Inorganica Chimica Acta, *164* (1989) 165–169

The Preparation of Metal Sulfides and Organo-metal Sulfides from Metal Alkyls and Hydrogen Sulfide

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(Received April 17, 1989)

Abstract

The room temperature reactions of homoleptic metal alkyl complexes with hydrogen sulfide in toluene solution have been investigated. The aluminum alkyls, AlR_3 (R = Me, Et and i-Bu), reacted with H_2S to form air-sensitive solids which are postulated to be mixtures of Al_2S_3 and $(RAlS)_n$. A species of the empirical formula CH_3GaS was produced when $GaMe_3$ was treated with H_2S. Reaction of $Cd(CH_2SiMe_3)_2$ with H_2S yielded cadmium sulfide which retained approximately 10 ppm of the alkyl group. At room temperature, $Hg(CH_2SiMe_3)_2$ was unreactive with H_2S. However at 150 °C the neat liquid reacted to form highly crystalline mercuric sulfide in the cubic crystalline form. The reactions of $MgEt_2$ and $Ti(CH_2SiMe_3)_4$ with H_2S are also described.

Introduction

Metal sulfide powders are important as lubricants, phosphors, catalysts [1] and precursors of optical ceramics [2]. We are investigating possible low temperature routes to metal sulfide powders as alternatives to traditional high temperature solid state methods. Low temperature routes may give products with smaller particle size and higher purity. Previous reports of the reaction of H_2S with metal alkyls have dealt primarily with high temperature metal-organic chemical vapor deposition [3, 4] or metal-organic vapor phase epitaxy [5]. The preparation of aluminum sulfide powder by the vapor phase reaction of $AlMe_3$ with H_2S, at temperatures in the range of 50–90 °C, has been reported [6]. ZnS powder doped with amine ligands has also been prepared from H_2S and the amine adduct of diethylzinc at room temperature [7]. In a separate paper we present a detailed study of the preparation of ZnS powders from diethylzinc and H_2S [8]. In this paper we have surveyed the reaction of metal alkyl complexes with H_2S. Closed shell (d^0 or d^{10}) metal complexes were chosen based on our interest in preparing optically transparent materials.

Experimental

General Information

All manipulations were performed under argon using Schlenk techniques or in a helium filled glove box. Infrared spectra were recorded on a Nicolet 60SX Fourier transform spectrophotometer using a Barnes diffuse reflectance cell. ^1H NMR spectra were obtained at 80.13 MHz from an IBM NR80 Fourier transform spectrometer. X-ray powder diffraction patterns were collected on a Scintag PAD V diffractometer. A Perkin-Elmer 2000 gas chromatograph, with a 3600 Data Station, equipped with either an Analabs 1/8″ × 6′ stainless steel Spherocarb column or a 1/8″ × 6′ stainless steel Porapak T column was used to record gas chromatograms. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Materials

The following materials were used as provided: hydrogen sulfide (99.5%) (Matheson Gas Products), cadmium iodide and mercuric chloride (J. T. Baker Chemical Company), trimethylsilylmethyl lithium (1.0 M in pentane), trimethylsilylmethyl magnesium chloride (1.0 M in ether) and titanium(IV) chloride (Aldrich Chemical Company), deuterium chloride (33% in D_2O, ICN Biomedicals), diethylmagnesium (1.45 M in diethyl ether) and trimethylgallium (Alfa Products). Trimethyl, triethyl and triisobutyl aluminum (Research Organic/Inorganic Chemicals) were distilled prior to use. All organic solvents were dried under argon over sodium benzophenone ketyl before use. $Ti(CH_2SiMe_3)_4$ [9], $Hg(CH_2SiMe_3)_2$ [10] and $Cd(CH_2SiMe_3)_2$ [11] were prepared as described in the literature.

General Procedure for the Reaction of Metal Alkyls with Hydrogen Sulfide

Typically, 15 mmol of metal alkyl were placed in a 100 ml Schlenk flask and diluted to 1 M with

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0020-1693/89/$3.50

toluene. This solution was added with stirring, via a 22 gauge cannula, to a 100 ml Schlenk flask containing 30 ml of an H_2S-saturated toluene solution over *c.* 30 min. During the addition, a continuous H_2S purge was maintained with the excess gas exiting through a mineral oil bubbler followed by two bubblers containing 6% NaOCl to destroy the H_2S. When addition of the metal alkyl solution was complete, the mixture was stirred for an additional 10 min under H_2S flow. After filtration, the solid was washed with two 10 ml portions of toluene, dried at 10^{-3} torr and 25 ℃ for 3 h, then heated to 80 ℃ and dried overnight to a final pressure of 2×10^{-4} torr.

Reaction of AlR_3 (R = Me, Et and i-Bu) with Hydrogen Sulfide

White solids precipitated after induction periods of 2, 1 and 10 min for R = Me, Et and i-Bu respectively. These solids partially dissolved in d_5-pyridine to give ^1H NMR spectra which exhibited two sets of peaks for each species. R = Me: δ −0.094(s); 0.17(s). R = Et: δ 0.46 (q, J = 8 Hz), 1.26 (t, J = 8 Hz); 0.72 (q, J = 8 Hz), 1.50 (t, J = 8 Hz). R = i-Bu: δ 0.46 (d, J = 7 Hz), 1.06 (d, J = 7 Hz), 2.19(m); 0.71 (d, J = 7 Hz), 1.14 (d, J = 7 Hz), 2.19(m).

Reaction of $GaMe_3$ with Hydrogen Sulfide

A white solid began to precipitate 15 min after the start of $GaMe_3$ addition to the H_2S saturated solution. *Anal.* Calc. for $GaSCH_3$: Ga, 59.68; S, 27.44; C, 10.28; H, 2.59. Found: Ga, 58.55; S, 27.31; C, 10.51; H, 2.77%. Diffuse reflectance infrared spectrum of 2975(w), 2910(w), 2863(w), 2769(w), 1772(w), 1395(w), 1205(m), 744(s), 576(s), 383(s), 352(m), 260(w) cm^{-1}.

Reaction of $Cd(CH_2SiMe_3)_2$ with Hydrogen Sulfide

$Cd(CH_2SiMe_3)_2$ formed an orange solid immediately upon contact with the H_2S-saturated solution. *Anal.* Calc. for CdS: Cd, 77.81; S, 22.19. Found: Cd, 78.28; S, 22.31; C, 0.24; H, 0.11%.

Reaction of $Hg(CH_2SiMe_3)_2$ with Hydrogen Sulfide

$Hg(CH_2SiMe_3)_2$ (11.1 mmol, 4.17 g) was loaded into a 100 ml Schlenk flask and a stream of H_2S was bubbled in through a syringe needle. The flask was then heated to 150 ℃ under an H_2S flow with rapid stirring. After 25 min, all of the liquid had been replaced by a black powder that was subsequently washed twice with 10 ml portions of toluene, filtered and dried *in vacuo*. The sample was dried further by heating to 90 ℃ overnight at 2×10^{-4} torr. *Anal.* Calc. for HgS: Hg, 86.22; S, 13.78. Found: Hg, 81.60; S, 14.24; C, <0.1; H, <0.1%.

Reaction of $MgEt_2$ with Hydrogen Sulfide

A 5 ml aliquot of an $MgEt_2$ solution (1.45 M in ether) was diluted with 30 ml of ether and cannulated into a Schlenk flask containing 40 ml of an H_2S-saturated ether solution as described in the general procedure. A white solid began to precipitate immediately. After addition of the metal alkyl solution was complete, the reaction mixture was stirred an additional 45 min and then allowed to sit under an H_2S atmosphere for 3 days. The solid was filtered, washed with ether and pentane, and then dried first at 10^{-3} torr for 3 h at room temperature and finally for 4 h at 73 ℃.

Hydrolysis and Gas Chromatography of the Sulfide Powders

Residual alkyl groups in the sulfide powders were measured by chromatography of the gas released by hydrolysis. Typically, 30 mg of the solid was placed in a 50 ml two neck round-bottom flask fitted with a septum and a vacuum valve adapter. The flask was evacuated to 2×10^{-4} torr and 0.5 ml of concentrated H_2SO_4 was added. The resulting mixture was stirred until gas evolution ceased. A 1.0 ml sample of gas was withdrawn into a gas-tight syringe that was then stoppered and the gas compressed to 0.50 ml giving a final pressure of 0.4 to 0.8 atmospheres. The syringe was opened briefly to the atmosphere and the sample injected into the gas chromatograph. The percentage of alkane present in the gas was determined by comparison with calibration standards of known hydrocarbon concentration. The total moles of alkane was then calculated by assuming ideal gas behavior. Assuming an empirical formula of $Al_2S_{3-x}R_{2x}$, the ratio of alkyl group to aluminum was determined.

Hydrolysis and ^1H NMR of $(MeGaS)_n$

A vial containing a stirbar was loaded with 24 mg of $(MeGaS)_n$ and 1 ml of C_6D_6. To this suspension was added 1 ml of 33% DCl in D_2O dropwise with stirring. After an additional 10 min of stirring, the aqueous and organic layers were transferred to separate NMR tubes. Spectra of both samples were recorded and then 5.0 μl of methanol and 2.0 μl of acetone were added as integration standards in the aqueous and organic layers, respectively. The benzene layer did not exhibit any resonances other than those of solvent and accompanying impurities. A singlet was observed in the spectrum of the aqueous layer 0.23 ppm downfield of DSS (3-trimethylsilyl-1-propanesulfonic acid sodium salt).

^1H NMR of the $Ti(CH_2SiMe_3)_4$ Reaction with Hydrogen Sulfide

$Ti(CH_2SiMe_3)_4$ (30 mg, 0.076 mmol) was pipetted into an NMR tube and dissolved in *c.* 1 ml of C_6D_6. An integration standard (2.0 μl toluene) was added and the spectrum recorded. Upon the addition of gaseous H_2S (5.0 ml, 0.18 mmol), a black solid formed. A spectrum of this mixture revealed only the presence of tetramethylsilane, the toluene standard, and dissolved H_2S.

Results and Discussion

Reaction of Aluminum Alkyls with Hydrogen Sulfide

The air-sensitive solids obtained from the reaction of aluminum alkyls with H_2S were hydrolyzed in concentrated sulfuric acid and the evolved hydrocarbon gas analyzed. In all cases the amount of alkane released was between 0.2 and 0.7 mol per mole of aluminum, indicating incomplete conversion of the trialkyl aluminum complex to aluminum sulfide (see Table 1). For the solid derived from $AlMe_3$, the Al:C ratio of 1:0.66, determined by elemental analysis, agreed with the amount of methane observed by hydrolysis.

TABLE 1. Alkyl group content of metal sulfide products[a]

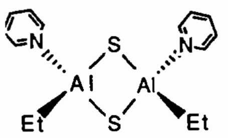
Precursor	Alkyl group/Metal atom
$AlMe_3$ [b]	0.66
	0.61
$AlEt_3$ [b]	0.34
	0.23
$Al(i\text{-}Bu)_3$ [c]	0.17
	0.14
$GaMe_3$	0.85[d]
$MgEt_2$	2.4×10^{-5}
$ZnEt_2$	1.0×10^{-5} [e]
$Cd(CH_2SiMe_3)_2$	1.0×10^{-5}
$Hg(CH_2SiMe_3)_2$	$<1.0 \times 10^{-6}$ [f]

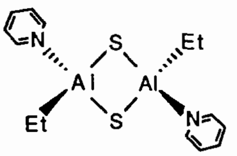
[a]All values, unless noted, were determined by gas chromatography of the hydrolysis products. [b]Results from two separate preparations. [c]Duplicate determination from one preparation. [d]$Ga-CH_3$ bond not hydrolyzed. Value determined by ^1H NMR of the hydrolysis product in 33% DCl. [e]Ref. 8. [f]None observed.

Previous reports have demonstrated [12, 13] that when $AlEt_3$ reacted with a deficiency of H_2S a species with the stoichiometry C_2H_5AlS was produced.

$$AlEt_3 + H_2S \xrightarrow{-78\ ^\circ C} \frac{1}{n}(EtAlS)_n + 2EtH \qquad (1)$$

The species formulated as $(EtAlS)_n$ dissolved in pyridine, forming an adduct which was postulated to have the structure of one of the two isomers below. The gas phase reaction of $AlMe_3$ with H_2S reportedly produced a mixture of 90% Al_2S_3 and 10% $(MeAlS)_n$ at 50 °C [6].





We believe that the powders produced in our reactions are mixtures of Al_2S_3 and $(RAlS)_n$, based on the residual alkyl group content and the following supporting results. The powders are partially soluble in pyridine. The product from $Al(i\text{-}Bu)_3$ had the lowest solubility in pyridine, consistent with the observation that it retained the least amount of unreacted alkyl group. Proton NMR spectra of the soluble components displayed two sets of resonances assignable to two different alkyl aluminum species. The ratios of the upfield to downfield peak heights were 2.3:1 for R = Me, 1.6:1 for R = Et, and 0.9:1 for R = i-Bu. The ^1H NMR spectrum of the pyridine adduct of $(EtAlS)_n$ was reported to contain two resonances separated by 49 Hz [12] (no chemical shifts were given). The two species we observed have peak separations ($\delta\ CH_3 - \delta\ CH_2$) of 48 Hz ($\delta$ 1.26, 0.46) and 47 Hz (δ 1.50, 0.72), when converted to a 60 MHz resonance frequency. To determine whether one of these species was the same as the one previously reported, we repeated the literature synthesis and found that the pyridine adduct of $(EtAlS)_n$ has resonances at 1.26 and 0.46 ppm. The identity of the second pyridine adduct observed from our synthesis remains unknown. Presumably, the different reaction temperature and/or stoichiometry account for the formation of the second adduct.

Reaction of $GaMe_3$ with Hydrogen Sulfide

$GaMe_3$ forms a complex with the empirical formula CH_3GaS. Unlike the case for the aluminum alkyls, the product obtained by treating $GaMe_3$ with H_2S at room temperature in toluene contained no binary metal sulfide. In fact, the remaining gallium–carbon bond is extremely inert, resisting hydrolysis with hydrochloric or concentrated sulfuric acid*. Hydrolysis of $(MeGaS)_n$ with concentrated sulfuric acid released only 4.3×10^{-3} mol CH_4 per mole of Ga. Upon treatment with a 33% DCl solution, $(MeGaS)_n$ released D_2S and formed a soluble species that displayed a singlet in the ^1H NMR at 0.23 ppm. The integrated intensity of this peak corresponded to 0.85 methyl groups per formula weight of MeGaS.

$(MeGaS)_n$ was insoluble in a number of solvents including toluene, tetrahydrofuran, methylene chloride and acetonitrile. However, it dissolved completely in pyridine forming a pyridine adduct. This is analogous to the formation of adducts by the addition of pyridine to the species $(RAlS)_n$ (*vide supra*). However, ^1H NMR of the gallium analog revealed only one species in d_5-pyridine with a singlet at 0.27 ppm.

$(MeGaS)_n$ could be partially sublimed at 390 °C and 2×10^{-4} torr. Continued heating to 450 °C

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*The etherate of $GaEt_3$ also displayed incomplete hydrolysis in concentrated HCl [14].

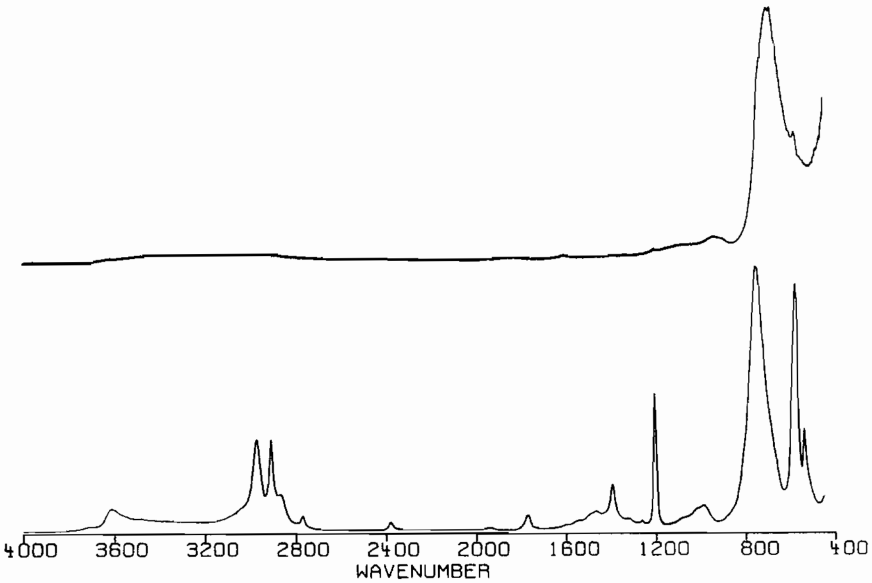

Fig. 1. Diffuse reflectance infrared spectra of: $(MeGaS)_n$ (lower trace) and product derived from $(MeGaS)_n$ by heating to 450 °C *in vacuo* overnight (upper trace).

caused the material to change color from white to yellow. The infrared spectrum of the X-ray amorphous yellow solid displayed very weak C–H stretching bands at 2982, 2918, 2883 and 2775 cm^{-1} similar in shape to those of $(MeGaS)_n$ as well as new peaks at 695(s), 687(s) and 580(sh) cm^{-1} (Fig. 1). After heating to 640 °C *in vacuo*, X-ray diffraction lines corresponding to GaS (not Ga_2S_3) were observed. Due to the insolubility of $(MeGaS)_n$, the value of n could not be ascertained. Given its sublimability, it is unlikely that $(MeGaS)_n$ is polymeric.

Reaction of $Cd(CH_2SiMe_3)_2$ with Hydrogen Sulfide

The orange solid produced by H_2S treatment of $Cd(CH_2SiMe_3)_2$ consisted of Cd and S in a 1.0:1.0 molar ratio. X-ray powder diffraction confirmed that the product was indeed the hexagonal (low temperature) form of cadmium sulfide. Gas chromatography of the hydrolysis product detected only 12 ppm of tetramethylsilane derived from the alkyl remaining in the solid.

A scanning electron micrograph (Fig. 2) of the CdS powder exhibits approximately spherical particles *c.* 0.1 μm in diameter. This powder has nearly identical particle size and residual alkyl group content as the ZnS produced from Et_2Zn and H_2S by the same method [8].

Reaction of $Hg(CH_2SiMe_3)_2$ with Hydrogen Sulfide

In contrast to the alkyl complexes of zinc and cadmium, bis(trimethylsilylmethyl)mercury did not react with H_2S at room temperature in toluene. However, when neat liquid $Hg(CH_2SiMe_3)_2$ was heated to 150 °C under a stream of H_2S, a fine black powder was formed. Sharp lines in the X-ray diffraction pattern indicated a highly crystalline substance consisting of mostly (>75%) metacinnabar (cubic HgS) with the remainder being the hexagonal form of mercuric sulfide (cinnabar).

Fig. 2. Scanning electron micrograph of cadmium sulfide powder from the reaction of $Cd(CH_2SiMe_3)_2$ and H_2S.

Scanning electron micrographs of the powder reveal sharply faceted particles that are 0.1 to 1 μm in diameter (Fig. 3). When hydrolyzed by concen-

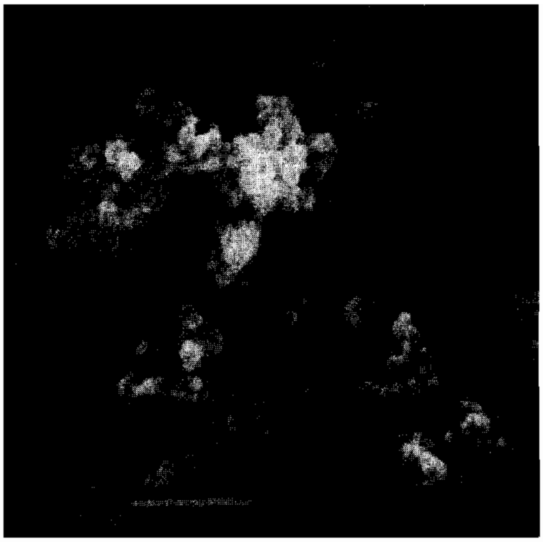

Fig. 3. Scanning electron micrograph of mercuric sulfide powder from the reaction of $Hg(CH_2SiMe_3)_2$ and H_2S.

trated sulfuric acid, no tetramethylsilane could be detected by gas chromatography down to the detection limit of *c.* 1 ppm. Although this result could be due to incomplete hydrolysis, the high crystallinity and the elemental analysis results argue in favor of complete conversion to mercury(II) sulfide.

Reaction of $MgEt_2$ with Hydrogen Sulfide

An ether solution of diethylmagnesium produced a white powder upon treatment with H_2S. An X-ray diffraction pattern of the powder displayed broad lines for MgS as well as other weak unassigned lines that are possibly derived from reactions with atmospheric oxygen and water. Hydrolysis of the solid liberated 24 ppm ethane. However, NMR examination of a hydrolysis indicates that the solid retained at least 2 mol% of ether even after drying at 73 °C for 4 h at 10^{-3} torr.

Reaction of $Ti(CH_2SiMe_3)_4$ with Hydrogen Sulfide

Addition of $Ti(CH_2SiMe_3)_4$ to an H_2S-saturated solution initially led to a color change from yellow to brown followed rapidly by the precipitation of an X-ray amorphous black solid. Hydrolysis of the solid produced only 18 ppm of tetramethylsilane. The extent of reaction of the titanium alkyl and H_2S was determined in a ^1H NMR experiment by measuring the tetramethylsilane liberated. In this case 84% of the original trimethylsilylmethyl groups were observed as tetramethylsilane. These results indicate that the reaction of $Ti(CH_2SiMe_3)_4$ and H_2S proceeds nearly to completion, with less than one alkyl group remaining per titanium.

Conclusions

The conversion of metal alkyls to sulfides by hydrogen sulfide treatment was essentially complete for the divalent metals Zn, Cd, Hg and Mg. While Zn, Cd and Mg alkyls reacted rapidly at ambient temperature, mercuric sulfide was formed only at elevated temperatures. Due to the inertness of the third alkyl–gallium and alkyl–aluminum bonds, pure binary sulfides could not be produced under conditions comparable to those employed for the divalent metals. Instead, alkyl metal sulfide oligomers were formed. For aluminum, the product was a mixture of Al_2S_3 and $(RAlS)_n$ while trimethylgallium was converted exclusively to the $(MeGaS)_n$ oligomer.

Acknowledgements

This work was supported by the Office of Naval Research. C.G.B. wishes to thank the American Society for Engineering Education/Office of Naval Technology for a postdoctoral fellowship. We also thank Dr D. C. Harris for helpful discussions, Dr C. Lowe-Ma and L. A. Zellmer for X-ray diffraction work, Dr M. P. Nadler for infrared spectra, J. H. Johnson for gas chromatography, R. W. Woolever for scanning electron microscopy, and D. K. Hickey for experimental assistance.

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