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.

(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.

CONTRIBUTION FROM PENNSALT CHEMICALS CORPORATION,
RESEARCH AND DEVELOPMENT DEPARTMENT,
KING OF PRUSSIA, PENNSYLVANIA

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

BY MEYER S. SILVERMAN

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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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(11) Just after this paper was submitted, a report on this high-pressure polymorph appeared: L. P. Towle, V. Oberbeck, B. E. Brown, and R. E. Stajdohar, *Science*, **154**, 895 (1966). It is interesting that the transformation from hexagonal $MoSe_2$ studied by Towle and co-workers is far more sluggish (incomplete reactions in 1 hr) than the synthesis directly from the elements (complete reactions in 1–5 min). This same difference was noticed in the Mo–S system described above; *i.e.*, more severe conditions are required for the hexagonal to rhombohedral transformation than for synthesis of the rhombohedral form from the elements.

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TABLE I

$MoSe_2$ X-RAY POWDER DIFFRACTION DATA

Hexagonal[a] d, A	Hexagonal[a] I	Rhombohedral h k l	Rhombohedral d, A (obsd)[b]	Rhombohedral I	Rhombohedral d, A (calcd)[c]
6.44	78				
2.839	63	0 0 3	6.4	100	6.46
2.369	100	1 0 1	2.81	30	2.82
1.914	39	1 0 4	2.46	50	2.46
1.641	49	1 0 5	2.29	70	2.30
1.152	33	1 0 7	1.98	50	1.99
		10 1 0	1.61	70	1.60
		2 0 5	1.34	30	1.34

[a] Reference 12. [b] Cu Kα radiation, λ 1.5418 A; intensities visually estimated. [c] Calculated from lattice constants a = 3.292 A and c = 19.392 A, obtained from ref 11.

products, obtained from the decomposition of WS_3, were always mixed with the hexagonal form. One attempt to prepare the rhombohedral form from the hexagonal form at a pressure of 44 kbars and 2000° for 5 min resulted in an incomplete reaction with a strong X-ray powder diffraction pattern of the starting material still evident.

The strongest lines in the X-ray pattern of uncontaminated rhombohedral WS_2 listed in Table II agree quite well with the *d* spacings calculated from Wildervanek and Jellinek's lattice constants.[13]

TABLE II

RHOMBOHEDRAL WS_2, X-RAY POWDER DIFFRACTION DATA

h k l	d, A (obsd)[a]	I	d, A (calcd)[b]
0 0 3	6.1	100	6.2
0 0 6	3.08	30	3.08
1 0 1	2.71	25	2.71
1 0 4	2.35	20	2.35
0 1 5	2.20	20	2.20
0 0 9	2.06	50	2.06
1 1 0	1.577	30	1.580
0 0 12	1.530	30	1.542

[a] Cu Kα radiation, λ 1.5418 A; intensities visually estimated. [b] Calculated from lattice constants a = 3.162 A and c = 18.50 A taken from ref 13.

Runs with 1:2 atomic ratio tungsten–selenium mixtures covering a very wide pressure–temperature profile up to 70 kbars and 2400° gave only the hexagonal diselenide. Neither was any change apparent when hexagonal WSe_2 was used as starting material. All high-pressure runs with Mo–Te and W–Te 1:2.1 atomic ratio mixtures either did not react or formed the known product hexagonal $MoTe_2$[14] or WTe_2 and the high-temperature form of $MoTe_2$ both reported recently by Brown.[15] The last was obtained in partial yields at 45 kbars, 1800°, and 3 min and in quantitative amounts at 60 kbars, 2200°, and 2 min. Brown[15] reported 900° as the dividing line at atmospheric conditions between hexagonal and high-temperature $MoTe_2$.

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CONTRIBUTION FROM ROHM AND HAAS COMPANY,
REDSTONE RESEARCH LABORATORIES,
HUNTSVILLE, ALABAMA 35807

The Chlorofluorination of Acetonitrile. Preparation of N-Chloro-N-fluoro-1,1-difluoroethylamine

BY MAX LUSTIG

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It has been recently reported that the fluorination of cyanogen chloride with elementary fluorine leads to the formation of N-chloro-N-fluorotrifluoromethylamine, CF_3NFCl,[1] the first member of the class of compounds having the general formula RNClF. Chlorine(V) fluoride (ClF_5),[2] whose chemistry has been substantially unexplored, also can be used to prepare a compound of the same type by its reaction with acetonitrile to produce N-chloro-N-fluoro-1,1-difluoroethylamine, CH_3CF_2NFCl, as the major product.

Experimental Section

Reagents.—Acetonitrile (Spectro Grade) was obtained from Eastman Organic Chemicals. Chlorine(V) fluoride was prepared by the literature method.[2]

Apparatus.—A $^5/_8$-in. o.d. copper tubing vacuum apparatus containing Hoke 413K valves and equipped with a Helicoid pressure gauge and a fractionation train consisting of three 65-ml Kel-F or Teflon traps was used for manipulating volatile compounds. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrometer using a 10-cm path length stainless steel gas cell with AgCl windows. Fluorine-19 and hydrogen-1 nmr spectra were taken with a Varian Model C4310 spectrometer operating at 40 Mc. Samples were measured neat in 5-mm o.d. Pyrex tubes at 25° using trifluoroacetic acid (TFA) and tetramethylsilane (TMS) as external standards for the ^{19}F and ^1H spectra, respectively. Mass spectra were obtained with a Consolidated Engineering Model 21-620 spectrometer operating with an ionization potential of 100 v.

Preparation of CH_3CF_2NFCl.—In a typical reaction both reactants, ClF_5 and CH_3CN (1.5 mmoles each), were charged into a Kel-F trap in the fractionation train at −196°. The mixture was allowed to warm to room temperature over a 1-hr period and then stand for an additional 0.5 hr to ensure completion of the reaction. [*Caution:* This reaction appeared to be smooth when Spectro Grade acetonitrile was used, but violent explosions occurred when distilled but non-Spectro Grade acetonitrile was employed.] The reaction mixture was cooled to −196° and a small amount of noncondensable material was pumped out.

The principal products were CH_3CF_2NFCl (1.2 mmoles or 80% yield), CH_3CF_3, and Cl_2. Smaller quantities of a compound tentatively identified as $CH_3CF_2NNCF_2CH_3$ (*ca.* 0.01 mmole), as well as CF_4 and N_2O, were also present; the latter presumably was formed from the small quantities of chlorine oxides and oxyfluorides present in the chlorine(V) fluoride. The results were substantially the same when a Monel cylinder was used as a reactor. The yields were based upon the quantity of acetonitrile originally used after measurement of the quantities of each purified product component. Purity was established by chromatography as well as by mass, nmr, and infrared spectroscopy. The quantity and per cent composition of gaseous samples were determined by *PVT* measurement and by mass spectrometric analysis. The spectrometer was calibrated with

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