Some Physical Properties of the Trimeric and Tetrameric Phosphonitrilic Fluorides

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A simple one-step synthesis of trimeric and tetrameric phosphonitrilic fluorides from the corresponding phosphonitrilic chlorides has been developed. The vapor pressures and heats of vaporizations, sublimations, and fusions for the trimer and tetramer have been determined and compared with the previously reported corresponding phosphonitrilic chlorides.

EXPERIMENTAL

Preparation of Trimeric and Tetrameric Phosphonitrilic Fluoride. Anhydrous, chemically-pure potassium fluoride (Baker Chemical) was dried in an oven at 316°C. for 36 hours. Anhydrous sulfur dioxide (Matheson Co.) was further dried through a column packed with phosphorus pentoxide and calcium sulfate. Technical grade phosphonitrilic chloride, approximately a 3 to 1 mixture of trimer to tetramer (Berkeley Chemical Corp.) was freed of moisture and nonvolatile impurities by several sublimations. A weighed amount of potassium fluoride and a trimer-tetramer mixture of phosphonitrilic fluorides was thoroughly pulverized and mixed together in an inert atmosphere chamber and loaded into a dry stainless steel bomb equipped with a valve. A calculated weight of sulfur dioxide was distilled into the bomb, which had been previously evacuated. The bomb was heated to between 120° and 125°C. in an oven for 67 hours, and then cooled to room temperature. After the volatiles were distilled from the bomb, pure tetramer and nearly pure trimer were isolated by several fractionations through cold U-traps held at the following temperatures: −22°, −45°, −63°, −83°, and −196° C. Pure trimer was isolated by fractional distillation through a vacuum-jacketed, helices-packed column. A typical run is shown below.

$$2KF + 2SO_2 + PNCl_2 \xrightarrow[67\ \text{hours}]{120^\circ - 125^\circ C.} PNF_2 + 2KCl + 2SO_2$$

Grams	30	80	27	14.6
Moles	0.52	1.33	0.233	0.176

The combined trimer and tetramer yield, based on $PNCl_2$ and PNF_2 monomer units, corresponds to 75.5%.

Analysis. Calculated for PNF_2: Phosphorus, 37.30; nitrogen, 16.83; and fluorine, 43.87. Found. Phosphorus, 37.02; nitrogen, 17.30; and fluorine, 45.68 (by difference). Molecular weights of the trimer and tetramer were measured by vapor densities as 251 and 333 (calculated 249 and 332). The measured data on which these values were based are tabulated below.

	Trimer	Tetramer
T, °K.	297	297
P, mm.	43.5	38.9
Wt., gram	0.0834	0.0991
V, liter	0.1414	0.1414

Table II. Vapor Pressure of Trimeric Phosphonitrilic Fluoride

Temp., °C.	Pressure, Mm. Obsd.	Pressure, Mm. Calcd.	ΔP, Calcd. − Obsd.
Solid Phase, Empirical Equation $\text{Log } P = \frac{-2806}{T} + 11.81$			
0.2	36.3	35.5	−0.8
2.5	43.2	43.6	+0.4
3.8	47.6	47.9	+0.3
5.4	55.5	55.0	−0.5
7.2	63.5	63.1	−0.4
9.3	75.5	75.9	+0.4
11.5	90.5	91.1	+0.6
13.3	105.0	104.7	−0.3
15.4	122.5	123.0	+0.5
17.4	143.1	141.1	−2.0
19.3	164.6	165.9	+1.3
21.7	195.7	195.0	−0.7
24.1	235.5	234.0	−1.5
25.8	266.8	269.0	+2.2
26.8	285.8	288.3	+2.5
27.3	296.6	295.0	−1.6
Liquid Phase, Empirical Equation $\text{Log } P = \frac{1679}{T} + 8.065$			
27.5	302.4	302.7	+0.3
29.5	331.5	329.6	−1.9
32.0	367.8	366.4	−1.4
34.0	397.5	398.1	+0.6
35.7	427.5	426.6	−0.9
37.8	466.0	463.4	−2.6
39.9	506.5	503.5	−3.0
42.0	547.2	547.0	−0.2
44.0	591.5	591.6	+0.1
46.3	644.3	645.7	+1.4
48.1	688.0	690.2	+2.2
50.2	741.0	746.5	+5.5

Table I. Melting Points, Boiling Points, Heats of Vaporization, Sublimation, and Fusion, and Trouton Constants of Phosphonitrilic Fluorides and Chlorides

Compound	M.P., °C.	B.P., °C. (760 Mm.)	ΔH vap., Kcal./Mole at 760 Mm.	ΔH vap./T, *E.U.* at 760 Mm.	ΔH_s Kcal./Mole	ΔH_f Kcal./Mole
$(PNF_2)_3$	26.8 27.2–27.4[b] (28.1)	(50.7)[a] 51.8	7.68	23.7	12.8	4.97
$(PNF_2)_4$	30.4 (32.1)	(89.6) 89.7	8.91	24.5	13.9	5.03
$(PNCl_2)$[c]$_3$	114 (114.9)	256	13.2	25.0	18.2	5.0
$(PNCl_2)$[c]$_4$	123.5	328.5	15.5 (*3*)	25.7	....	....

[a] Boiling points in parenthesis calculated from the empirical equations; those not in parenthesis found experimentally by other investigators (*1, 5*).

[b] Melting point determined by capillary tube method. Melting points in parenthesis evaluated from solid-vapor and liquid-vapor equations.

[c] Physical properties for phosphonitrilic chlorides extracted from work of Audrieth, Steinman, and Toy (*1*).

Table III. Vapor Pressure of Tetrameric Phosphonitrilic Fluoride

Temp., °C.	Pressure, Mm. Obsd.	Pressure, Mm. Calcd.	ΔP, Calcd. − Obsd.
Solid Phase, Empirical Equation $\log P = \frac{-3046}{T} + 11.85$			
0.1	4.0	5.0	+1.0
6.3	9.1	8.9	−0.2
11.5	13.9	14.1	+0.2
15.6	18.0	20.0	+2.0
19.6	28.0	28.2	+0.2
23.0	34.3	37.2	−0.1
29.6	62.3	61.7	−0.6
Liquid Phase, Empirical Equation $\log P = \frac{-1947}{T} + 8.247$			
32.2	73.3	74.6	+1.3
36.0	89.0	89.1	+0.1
39.1	103.0	102.2	−0.8
43.7	125.7	126.4	+0.7
47.6	150.5	150.5	0.0
49.9	165.4	166.2	+0.8
53.5	197.0	193.5	−3.5
56.6	224.0	221.0	−3.0
59.2	250.0	245.5	−4.5
62.3	282.0	277.2	−4.8
65.2	317.0	312.0	−5.0
69.0	364.7	361.0	−3.7
72.2	411.0	407.0	−4.0
75.2	459.4	456.0	−3.4
77.8	501.5	501.0	−0.5
80.5	551.7	553.0	+1.3
83.5	610.5	616.0	+5.5
86.5	673.4	682.0	+8.6
89.0	732.3	743.3	+11.0

Physical Properties. Melting Points. The melting points of the first two homologs were determined using the magnetic plunger method described by Stock (*4, 6*). The melting point for the trimer determined by this method was found to be slightly lower than the value first reported by Seel and Langer (*5*); however, the capillary tube method gave a slightly higher value than that reported by the same investigators. A Harshaw 0.2° graduated thermometer, checked at the freezing point and boiling point of distilled water, was used for melting point determinations (Table I).

Vapor Pressures of Trimer and Tetramer. A water bath equipped with an efficient stirrer and two heaters, one having a thermoregulator, was used for all the measurements. The temperatures were read from Harshaw 50°, 0.2° graduated, thermometers, and the pressures were read from a mercury manometer with a cathetometer. All the vapor pressures were determined using a tensimeter similar to that described by Burg and Schlesinger (*2*). The results are summarized in Tables II and III. The constants to the empirical equations were determined by plotting log P vs. $1/T$ and drawing the best straight line. The heats of vaporization and sublimation were calculated from the corresponding empirical equations, and the heat of fusion was calculated from the differences of heats of vaporization and sublimation. Comparative physical data for the trimer and tetramer are summarized in Table I.

ACKNOWLEDGMENT

Thanks are due to A. J. Bilbo for his assistance during the fractional distillation of the trimer and C. M. Douglas during the preparation of this article.

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Received for review October 14, 1957. Accepted April 25, 1958. Research conducted under sponsorship of the Bureau of Ordnance, Foundational Research Fund.

Preparation and Comparison of the Physical Properties of Alkyl and Alkforyl Silicates

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Normal alkyl and alkforyl alcohols reacted with silicon tetrachloride to produce tetraalkyl and tetraalkforyl silicates (*8*) as well as hexaalkoxy and hexaalkforyloxy disiloxanes. Differences were noted in their mode of reaction and physical properties.

A comparison of the physical properties of the three series of organosilicates exhibited some unusual variations. Unfortunately, a more complete comparison was not possible because of the unavailability or the high cost of the alkforyl alcohols in this homologous series. Nonetheless, generalizations may be made concerning the three series from the available data.

Although the alkyl silicates are stable thermally (*1,2*), the object of this study was to compare the thermal stability, physical properties, and hydrolytic stability of these with the 1,1,(*n* + 2)-trihydroalkforyl silicates and the 1,1-dihydroalkforyl silicates. These silicates may be represented by the following general formulas:

Tetra-*n*-alkyl silicate

$$\left[H_3C(CH_2)_N-CH_2-O\right]_4 Si$$

Tetra-1,1(*n* + 2)-trihydroalkforyl silicate

$$\left[HF_2C(CF_2)_N-CH_2-O\right]_4 Si$$

Tetra-1,1-dihydroalkforyl silicate

$$\left[F_3C(CF_2)_N-CH_2-O\right]_4 Si$$

Hexa-*n*-alkoxy disiloxane

$$\left[H_3C(CH_2)_N-CH_2-O\right]_3 Si-O-Si\left[O-CH_2(CH_2)_N-CH_3\right]_3,$$