*z*) and by heating a solution of mercuric chloride to which had been added sodium thiosulfate (*w*). These samples contained 99.5% of mercuric sulfide. The samples of the red modification were a commercial product (M_A and P_R) containing 99.6 and 98.7% of the sulfide, respectively.

Analysis.—The samples of the mercuric sulfide were dried for an hour at 106° and analyzed according to a modification of the method described by Rupp and Muller.[5]

(*) This work was started at the University of Illinois during the summer of 1935.

(1) Original manuscript received March 22, 1937.

(2) Quam, THIS JOURNAL, **47**, 105 (1925).

(3) Ostwald, "Fundamental Principles of Chemistry," Longmans, Green & Co., New York, N. Y., 1917, p. 92.

(4) Franklin, "The Nitrogen System of Compounds," Reinhold Publishing Corp., New York, N. Y., 1935, p. 25.

(5) Rupp and Muller, *Z. anal. Chem.*, **67**, 20-23 (1925).

TABLE I

SUMMARY OF ACTION OF VARIOUS CONCENTRATIONS OF REAGENTS ON 2-G. SAMPLES OF RED HgS (SAMPLE M_A)

M_{NH_3}	M_{H_2S}	M_{HgS}/M_{H_2S}	Color	Treatment for analysis	HgS analysis, %	Time change Red–Black	X-Ray pattern
0.144	0.044	0.20	Black			1 hr.	
.144	.032	.27	Black	28 hrs. *vacuo* 27° 2 days *vacuo* 50°	94.9% HgS 99.3% HgS[c]	12 hrs.	
.137	.027	.32	Black	Wash liq. NH_3	95.2% HgS 15.6% S	1 day	
.132	.027	.32	Black				
.12	.027	.32	Black	*Vacuo* 27°	95.0% HgS	3 hrs.	Complex
.12[a]	.027	.32	Black	Wash liq. NH_3	94.7% HgS	4 days	Complex
.17	.026	.22	Black	Wash liq. NH_3	94.6% HgS[d]	1 day	
.043	.026	.33	Black	8 days *vacuo* 50°	99.4	4 hrs.	
.096	.022	.39	Black	Wash H_2O	99.2[c]	1 day	Black
.144	.018	.48	Black	Wash liq. NH_3	94.8% HgS 16.0% S	1 day	
.274	.0084	1.0	Black			15 days	
.292	.0056	1.5	Black			15 days	
.264	.0048	1.8	Black	Wash liq. NH_3	94.8% HgS	15 days	
.26	.0038	2.3	Black	Wash liq. NH_3	95.0%	15 days	
.14	.0019	4.5	Nearly all black	Wash liq. NH_3	94.9%	34 days	
.18[b]	.00185	4.7	Black			30 days	
.264	.00064	13.5	Red	Wash liq. NH_3	99.2	25 days	

[a] Red cake 2 days. [b] Red cake 10 days. [c] Found: 2.5% NH_4. Calculated for $(NH_4)_2S\cdot 6HgS$: NH_4 2.5%, Hg 95.2% and S 15.3%. [d] Average of two values differing by 1.5%.

The details of the method will be described elsewhere. Since the ammonium thiohexamercurate is sensitive to moisture, samples were weighed as soon as possible after exposure to the air. The mercury content of the samples expressed as the percentage of mercuric sulfide is given in column 7 of Table I. Ammonia was determined by treating the samples with potassium hydroxide, collecting the ammonia in standard sulfuric acid and titrating the excess of sulfuric acid. To determine sulfur, weighed samples were sealed in tubes containing fuming nitric acid and heated to 300°. Hydrochloric acid was added to the tubes and the contents, after transfer to a beaker and the addition of 10 mg. of sodium carbonate, were evaporated to dryness to remove the nitric acid. The residue was dissolved in water and the analysis for the sulfate ion was carried out in the usual manner.

X-Ray Examination.—The X-ray examination of the samples was made through the courtesy of Dr. J. Dorn using the apparatus described by Dorn and Glockler.[6]

Results

Samples of the black form sealed in tubes containing liquid hydrogen sulfide became red. That the samples had actually changed to the red modification was shown by chemical analysis and a comparison of the X-ray diagrams with those of cinnabar. No change in the color, composition or structure of either the red or black modification was observed when samples were treated with anhydrous ammonia. However, samples of the red modification sealed in tubes containing liquid ammonia to which hydrogen sulfide had been added, began to darken at −80°. The results are summarized in Table I. The X-ray patterns were much more complicated than those of either cinnabar or meta cinnabar. The compound is decomposed by water or by heating above 50° *in vacuo*, yielding a residue of the black form of mercuric sulfide. It is stable when suspended in liquid ammonia or kept *in vacuo* at room temperature. To remove the possibility that the energy required for the endothermal process $HgS_r \longrightarrow HgS_b$ was supplied by the reaction between ammonia and hydrogen sulfide, tubes were prepared in which anhydrous hydrogen sulfide and ammonia in varying proportions were allowed to react and, after breaking a capillary, the cooled liquid was permitted to fall on the red form. A black substance was formed over a wide range of concentration of ammonium sulfide.[7] In many cases a red cake formed before the solid be-

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[6] Dorn and Glockler, *Rev. Sci. Instruments*, **7**, 391–393 (1936).

[7] The nature of the system—anhydrous ammonia to which even a small amount of hydrogen sulfide has been added—is in doubt. Some investigators state that a solution of normal ammonium sulfide in ammonia is formed. Scheflan and McCrosky [THIS JOURNAL, **54**, 193 (1932)] from their investigation of the temperature–pressure-composition diagrams conclude that the normal sulfide does not exist above −18°. However their investigations do not exclude the existence of a solution of the normal sulfide in liquid ammonia. Furthermore, the excess of ammonia would tend to shift the equilibrium to increase the amount of the normal sulfide. Then, too, the normal sulfide may be stabilized by coördination with the mercuric sulfide similar to the stabilization of cupric iodide or hypophosphite by coördination with two molecules of ethylenediamine. (*Cf.* Morgan and Burstall, "Inorganic Chemistry," Chemical Publishing Co., New York, N. Y., 1937, p. 66.)

came black. No change in temperature was noted on adding the solution of ammonium sulfide to the mercuric sulfide.

Analyses of the black crystals obtained when the ratio of ammonium sulfide to mercuric sulfide varied over a wide range, indicate the existence of a compound having the formula $(NH_4)_2S \cdot 6HgS$ or $[NH_4HS \cdot 6HgS]NH_3$. The slightly lower value of the mercury content than that corresponding to these formulas is undoubtedly due to its sensitivity toward moisture. The complete analysis (run 3, Table I) made after a technique had been perfected to reduce the exposure to air and moisture to a minimum, agreed with that demanded by the formula. The first formula seems to be the more reasonable, since the large excess of ammonia present favors the formation of the normal rather than the hydrosulfide. If this view is correct, the double salt should not be formed when the red modification is suspended in a solution which does not contain the normal ammonium sulfide. A solution of ammonium hydrosulfide may be prepared by adding a small amount of ammonia to hydrogen sulfide. Since no change in the color or composition of samples of the red modification suspended in the solution containing ammonium hydrosulfide occurs, the formula $(NH_4)_2S \cdot 6HgS$ is preferred. The compound will be called ammonium thiohexamercurate. The chemical changes involved are

$$\begin{tikzcd}[column sep=small] & & \mathrm{HgS_{black}} + (x + 2)\mathrm{NH_3} + \mathrm{H_2S} \\ \mathrm{HgS_{red}} + \mathrm{NH_3} + \mathrm{H_2S} \arrow[r] & (\mathrm{NH_4})_2\mathrm{S}\cdot 6\mathrm{HgS}\cdot x\mathrm{NH_3} \arrow[ur] \arrow[dr] & \\ & & (\mathrm{NH_4})_2\mathrm{S}\cdot 6\mathrm{HgS_{black}} + x\mathrm{NH_3} \end{tikzcd}$$

Thus through the intermediate formation of a compound, a stable modification has been changed to a metastable form at temperatures far below the transition point.

The energy necessary to change the structure is undoubtedly available from the heat of formation of the thiohexamercurate from ammonium sulfide and mercuric sulfide.

Ditte[8] reported compounds whose compositions may be expressed by the formulas: $K_2S \cdot 5HgS \cdot 5H_2O$, $K_2S \cdot HgS \cdot 7H_2O$ and $K_3S \cdot HgS \cdot H_2O$. Since the ionic radii of potassium and ammonium ions are very nearly the same, the formation of similar ammonium compounds may be expected. The compound $K_2S \cdot 5HgS \cdot H_2O$ exists in two modifications—red and black. The red cake which forms just before the change to the black ammonium thiohexamercurate is not a red modification. The volatile constituents of a reaction mixture made by mixing 0.156 M NH_3, 0.027 M H_2S and 0.0086 M HgS were removed by inverting the sealed tube in liquid air. The residue contained only 96.5% of mercuric sulfide but the X-ray pattern was identical with that of cinnabar.

Summary

Black mercuric sulfide is changed to the red modification in liquid hydrogen sulfide.

Red mercuric sulfide reacts with a solution of ammonium sulfide in liquid ammonia forming $(NH_4)_2S \cdot HgS$. This compound is unstable in the presence of moisture, losing H_2S and NH_3. The residue is identical with the metacinnabarite.

MINNEAPOLIS, MINN. RECEIVED NOVEMBER 8, 1937

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[8] Ditte, *Compt. rend.*, **98**, 1271, 1380 (1889).