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# Thermal Decomposition Studies of Selected Transition Metal Polysulfide Complexes. II. Effect of Atmosphere on Decomposition

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## Abstract

Initial studies involved the thermal decomposition profile of five polysulfide complexes in air up to 550°C. Since our first report to the Academy in 1990, we have obtained the capability to run samples up to 1500°C under various gases. Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) of a series of transition metal polysulfide complexes are presented. Compounds analyzed included  $\text{Cp}_2\text{TiS}_5$ ,  $\text{MoS}_9^{2-}$ ,  $\text{MoOS}_8^{2-}$ ,  $\text{Zn}(\text{S}_x)^{2-}$ ,  $\text{Cd}(\text{S}_x)^{2-}$ ,  $\text{Fe}_2\text{S}_{12}^{2-}$  and  $\text{NiS}_8^{2-}$ .

## Introduction

Binary and tertiary metal sulfides have many important uses including catalysis, batteries and electrical devices (Greenwood and Earnshaw, 1984). More efficient methods for preparing these materials may employ the use of a large class of compounds known as transition metal polysulfides as precursors. Though polysulfide complexes are known for most transition metals (Draganjac and Rauchfuss, 1985), few studies have focussed on the reactivity and applicability of these compounds. Our interests involve possible use of metal polysulfides as sulfur transfer reagents, particularly in the vulcanization of rubber. To understand their usefulness in this capacity, we have begun a systematic study of the thermal stability of a series of transition metal polysulfides. Herein, we report on the thermal decomposition profiles for several of the transition metal polysulfide complexes.

## Methods and Materials

Reactions were carried out on a dual manifold vacuum line using Schlenk techniques, Kewaunee Inert Atmosphere Box or in a Vacuum Atmosphere Dual Station Dry-Box under  $\text{N}_2$ . Reagents were used as purchased without further purification. Polysulfide complexes were prepared as described in the literature:  $\text{Cp}_2\text{TiS}_5$  (Kopf et al., 1968),  $(\text{Et}_4\text{N})_2\text{MoS}_9$ ,  $(\text{Ph}_4\text{P})_2\text{MoOS}_8$  (Draganjac, 1983),  $(\text{Ph}_4\text{P})_2\text{Fe}_2\text{S}_{12}$  (Coucovanis et al., 1979),  $(\text{Et}_4\text{N})_2\text{ZnS}_8$ ,  $(\text{Ph}_4\text{P})_2\text{CdS}_{10}$  and  $(\text{Ph}_4\text{P})_2\text{NiS}_8$  (Coucovanis et al., 1985). The polysulfide complexes were characterized and compared with literature values to assure the identity of the products before thermal analysis. Thermal gravimetric analyses (TGA) were obtained on a Seiko TG/DTA 320 instrument. All samples were run at heating rates of 20°C/min up to 1000°C. Gas flow rates

(either air or  $\text{N}_2$ ) were set at 300 mL/min. Scanning Electron Microscopy (SEM) X-ray Fluorescence measurements were obtained on a JEOL-100CX II with Tracor Northern 2000 X-ray detection system.

## Results and Discussion

Depending on the atmosphere employed (air vs. nitrogen), differences occurred in the thermal decomposition of the transition metal polysulfides. All of the samples run in air flow showed exothermic behavior in the Differential Thermal Analysis (DTA). This could be explained by the burning of the C- and S-containing moieties. The differences in the mass loss can also be explained by the reaction of  $\text{O}_2$  with the polysulfide complexes.

Figure 1 shows the Thermal Gravimetric Analysis (TGA) curves for  $\text{Cp}_2\text{TiS}_5$ . Under  $\text{N}_2$ , a total of 33.7% mass loss has occurred by 1000°C. The compound is still losing mass at this temperature. Loss of two  $\text{CpS}_{1.5}$  units and subsequent coupling of the remaining Ti fragments to give to  $\text{Cp}_2\text{TiS}_7$  species would account for 33.5% mass loss. Giolando and Rauchfuss (1984) have demonstrated Cp migration from the Ti in  $\text{Cp}_2\text{TiS}_5$  to the pentasulfide ring at elevated temperature (boiling xylenes, b.p. 137-144°C for 24 hr under  $\text{N}_2$ ). Mass change in  $\text{Cp}_2\text{TiS}_5$  begins at 132°C. Further decomposition to  $\text{TiS}_x$  would be expected at higher temperatures. In air, the total mass loss of 77.8% approximates the formation of  $\text{TiO}_2$  (76.4%). The decomposition left a white powder in the sample pan. SEM X-ray fluorescence measurements showed presence of Ti and a trace of S. A large exotherm at 563.9°C is seen in the DTA plot for  $\text{Cp}_2\text{TiS}_5$  in air.

Figure 2 shows the TGA curves for  $(\text{Et}_4\text{N})_2\text{MoS}_9$ . In  $\text{N}_2$ , beginning at 153.0°C, a total mass loss of 67.0% is observed. SEM measurements show only Mo. Due to

II. Effect of Atmosphere on Decomposition

overlap of the Mo and S peaks, it is not possible to conclude the presence of S. The gray appearance of the decomposition product suggests  $\text{MoS}_x$ . Calculations based on  $\text{MoS}_3$  would indicate a 70.2% mass loss. An extremely bad odor was given off during this reaction. In air,  $\text{MoS}_9^{2-}$  shows a step-wise decomposition. The first step at 183.5°C could be a possible loss of two  $\text{Et}_3\text{N}$  and five eq. of S atoms leaving  $(\text{EtS})_2\text{MoS}_2$  (56.2% loss). Further heating associated with the exotherm at 579.5°C is explained by the formation of  $\text{MoO}_3$ . A small endotherm corresponds with the melting of  $\text{MoO}_3$  at 795°C. Under the flow of air, possibly the  $\text{MoO}_3$  is vaporized, explaining the total mass loss of 98.5%.

The TGA curves for  $(\text{Ph}_4\text{P})_2\text{Fe}_2\text{S}_{12}$  (Fig. 3) show greater mass loss for the run under  $\text{N}_2$  than in air. Under  $\text{N}_2$ , the final product appears to be  $\text{FeS}_2$ . The total mass loss of 80.6% agrees with the calculated value of 80% for the iron disulfide. In air, the decomposition product had a reddish color and the SEM showed only the presence of Fe and P. A mixture of iron oxides and phosphates is proposed at this time. Further study of the decomposition products is underway.

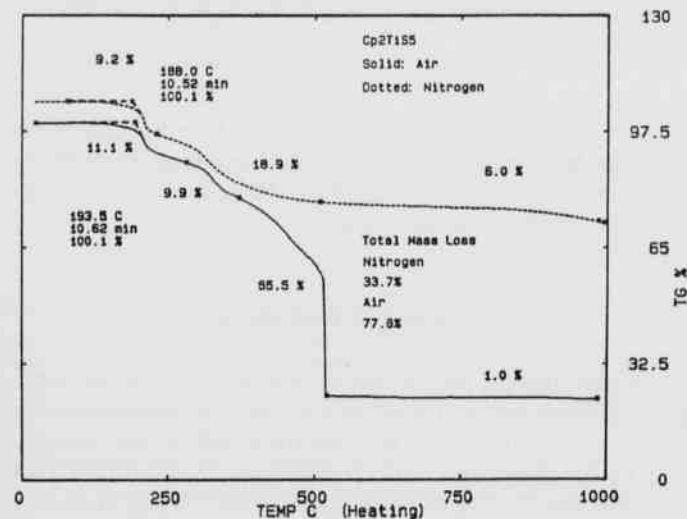


Fig. 1. TGA curves for  $\text{Cp}_2\text{TiS}_5$ . The air curve has been offset by -6%.

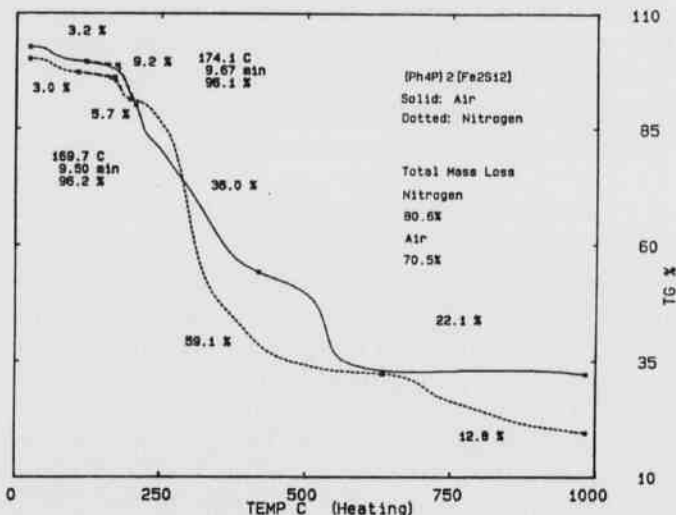


Fig. 3. TGA curves for  $(\text{Ph}_4\text{P})_2\text{Fe}_2\text{S}_{12}$ . The  $\text{N}_2$  curve has been offset by -2.5%.

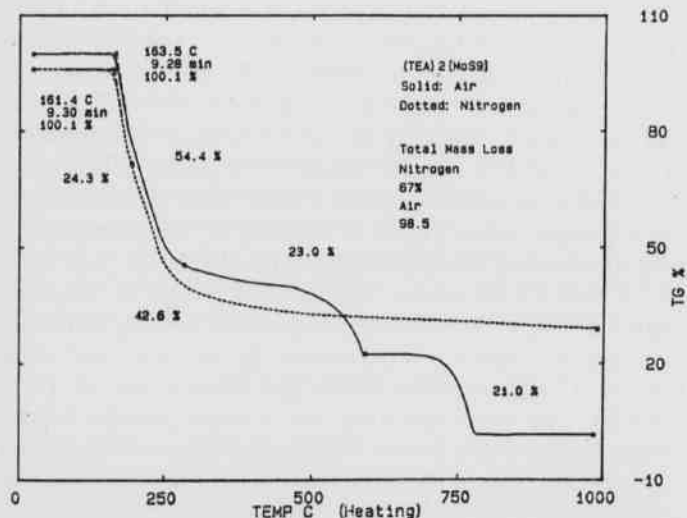


Fig. 2. TGA curves for  $(\text{Et}_4\text{N})_2\text{MoS}_9$ . The  $\text{N}_2$  curve has been offset by -4%.

The decomposition curves for  $(\text{Ph}_4\text{P})_2\text{MoOS}_8$  (Fig. 4),  $(\text{Et}_4\text{N})_2\text{ZnS}_8$  (Fig. 5),  $(\text{Ph}_4\text{P})_2\text{CdS}_{10}$  (Fig. 6) and  $(\text{Ph}_4\text{P})_2\text{NiS}_8$  (Fig. 7) are shown for comparison. Calculations based on expected products do not conform to total mass loss for these four compounds.

The authors caution the readers that the proposed intermediate and product structures in the discussion above are speculative at best. Attempts to isolate and characterize the intermediates and final decomposition products for all seven of the polysulfide complexes will be undertaken. The main intent of this report is to show the effect of differing atmospheres on the decomposition profiles. Due to their ease of preparation,  $\text{Cp}_2\text{TiS}_5$  and  $(\text{Et}_4\text{N})_2\text{MoS}_9$  are currently being tested for their ability to vulcanize rubber.

Acknowledgements

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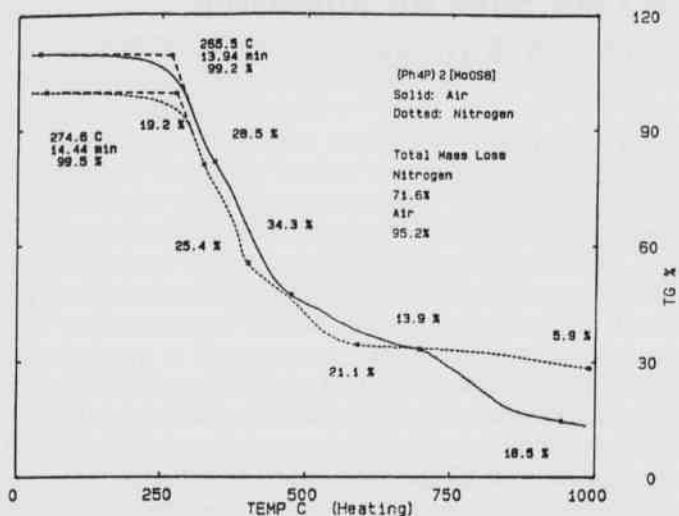


Fig. 4. TGA curves for  $(\text{Ph}_4\text{P})_2\text{MoOS}_8$ . The air curve has been offset by +5%.

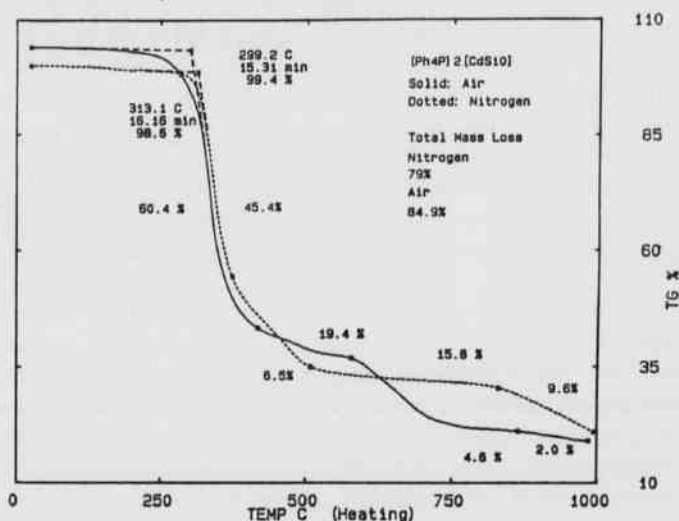


Fig. 6. TGA curves for  $(\text{Ph}_4\text{P})_2\text{CdS}_{10}$ . The air curve has been offset by +5%.

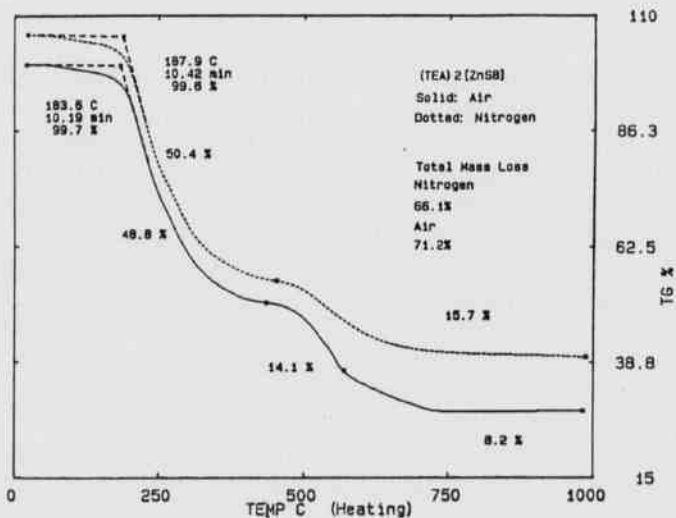


Fig. 5. TGA curves for  $(\text{Et}_4\text{N})_2\text{ZnS}_8$ . The  $\text{N}_2$  curve has been offset by +6%.

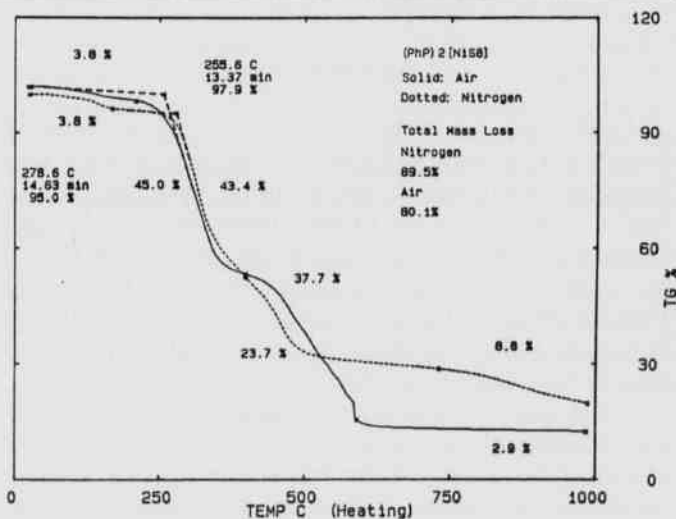


Fig. 7. TGA curves for  $(\text{Ph}_4\text{P})_2\text{NiS}_8$ . The air curve has been offset by +2%.

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