TABLE III

FUNDAMENTAL FREQUENCIES (CM.$^{-1}$) OF GeF_6^{2-}

No.	Species	Intensity	Activity	Assignment
1	a_{1g}	s	Raman	627
2	e_g	w	Raman	454
3	f_{1u}	s	Infrared	600
4	f_{1u}	s	Infrared	350
5	f_{2g}	m	Raman	318
6	f_{2u}	..	Inactive	...

metrical for Rb_2GeF_6 than for K_2GeF_6, where the appearance of a higher frequency contribution to the intensity indicates two bands at 602 and 635 cm.$^{-1}$. Moreover, a very weak band near 465 cm.$^{-1}$ in the spectrum of the potassium salt correlates with the similar band observed at 452 cm.$^{-1}$ in the spectrum of $BaGeF_6$.

On the basis of the above evidence, it would seem that additional bands, over that expected for a regular octahedral ion, indicate a lowered site symmetry. The opposite may not always be precisely true, however. It also follows that when additional bands are observed in the spectra of complex molecules which contain very symmetrical ions, the spectral complexities do not necessarily arise from structural changes in the ions but may only reflect changes in their site symmetries.

Assignments.—The observed Raman and infrared spectral data of fluorogermanic acid solutions and of solid Cs_2GeF_6 are useful for establishing the fundamental frequencies of the hexafluorogermanate ion. The Raman line at 627 cm.$^{-1}$ is the strongest in the spectrum and is therefore assigned to the totally symmetric a_{1g} stretching vibration. The weak and broad band centered at 454 cm.$^{-1}$ is assigned to ν_2 (e_g) because, in general, such a stretching vibration occurs at a higher frequency than the bending mode, ν_5, of the f_{2g} species.

TABLE IV

INFRARED SPECTRA OF $(NH_4)_2GeF_6$ AND $BaGeF_6$[a]

$(NH_4)_2GeF_6$ (O^5_h)			$BaGeF_6$ (D^3_{3d})		
No.	Species	Assignment	No.	Species	Assignment
1	a_{1g}	...	1	a_{1g}	...
2	e_g	...	2	a_{1g}	...
3	f_{1u}	598	3	a_{1u}	Inactive
4	f_{1u}	349	4	a_{2u}	602
5	f_{2g}	...	5	a_{2u}	337
6	f_{2g}	Inactive	6	e_u	635
			7	e_u	452
			8	e_u	367
			9	e_g	...
			10	e_g	...

[a] Frequencies are given in cm.$^{-1}$.

By the same reasoning, the infrared active bands at 600 and 350 cm.$^{-1}$ are assigned to ν_3 and ν_4, respectively. The remaining fundamental, ν_6 (f_{2u}), is inactive. The assignments are summarized in Table III and the data and assignments for the ammonium and barium hexafluorogermanate salts are listed in Table IV. For the barium salt, e_u and a_{2u} fundamentals are assigned arbitrarily for we have no reasonable means of establishing which is which at this time. Individual data for K_2GeF_6 and Rb_2GeF_6 appear in the text but are not reproduced again in tabular form.

Acknowledgments.—We are grateful to Drs. G. E. Walrafen and L. H. Sharpe for the use of the Raman and infrared spectrophotometers. The generous gift of samples of K_2GeF_6 and Rb_2GeF_6 from Sylvania Electric Products, Inc., is gratefully acknowledged. We also wish to thank an anonymous referee for suggesting that infrared spectra of samples in Nujol mulls would eliminate or confirm the possibility of double decomposition occurring during the preparation of CsI pellets.

CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY,
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Preparation and Crystal Data for Lanthanide and Actinide Triiodides[1]

BY L. B. ASPREY, T. K. KEENAN, AND F. H. KRUSE

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Lattice parameters and crystal structure types for twelve lanthanide triiodides (excepting only promethium and europium) have been determined. Similar data have been obtained for yttrium, americium, and plutonium triiodides. Two structure types occur in the lanthanide triiodides. The lighter members, LaI_3 through NdI_3, have orthorhombic symmetry ($PuBr_3$ type) while the heavier members of the series are hexagonal (BiI_3 type). An analogous transition is observed in the actinide series between PuI_3 and AmI_3, the former being orthorhombic and the latter hexagonal. Treatment of AmI_3 with hydrogen at elevated temperatures gave no evidence of a divalent compound of americium.

Introduction

Though most of the lanthanide and many actinide trifluorides, trichlorides, and tribromides have been prepared and identified, few investigations of the chemistry of the corresponding triiodides have been published. The triiodides of lanthanum, neodymium, uranium, neptunium, plutonium, and americium were reported to have an orthorhombic structure.[2] Druding

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] W. H. Zachariasen, *Acta Cryst.*, **1**, 265 (1948).

and Corbett[3] stated that NdI_3 underwent a phase transition from orthorhombic to hexagonal at 574°; this was confirmed by Dworkin and Bredig.[4] Another study by Krause, *et al.*,[5] indicated that YI_3 has the hexagonal BiI_3 structure type.

Previous studies of the lanthanide trihalides show that a change in structure type takes place near the midpoint of the series. Such a change is observed in the lanthanide trifluorides,[6] trichlorides,[7,8] and tribromides,[2,9] although complete crystallographic data have not always been reported for all members of the series of a given trihalide. In fact, a recent crystal structure analysis of $TbCl_3$[10] revealed a third structure type appearing at the point of "transition" [*i.e.*, $GdCl_3$ (UCl_3 type) $\rightarrow$ $TbCl_3$($PuBr_3$ type) $\rightarrow$ α-$DyCl_3$(YCl_3 type)]. Of the actinide trihalides which have been reported, a change in structure type has been noted only for the tribromides. The transition occurs at neptunium tribromide, which is dimorphic; α-$NpBr_3$ shows hexagonal symmetry while β-$NpBr_3$ is orthorhombic.[2,9] In order to expand our knowledge of these transitions and the related chemistry of triiodides, it was decided to prepare as many as possible of the lanthanide and actinide triiodides. With the latter, microscale preparations were necessary because of radiation and health hazards.

Experimental

General.—Unless otherwise stated, all chemicals were A.R. grade and used without further purification. The lanthanide metals were obtained from various sources, including Lindsay Rare Earth Chemicals, Semi-Elements, Inc., and Research Chemicals Company, and exceeded 99.5% purity. Plutonium metal of >99.5% purity was available at Los Alamos. (Plutonium supplied by Joseph Leary of this laboratory.) Americium stock solutions contained <0.5% total cation impurity. Tank hydrogen was purified by passage through a heated silver–palladium alloy valve prior to use.

Several methods are available to prepare anhydrous lanthanide halides. These are summarized in several recent review papers[11-13]; however, we found that a technique described by Asprey and Kruse[14] gave excellent results with relative ease of manipulation. This method involves the reaction of a lanthanide metal with mercuric iodide, *i.e.*

$$2\text{Ln (any lanthanide metal)} + 3HgI_2 \xrightarrow{\Delta} 2LnI_3 + 3Hg$$

In addition to yielding an excellent triiodide product, the principal advantages of this method are: (1) the reactant, HgI_2, is stable at room temperature and can be weighed in air, and (2) the byproduct Hg can easily be separated by distillation from the triiodide.

Preparation of LaI_3, CeI_3, PrI_3, NdI_3, GdI_3, TbI_3, HoI_3, ErI_3, TmI_3, LuI_3, YI_3, and PuI_3 by the Reaction of HgI_2 with the Metallic Element.—In a typical run, *ca.* 0.2–0.5 mg.-atom of the reactant metal was used with a slight deficiency of HgI_2 (*ca.* 99% of theoretical). The two reactants were placed in a 7 × 50 mm. quartz tube which was evacuated to *ca.* 5×10^{-6} mm. and sealed. The tube was placed in a muffle furnace; the temperature was slowly raised and held at 500° for 2 hr., followed by slow cooling for 8 hr. The absence of the orange-red HgI_2 indicated completion of the reaction. One end of the tube was then placed in a small furnace to distil free mercury from the desired triiodide product. The tube was transferred to an inert-atmosphere (helium) glove box, opened, the triiodide ground in a mortar, and an X-ray capillary loaded. In the experiment involving plutonium, all such operations were carried out in a conventional radiochemical glove box containing an inner polyethylene bag with integral glove forms.[15] Dry helium was used to flush oxygen and water vapor from this device prior to opening the reaction tube.

Preparation of SmI_3, YbI_3, and Attempted Preparation of EuI_3 by the Reaction of the Metallic Element with Elemental Iodine.—The reaction with HgI_2 was not satisfactory when used with samarium, ytterbium, and europium. It was necessary to utilize the thermodynamically more favorable system involving direct reaction of the lanthanide metal with iodine. In a typical run, 0.5 mg.-atom of metal was placed in a heavy-walled quartz reaction tube. This tube was formed from 10-mm. quartz tubing having a wall thickness of 2.5 mm. An amount of iodine required to give the desired pressure at the experimental temperature was then introduced. The equilibrium pressure was estimated, assuming ideal gas behavior, from the known volume of the tube and the observed temperature. With the iodine cooled in an ice bath, the reaction tube was evacuated to 0.001 mm. and sealed off. For protection against possible explosion or implosion, the quartz tube was placed in a steel pipe capped at both ends with a vented cover. The tube assembly was placed in a muffle furnace.

Following a run, the excess iodine was distilled to one end of the tube by warming the opposite end. The reaction tube was transferred to the inert atmosphere box, opened, and the product removed. The sample was ground to a fine powder and an X-ray capillary prepared as before.

The following conditions were found adequate to yield satisfactory samples of samarium and ytterbium. Samarium: slow heating to 500° over 8 hr., holding at 500° for 2 hr. with an iodine pressure of 5 atm. at 500°. Ytterbium: slow heating to 500° over 8 hr., holding at 500° for 16 hr. with an iodine pressure of 30 atm. at 500°.

Similar experiments with europium, involving temperatures as high as 600° and pressures of 100 atm. of iodine, gave an unidentified product not isostructural with other lanthanide triiodides.

Preparation of AmI_3 by the Reaction of $AmCl_3$ with NH_4I.—Americium triiodide was not prepared by either of the previous methods because of the difficulty in obtaining pure americium metal. Using an X-ray capillary as a container, the metathetical reaction, $AmCl_3 + 3NH_4I \xrightarrow{\Delta} AmI_3 + 3NH_4Cl$, was carried out *in situ* using a flow system to sweep the volatile NH_4Cl away from the triiodide.

The starting material was an anhydrous mixture of $AmCl_3$ in a matrix of NH_4Cl. This was obtained by evaporation of an HCl solution containing a 10:1 mole ratio of NH_4Cl:$AmCl_3$. Such a salt mixture is quite stable in air and may be ground and handled without deliquescence. After preparation and grinding a small quantity of this material (*ca.* 50 μg. of americium) was introduced into a quartz capillary, which was drawn from an 18/9 semi-ball joint. Figure 1 shows a diagram of the experimental apparatus. The furnace was mounted on wheels and could be moved as desired. A large excess of NH_4I was added to the tube containing the NH_4Cl–$AmCl_3$ mixture and the joint sealed with Apiezon-

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(3) L. F. Druding and J. D. Corbett, *J. Am. Chem. Soc.*, **83**, 2462 (1961).

(4) A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.*, **67**, 697 (1963).

(5) B. H. Krause, A. B. Hook, and F. Wawner, *Acta Cryst.*, **16**, 848 (1963).

(6) A. Zalkin and D. H. Templeton, *J. Am. Chem. Soc.*, **75**, 2453 (1953).

(7) D. H. Templeton and G. F. Carter, *J. Phys. Chem.*, **58**, 940 (1954).

(8) D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 5237 (1954).

(9) A. J. C. Wilson, "Structure Reports," Oosthoek, Utrecht, Netherlands, 1948, Vol. 11, pp. 276 and 282.

(10) J. D. Forrester, A. Zalkin, D. H. Templeton, and J. C. Wallman, *Inorg. Chem.*, **3**, 185 (1964).

(11) M. D. Taylor, *Chem. Rev.*, **62**, 503 (1962).

(12) M. D. Taylor and C. P. Carter, *J. Inorg. Nucl. Chem.*, **24**, 387 (1962).

(13) N. H. Kiess, *J. Res. Natl. Bur. Std.*, **67A**, 343 (1963).

(14) L. B. Asprey and F. H. Kruse, *J. Inorg. Nucl. Chem.*, **13**, 32 (1960).

(15) This is a polyethylene bag with molded glove forms with appropriate provision for entry and escape of gas. They are manufactured by Instruments for Research and Industry, Cheltenham, Pa.

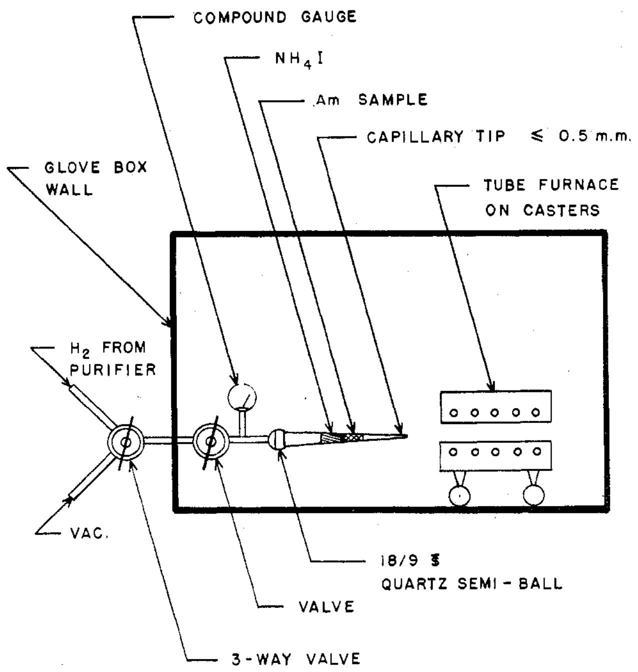

Fig. 1.—Apparatus for preparation of actinide triiodides.

W to the vacuum manifold. The system was evacuated to $<5 \times 10^{-6}$ mm. The furnace was placed around the sample and held at 100–130° for 1 hr. under vacuum to remove any residual moisture. The system was then pressurized with hydrogen to ca. 3 p.s.i. and the tip of the capillary was clipped with a scissors. (The samples adhered to the capillary and usually did not blow out the open tip in the hydrogen stream.) The furnace was heated to 400° and moved slowly upstream from the open tip. The NH_4Cl was sublimed away first from the NH_4Cl–$AmCl_3$ mixture, and then the NH_4I was sublimed over the $AmCl_3$, converting it to the triiodide. After the NH_4I was removed the hydrogen pressure was lowered to slightly over atmospheric, the open tip of the capillary was sealed with a torch, and the system was evacuated again. The furnace was again placed around the sample and heated to 400° to ensure that any residual ammonium halide was sublimed away from the americium triiodide. The capillary was sealed under vacuum and removed for X-ray analysis. Very little trouble was experienced with α activity on the outside of such capillaries.

X-Ray Diffraction Techniques.—In all cases, the triiodide products were identified by X-ray powder diffraction photographs. Diffraction equipment included a basic Norelco X-ray unit using filtered copper radiation, 114.6-mm. Debye–Scherrer cameras, and Ilford Type G film. Since the structure type for each triiodide was known or could be postulated, it was possible to compute a typical pattern (hkl, I_0, 2θ, d-spacing) for indexing the X-ray patterns. Subsequently, another computer program was employed to obtain a least-squares refinement of the lattice dimensions. Normally, two cycles with these programs sufficed to give the final parameters. The powder pattern generating program was the POWD code supplied by Smith[16]; the least-squares program was the MET-124 code supplied by Mueller and Heaton.[17] Both programs were used on an IBM-7094 computer.

Results

Analysis of the powder diffraction data shows that every lanthanide and actinide iodide examined falls into one of two structure types. The lighter lanthanide and actinide triiodides are orthorhombic, $PuBr_3$ structure type.[9] The triiodides of the heavier members of the series are hexagonal, BiI_3 structure type.[5] It should be pointed out that more than one hexagonal structure for BiI_3 can by found in the crystallographic literature. The structure described by Wyckoff[18] produced a calculated powder pattern in agreement with the pattern we obtained from purified BiI_3 as well as the BiI_3-type rare earth triiodides. The change in structure type from orthorhombic to hexagonal takes place between neodymium and samarium triiodides in the lanthanide series and between plutonium and americium triiodides in the actinide series. Table I lists lattice constants and molecular volumes for the compounds studied; the error limits shown are standard deviations. Partial powder X-ray diffraction patterns for typical orthorhombic (CeI_3) and hexagonal (DyI_3) types are presented in Table II. The variation in molecular volume with atomic number for the known lanthanide iodides is plotted in Fig. 2. The abrupt change in molecular volume accompanying the change in structure type is clearly shown. A similar abrupt change is found in the actinide triiodides; the molecular volume of plutonium triiodide (orthorhombic) is 150.4 Å.³ and that of americium triiodide (hexagonal) is 163.3 Å.³.

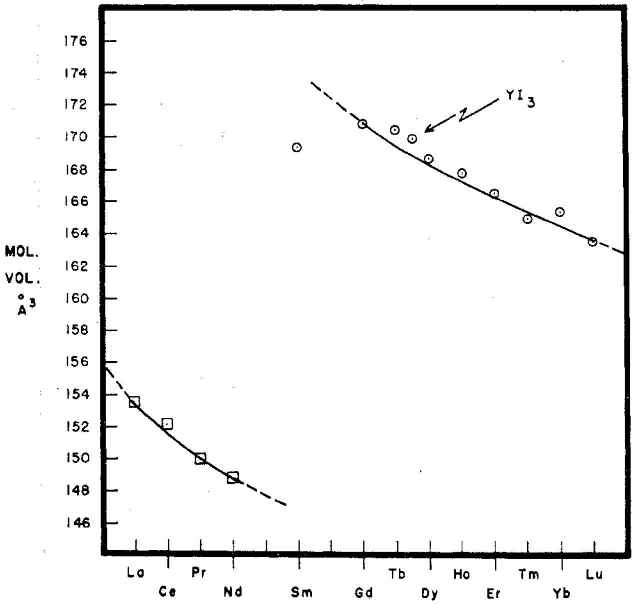

Fig. 2.—Variation of molecular volume with atomic number for lanthanide trihalides.

No evidence was obtained for the preparation of an orthorhombic AmI_3 phase as reported some years ago[2] (no details were given for the preparation of that americium compound). In any event, under widely varying conditions, we always obtained AmI_3 of hexagonal

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[16] D. K. Smith, "A Fortran Program for Calculating X-Ray Powder Diffraction Patterns," University of California Report UCRL-7196 (1963).

[17] M. H. Mueller and L. Heaton, "Determination of Lattice Parameters with the Aid of a Computer," Argonne National Laboratory Report ANL-6176 (1961).

[18] R. W. G. Wyckoff, "Crystal Structures," Interscience, New York, N. Y., 1960, V, text p. 12.

Table I

Lattice Constants and Molecular Volumes of Some Lanthanide and Actinide Triiodides

(1) Structure Type $PuBr_3$

Orthorhombic; $n = 4$; space group Cmcm-D^{17}_{2h}

Compound	a_0, Å.	b_0, Å.	c_0, Å.	Mol. vol., Å.^{3}
LaI_3	4.37 ± 0.02	14.01 ± 0.02	10.04 ± 0.01	153.6
CeI_3	4.341 ± 0.008	14.00 ± 0.01	10.015 ± 0.004	152.2
PrI_3	4.309 ± 0.008	13.98 ± 0.01	9.958 ± 0.008	150.0
NdI_3	4.284 ± 0.004	13.979 ± 0.008	9.948 ± 0.004	148.9
PuI_3	4.33 ± 0.02	13.95 ± 0.03	9.96 ± 0.02	150.4

(2) Structure Type BiI_3

Hexagonal; $n = 6$; space group R$\bar{3}$-C^2_{3i}

Compound	Hexagonal dimensions		Rhombohedral dimensions		Mol. vol., Å.
	a_0, Å.	c_0, Å.	a_0, Å.	α^0	
SmI_3	7.490 ± 0.008	20.80 ± 0.04	8.172	54.44	168.4
GdI_3	7.539 ± 0.008	20.83 ± 0.02	8.196	54.77	170.8
TbI_3	7.526 ± 0.004	20.838 ± 0.008	8.193	54.68	170.4
DyI_3	7.488 ± 0.004	20.833 ± 0.008	8.179	54.48	168.6
HoI_3	7.474 ± 0.004	20.817 ± 0.008	8.171	54.43	167.8
ErI_3	7.451 ± 0.008	20.78 ± 0.02	8.155	54.37	166.5
TmI_3	7.415 ± 0.004	20.78 ± 0.03	8.141	54.18	164.9
YbI_3	7.434 ± 0.008	20.72 ± 0.03	8.132	54.40	165.3
LuI_3	7.395 ± 0.008	20.71 ± 0.02	8.117	54.20	163.5
AmI_3	7.42 ± 0.03	20.55 ± 0.08	8.08	54.67	163.3
YI_3	7.505 ± 0.004	20.88 ± 0.01	8.198	54.48	169.8

Table II

Partial Powder X-Ray Patterns

(A) CeI_3—Orthorhomic ($PuBr_3$-type)

hkl	d_{obsd}, Å.	d_{calcd}, Å.	I/I_0[a]
020	6.93	7.00	4
040	3.48	3.50	2
041	3.29	3.30	3
112 130	3.19	3.18 3.17	7
131	3.030	3.030	10
023	3.000	3.012	9
042	2.860	2.869	6
132	2.680	2.684	2
113	2.601	2.600	6
004	2.498	2.504	2
024	2.351	2.357	1
133 151	2.296	2.302 2.291	4
061	2.266	2.272	2
200	2.179	2.171	4
152	2.130	2.130	1
062	2.111	2.115	7

(B) DyI_3—Hexagonal (BiI_3-type)

hkl	d_{obsd}, Å.	d_{calcd}, Å.	I/I_0[a]
003	7.00	6.94	4
015 006	3.46	3.51 3.47	5
113	3.29	3.30	10
116	2.54	2.55	8
122	2.31	2.39	1
300	2.165	2.162	6
303	2.068	2.064	2
119	1.968	1.969	9
306	1.837	1.835	3
223	1.810	1.807	4
00·12	1.736	1.736	6
226	1.651	1.648	4
039	1.580	1.580	1
229	1.458	1.457	3
413	1.389	1.389	4
30·12	1.355	1.354	5

[a] Relative visual intensities based on scale of 10 as maximum.

symmetry. No evidence was obtained for divalent americium. Under conditions which produced SmI_2, EuI_2, and YbI_2, only hexagonal AmI_3 was prepared. Some evidence was also obtained for the expected hexagonal symmetry in CmI_3. However, a more complete study of the halides of americium and curium is currently under way in this laboratory and the results will be announced in the near future.

The high pressure I_2 experiments with europium did not give a product whose X-ray powder pattern could be indexed as either the orthorhombic or hexagonal forms of triiodide. Either EuI_3 was not formed or, possibly, it has a new and different structure.

Forrester, *et al.*,[10] found that $TbCl_3$ and a polymorph of $DyCl_3$ had the orthorhombic $PuBr_3$ structure type, not exhibited by any other rare earth trichloride. A detailed study of the tribromides and triiodides of Sm, Eu, and Gd should clarify the changes in phase type taking place in this series.

In Table I the molecular volume of the hexagonal compound, SmI_3, is 168.4 Å.^{3}, somewhat less than that of GdI_3. This suggests that the SmI_3 compound may have contained some SmI_2 in solid solution, or the lower value may be due to effects yet unidentified.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, AND INORGANIC MATERIALS RESEARCH DIVISION OF THE LAWRENCE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA

Disilanylphosphine and Disilylphosphine

BY SUDARSHAN D. GOKHALE AND WILLIAM L. JOLLY

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Disilanylphosphine, $Si_2H_5PH_2$, and disilylphosphine, $(SiH_3)_2PH$, have been prepared and identified by n.m.r. spectroscopy. Disilanylphosphine has been isolated and characterized by determination of its infrared spectrum, its vapor pressure, and the products of its hydrolysis and pyrolysis.

Introduction

Silylphosphine, SiH_3PH_2, was first prepared by the pyrolysis of a mixture of silane and phosphine.[1,2] Trisilylphosphine, $(SiH_3)_3P$, was prepared by the reaction between bromosilane and potassium dihydrogen phosphide.[3]

$$3SiH_3Br + 3KPH_2 \rightarrow (SiH_3)_3P + 2PH_3 + 3KBr$$

Both silylphosphine and a material of empirical composition Si_2PH_7 were detected in the products of the decomposition of a mixture of silane and phosphine in a silent electric discharge.[4] The compound Si_2PH_7 intrigued us because of the possibility of the existence of two structural isomers. The purpose of the present investigation was to prepare macroscopic amounts of the material and, if possible, to identify, separate, and characterize the isomers.

Experimental

A mixture of silane and phosphine in a mole ratio of 2:1 was circulated in a closed system through an ozonizer-type electric discharge tube at $-78°$ followed by a trap at $-95°$ (toluene slush) until practically all the reaction gases were consumed. A similar method had been used earlier for the preparation of higher silanes,[5,6] germanes,[7] and "mixed" (ternary) hydrides.[4,8] The products of the reaction were first subjected to fractional condensation in a series of traps at $-63°$ (chloroform slush), $-95°$ (toluene slush), $-130°$ (*n*-pentane slush), and $-196°$ (liquid nitrogen). The unreacted silane and phosphine condensed in the $-196°$ trap, and disilane and silylphosphine condensed in the $-130°$ trap. Diphosphine, trisilane, and part of the Si_2PH_7 condensed in the $-95°$ trap. The trap at $-63°$ contained the higher silanes, higher ternary hydrides, and the remainder of the Si_2PH_7. The condensate in the $-95°$ trap was allowed to stand at room temperature for 1 week, during which time the diphosphine decomposed almost completely. After pumping out a little hydrogen which had formed, the mixture was fractionally condensed in a trap at $-83°$ (ethyl acetate slush) followed by a trap at $-196°$. Phosphine, trisilane, and only a trace of Si_2PH_7 collected in the $-196°$ trap. The proton n.m.r. spectrum of the material collected in the $-83°$ trap showed clearly the presence of both $(SiH_3)_2PH$ and $Si_2H_5PH_2$ in approximately equal amounts, as well as some trisilane. The condensate in the $-63°$ trap was passed through a $-45°$ trap (chlorobenzene slush) in order to remove most of the higher molecular weight compounds from the Si_2PH_7. The Si_2PH_7-rich condensates were injected into a gas chromatographic column containing silicone oil on firebrick at 70°. We were never able to elute disilylphosphine from the column; we assume that it was thermally decomposed on the column. The observed presence of small amounts of phosphine and silylphosphine in all the elution fractions is consistent with this interpretation. The method of injecting the mixture in the chromatographic apparatus and of collecting the different fractions was similar to that used in the preparation of the tetrasilanes.[6] It was found that ordinary injection needles became clogged in spite of all reasonable precautions. Gas-tight syringes with Teflon-tipped plungers and 22- or 23-gauge needles were more satisfactory. When syringes with removable needles were used, a little grease had to be used at the joints to make them gas-tight. The chromatograms showed that the retention times of Si_3H_8 and $Si_2H_5PH_2$ were in the proportion of roughly 1:2. The peak of $Si_2H_5PH_2$ preceded the peaks of the tetrasilanes. It was found that the $SiH_3SiH_2PH_2$ was contaminated with a small amount of $(Si_2H_5)_2O$. By keeping the contaminated product in a trap at $-78°$ and by pumping out the vapors into a trap at $-196°$, it was possible to recover pure disilanylphosphine. Starting with 250 mmoles of the SiH_4–PH_3 mixture, about 3 mmoles of $Si_2H_5PH_2$ was obtained.

The proton n.m.r. spectra were obtained with a Varian Associates A-60 n.m.r. spectrometer, and the infrared spectra with Perkin-Elmer Infracord spectrophotometers (NaCl Model 137B and KBr Model 137). The n.m.r. spectrum for pure liquid $SiH_3SiH_2PH_2$ is given in Fig. 1. Although $(SiH_3)_2PH$ was not obtained in pure form, the relevant portions of the spectrum of a mixture containing about 30% $(SiH_3)_2PH$ are given in Fig. 2 and 3. The infrared spectrum of disilanyl phosphine shows absorptions, as seen in Fig. 4, at the following frequencies (cm.$^{-1}$): 2300 (w), 2150 (s), 1070 (sh, w), 990 (w), 942 (m), 932 (m), 888 (s), 877 (s), 790 (sh, s), 784 (s), 736 (w), 728 (w), 724 (w), 637 (w), 628 (w), and 475 to 515 (w, br).

The vapor pressure of disilanylphosphine was found to be 31 ± 1 mm. at 0° and 81 ± 1 mm. at 20°. It was found during the fractional condensation that the isomers $(SiH_3)_2PH$ and $Si_2H_5PH_2$ could not be separated from each other even partially. Thus we conclude that the volatilities of the two isomers are very similar. Gas-density molecular weights of 92.1, 95.5, and 96.0 were obtained for three different samples at room temperature (calculated for Si_2PH_7: 94.2). The mass spectrum of disilanylphosphine showed bands corresponding to the fragments Si_2P^+–$Si_2PH_7^+$, Si_2^+–$Si_2H_6^+$, SiP^+–$SiPH_5^+$ (uncertain because of ambiguity with $Si_2H_x^+$), Si^+–SiH_4^+, and P^+–PH_3^+.

In several experiments, $Si_2H_5PH_2$ vapor was allowed to remain in contact with an excess of water vapor for several hours. Analysis showed that the main hydrolysis products were phosphine and bisdisilanyl oxide, and that very small amounts of disilane and silane were formed. The glass walls of the reaction tubes became coated with a very thin white deposit. In one experiment 0.204 mmole of $Si_2H_5PH_2$ and 0.147 mmole of H_2O were allowed to react for 4 hr. at room temperature, yielding 0.208 mmole of PH_3, 0.126 mmole of a mixture of H_2O and $(Si_2H_5)_2O$ (it was not possible to separate these two), and a trace of Si_2H_6 and SiH_4. The products were identified by their infrared spectra.

Traces of phosphine and disilane were formed when disilanyl-

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