of linear portions of the curves as suggested by Findlay.[4] Liquidus points could not be determined accurately from cooling curves because of supercooling effects and the heat-transfer characteristics of the sample block assembly. All data accepted as measures of the solidus and liquidus points were obtained from the records of melting determinations.

All mixtures melted at temperatures between the melting points of the pure compounds. There was no evidence for the formation of constant-melting mixtures.

Figure 1, a plot of the solidus and liquidus temperatures against composition, shows the lens-shaped diagram characteristic of a continuous series of solid solutions. Each of the points in Figure 1 representing solidus and liquidus temperatures is an average of two to five determinations, and the uncertainty values are standard deviations of the averages. Two minor correction terms were applied to the values of mole fraction of UF_6 calculated from the initial weights of the components: A correction for change in composition owing to partial vaporization of the hexafluorides was made by assuming that the liquid and solid solutions both follow Raoult's law. An exact correction could not be made for the change in composition resulting from destruction of the hexafluoride molecules by the α radiation of the plutonium, but an upper limit for this correction term was calculated by assuming that the destruction of PuF_6 in the condensed phase occurs at a rate of 2%/day.[5]

A review of the physical properties of UF_6 and PuF_6, in the light of Hildebrand and Scott's discussion[6] of the influence of physical properties on solid miscibility, suggests that solid miscibility in the system UF_6–PuF_6 is to be expected. Since the crystals of UF_6 and PuF_6 are isomorphous,[7,8] and the difference between the calculated unit cell volumes is small,[7] both the heat of mixing[9] and the distortion energy will be small,[6] and compatibility of mixtures of UF_6 and PuF_6 crystals is indicated.

The curves in Figure 1 representing the locus of ideal solidus and liquidus temperatures were calculated from the equations developed by Seltz.[10] For the system UF_6–PuF_6, the observed liquidus points all lie in the vicinity of the ideal liquidus curve, whereas the observed solidus points all lie below the ideal solidus curve. Possible causes of the apparent bias of observed solidus points with respect to the ideal solidus curve are soluble impurities, fractional crystallization, and thermodynamic deviation from ideality.

Soluble impurities can lower the solidus points of mixtures with little effect on the liquidus points. In the present work, however, a soluble impurity is an unsatisfactory explanation of the deviation because an impurity also would produce a lowering of the end points of the observed solidus curve, and this behavior was not observed. If equilibrium is not established between solid and liquid phases as a mixture cools, fractional crystallization occurs, resulting in an observed solidus curve which is lower than the true value. In order to avoid the effects of fractional crystallization, it is recommended that a mixture be annealed at a temperature just below the solidus point.[11] Annealing was not considered for the system UF_6–PuF_6 because of the undesirable effects of extensive radiation decomposition of PuF_6, which would have occurred during the time sufficient for solid-state annealing. Since the mixtures were not annealed, a treatment of the deviation of the observed solidus points from ideality in terms of thermodynamic activity coefficients would not be justified.

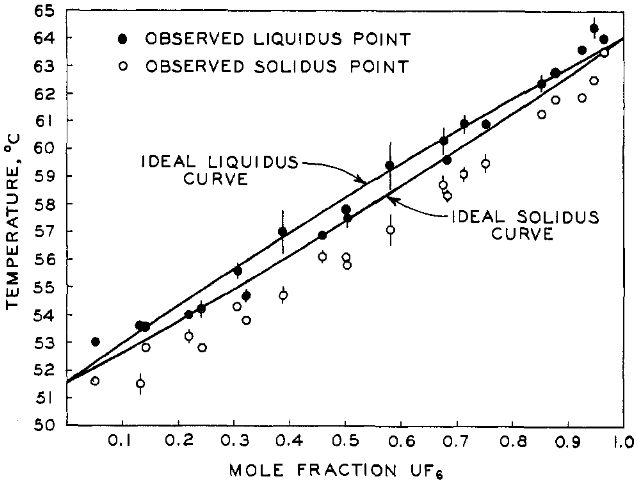

Figure 1.—Melting-point diagram for the system UF_6–PuF_6.

Acknowledgment.—The authors wish to thank Mr. Irving Knudsen, for providing the sample of UF_6, Mr. James Riha, for contributing to the design of the sample tubes, Mr. George Redding and Mr. Milton Haas, for some of the instrumental operations, and Dr. John Barghusen for comments on the paper.

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Reactions of Triphenyltin Azide

BY W. L. LEHN

Received December 3, 1966

Over the past 5 years there has been a marked increase in the number of publications appearing dealing with organometallic azides. During the course of this investigation a review article[1] appeared covering the preparation, physical properties, and chemical properties of these materials. For the sake of discussion and comparison, Thayer classified the organometallic azides as either type A or type B based upon certain chemical and physical properties and has classified triphenyltin azide (I) as type B.

The type-B classification of I appears based at least in part upon the observations of Thayer and West[2] and Reichle[3] that I would not react with triphenylphosphine (IIa) to form the corresponding phosphinimine, P,P,P-triphenyl-N-(triphenylstannyl)phosphinimine (IIIa), eq 1. Reaction according to eq 1 was

$$\begin{array}{lcl} (C_6H_5)_3SnN_3 + R_3P & \longrightarrow & (C_6H_5)_3SnN{=}PR_3 + N_2 \qquad (1) \\ \quad\text{I} \qquad\qquad \text{II} & & \qquad\quad \text{III} \\ \text{IIa, R} = C_6H_5 & & \text{IIIa, R} = C_6H_5 \\ \text{b, R} = C_8H_{17} & & \text{b, R} = C_8H_{17} \\ \text{c, R} = C_4H_9 & & \text{c, R} = C_4H_9 \end{array}$$

reported to have failed even when I and IIa were fused together at 180°. The corresponding reactions involving triphenylgermanium azide and triphenylsilyl azide are reported to give stable phosphinimines, $(C_6H_5)_3MN{=}P(C_6H_5)_3$. It should be noted that the evidence for the formation of the germanium derivative is based upon only infrared evidence with no supporting analytical data in one instance[2] and upon analytical data in the other.[3]

The abrupt change in reactivity reported as one proceeds from the germanium to the tin analog and the nature of the available information prompted a reinvestigation of the reaction of I with IIa–c.

Initial experiments were performed by simply noting the behavior of samples I and IIa and of an equimolar mixture of I and IIa contained in melting point capillaries and heated in a melting point bath. As expected, the samples were observed to melt as the temperature of the bath was slowly raised to temperatures above their respective melting points. However, when the temperature reached and exceeded 160°, gas evolution was observed in the capillary tube containing the mixture. Further experiments were performed by measuring the quantities of gas evolved when known amounts of I, IIa, or mixtures of I and IIa were heated to 200°. While little or no gas evolution was noted from the heating of either pure I or IIa, the theoretical amount of gas corresponding to eq 1 was observed from mixtures of I and IIa. Gas evolution was rapid and was essentially complete in 5 min. The addition of equimolar quantities of I or IIa to preheated, 200° samples of IIa or I, respectively, also resulted in essentially quantitative gas evolution within 5 min. The reaction was repeated on a larger scale by slowly heating equimolar quantities of I and IIa from 160 to 260°. The amount of nitrogen evolved was 94% of the theoretical amount based upon eq 1. The expected product, IIIa, was obtained from *n*-hexane; yield, 55%; mp 132.5–134.0°. *Anal.* Calcd for $C_{36}H_{30}NSnP$: C, 69.03; H, 4.83; N, 2.24; mol wt, 626. Found: C, 69.02, 69.26; H, 4.91, 4.61; N, 1.99, 1.84; mol wt, 626. A small amount of material having an infrared spectrum identical with that of tetraphenyltin was also isolated. The product, IIIa, gives an alkaline reaction with wet red litmus and the odor of NH_3. Triphenyltin hydroxide, identified by comparison of its infrared spectrum with that of an authentic sample, and triphenylphosphine oxide, identified by comparison of its infrared spectrum with that of an authentic sample and by melting point and mixture melting point, have been identified among the hydrolysis products of IIIa.

Tri-*n*-octylphosphine (IIb) was also found to react with I at 200° as indicated to give P,P,P-tri-*n*-octyl-N-(triphenylstannyl)phosphinimine (IIIb) as a viscous oily product. *Anal.* Calcd for $C_{42}H_{66}NSnP$: C, 68.66; H, 9.05; N, 1.91; mol wt, 734. Found: C, 68.50, 68.73; H, 9.31, 9.34; N, 1.67, 1.69; mol wt, 734.

Tri-*n*-butylphosphine (IIc) was also found to react with I. A neat mixture of I and IIc was heated by inserting the reaction tube into an oil bath preheated to 200°. A very vigorous reaction occurred with rapid gas evolution. The volume of gas evolved was equal to the theoretical amount. The product appeared to be hydrolytically unstable. Analysis of the product by vapor-phase chromatography indicated that only a minor amount of unreacted phosphine was present along with a still smaller quantity of the corresponding phosphine oxide; the ratio of peak heights is 3:1 for phosphine:phosphine oxide. Addition of 1 drop of water to the test solution and vapor-phase chromatographic analysis of the resulting mixture less than 10 min later showed no change in the quantity of phosphine present while the ratio of phosphine to phosphine oxide based upon peak heights had changed from 3:1 to 1:4.7. This is considered to be indirect evidence for the presence of and the ease of hydrolysis of the desired phosphinimine, P,P,P-tri-*n*-butyl-N-(triphenylstannyl)-phosphinimine (IIIc). Owing to the hydrolytic instability of this material, no attempt was made to isolate it in a pure state.

The infrared spectra of these materials were obtained on a Model 137 Perkin-Elmer Infracord, IIIa in a KBr pellet and IIIb and c as smears of the neat product between salt plates. While the P=N stretching bond is reported[4] to exhibit characteristic frequencies in the neighborhood of 1260 cm^{-1}, these materials exhibited only very small peaks in this region. The major absorption in this region was a broad, very strong peak centered at about 1160–1170 cm^{-1}. This peak which extended from 1120 to 1200 cm^{-1}, was common to all three spectra, and appeared to be composed of at least three major absorptions.

It is interesting to note that, during the preparation of I according to the procedure of Thayer and West,[2] in one instance, the ether extracts were inadvertantly dried over calcium chloride. The major product iso-

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lated was triphenyltin chloride, the azide apparently having undergone an exchange reaction regenerating the starting chloride.

As a result of this work, it is obvious that I was incorrectly characterized according to the "type" classification.[5]

The investigation of these materials is being continued and will be reported in more detail in a later publication.

Acknowledgment.—This work was supported, in part, by AFML Laboratory Director's Discretionary Funds.

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(5) A referee has pointed out that even before this work, the "type A" and "type B" characterizations of azides did not appear to be very good and that he would not help perpetuate this classification.

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Ultrahigh Pressure-High Temperature Synthesis of Rhombohedral Dichalcogenides of Molybdenum and Tungsten

BY MEYER S. SILVERMAN

Received November 17, 1966

Synthesis of rhombohedral MoS_2 has been discussed by Bell and Herfert,[1] Jellinek, *et al.*,[2] Zelikman, *et al.*,[3] and Semiletov.[4] Occurrence of this form in nature has been reported by Traill,[5] who found it in quartz-feldspar porphyry at the Con mine in Canada, and by Clark,[6] whose find was in a greisenized granite at the Minas da Panasqueira in Portugal. Recently, Arutyunyan and Khurshudyan[7] synthesized amorphous, hexagonal, and rhombohedral molybdenum disulfide from thiomolybdate solutions under hydrothermal conditions in an autoclave. Because of environmental and reaction time differences in their work and ours, a realistic comparison of results is not possible.

Ultrahigh-pressure, high-temperature treatment of elemental Mo–S, W–S, and Mo–Se mixtures in our laboratory resulted in the synthesis in each system of the rhombohedral form of the respective dichalcogenide. In addition, hexagonal molybdenite was transformed directly to the rhombohedral form at extreme temperatures and pressures.

The NBS design tetrahedral anvil apparatus[8] was used for all high-pressure runs. Sample assembly[9] and detailed experimental procedures,[10] including discussion of pressure and temperature calibrations, have been reported earlier. Phase identification was made principally by X-ray powder diffraction methods.

Synthesis of the rhombohedral form of MoS_2 from the elements appears to be mainly temperature dependent though in most reactions very high pressures were necessary to contain the volatiles at temperatures orders of magnitude above their atmospheric vaporization points. For example, when a 1:2 elemental Mo–S mixture was hot pressed at 27 kbars, 900°, and also at 47 kbars, 800°, only hexagonal molybdenite formed after a 5-min treatment. At 47 kbars, 1050°, 74 kbars, 1100°, and up to 70 kbars, 2000°, quantitative yields of the rhombohedral form were obtained.

With a 1:1 atomic ratio Mo–S mixture, only Mo_2S_3 was produced over pressure and temperature ranges of 10–75 kbars and 800–2200°. The starting mixture stoichiometry appears to be an important factor in determining the final product.

Normal hexagonal molybdenite was completely transformed to the rhombohedral form at 40–75 kbars, 1900–2000°, in 1–5 min. The temperatures required for this direct transformation were much higher than those needed for synthesis of the rhombohedral form from the elements.

A new phase that analyzed very closely to stoichiometric $MoSe_2$, and is also rhombohedral,[11] was synthesized from an elemental Mo–Se 1:2 atomic ratio mixture. Below about 800° from 17 to 78 kbars, only the hexagonal form was prepared; from 1100 to 1400°, over the same pressure range, mixed products containing hexagonal and rhombohedral phases were found. At 47 kbars, 1700°, and at 70 kilobars, 2000°, complete reactions occurred as indicated by X-ray powder diffraction patterns of the high-pressure solids. The major lines as reported by James and Lavik[12] for hexagonal $MoSe_2$ are compared in Table I with those obtained from samples treated above 1100° at ultrahigh pressure. Our *d*-spacing data are in good agreement with calculations we have made from lattice constants reported by Towle, *et al.*[11]

When the rhombohedral $MoSe_2$ obtained from a high-pressure run was heated *in vacuo* at 1000° in a quartz tube, it reverted to the stable hexagonal form, as indicated by the X-ray powder pattern of the residue.

When a W–S 1:2 mixture was compressed at 45 kbars and heated to 1800° for 2–3 min, a silver-gray soft product formed which was completely rhombohedral. This form of tungsten disulfide had been reported earlier by Wildervanek and Jellinek;[13] however, their

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