TABLE X

THE MOLAL ENTROPY OF BENZOTRIFLUORIDE IN CAL. DEG.$^{-1}$

T, °K.	334.22	353.31	375.21
S_{satd}(liq.)	70.21[a]	72.92[a]	75.97[b]
$\Delta Hv/T$	25.27	23.07	20.79
S(ideal) − S(real)[c]	0.11	0.17	0.25
Compression, $R \ln P$[c]	−2.75	−1.38	0.00
$S°$(obsd.)(±0.20)	92.84	94.78	97.01

[a] Interpolated from Table VI. [b] Extrapolated by use of eq. 1. [c] Calculated by use of eq. 3 and 5.

The heat of vaporization was calculated to be $\Delta Hv_{298.16}$ = 8.96 kcal. mole^{-1} from a thermodynamic network that utilized the thermodynamic functions of Table III. Alternate calculations by extrapolation of eq. 4 and by use of the Clapeyron equation with eq. 3 and 5 gave results that agreed within 0.02 kcal. mole^{-1}. The standard heat of vaporization was calculated to be $\Delta Hv°_{298.16}$ = 8.98 kcal. mole^{-1} from eq. 3 and 5 and the relationship $\Delta Hv° = \Delta Hv - BRT/V + (\mathrm{d}B/\mathrm{d}T)RT^2/V$. This value was used to obtain the standard heat of formation of the vapor, $\Delta Hf°_{298.16} = -138.8_7$ kcal. mole^{-1} for the reaction

$$7\ \mathrm{C(c,\ graphite)} + 5/2\ \mathrm{H_2(g)} + 3/2\ \mathrm{F_2(g)} = \mathrm{C_7H_5F_3(g)}$$

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF FLORIDA]

The Novel Synthesis of $(PNF_2)_3$ and $(PNF_2)_4$ from P_3N_5[1]

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Both $(PNF_2)_3$ and $(PNF_2)_4$ can be prepared at 700° by treating P_3N_5 with a source of fluorine, in this case CF_3SF_5 or NF_3. Infrared assignments of these two phosphonitrilic fluorides are presented.

Both the trimer and tetramer of PNF_2 have recently been reported,[2] having been prepared by treating the corresponding chlorides with KSO_2F. Prior attempts to prepare the fluorides from the chlorides using the so-called more conventional fluorine exchange agents such as PbF_2 were only partially successful in that the trimer chloride gave $P_4N_4Cl_2F_6$ and $(PNClF)_4$.[3,4] In this work, quantities of $(PNF_2)_3$ and $(PNF_2)_4$ were obtained in the same reaction when P_3N_5 reacted with either CF_3SF_5 or NF_3. At temperatures 100 to 150° below 700° the conversions to the phosphonitrilic fluorides are vanishingly small and at temperatures 100° above 700° the conversion drops off slightly and the products are contaminated.

Preliminary experiments on P_3N_5 alone confirmed the fact that N_2 is evolved when P_3N_5 is heated above 550° *in vacuo*. A similar phenomenon was observed by Moureau and Rocquet.[5] They also reported the existence of pure PN in a red (α) form and a yellow (β) form. Other workers[6] have suggested that PN probably exists as a monomeric vapor at elevated temperatures.

Experimental

Materials.—CF_3SF_5 was prepared electrochemically from methyl sulfide in anhydrous HF.[7] The samples used had a purity of not less than 99% by wt. as established by vapor phase chromatographic analysis and boiled at −20.5°.

The NF_3 was prepared electrochemically from pyridine in anhydrous HF.[8] It was freed of acid contaminants by passage through concd. NaOH and of OF_2 by passage through KI solution and a further wash with base to remove any entrained iodine. The gas was dried over P_2O_5 and degassed at considerable length until the vapor pressure of a recondensed sample was less than 2 mm. at liquid air temperatures. Chromatographically, it showed a minor impurity of about 1% by wt. which was presumed to be CF_4. The mol. wt. was 71–72.

P_3N_5 was purchased from Chemicals Procurement Co. (New York). Its purity was questionable as Kjeldahl nitrogen analysis was only 38.5% (theo. 42.9). However, except for the heat treatment noted below, it was used as shipped.

Equipment.—Vapor phase chromatographic analyses were performed on a Perkin-Elmer Fractometer, Model 154. The developer gas was always N_2. The stationary phases used will be indicated at the proper place in this discussion.

Infrared spectra were performed on a Model 21 Beckman Spectroscope using a 5 cm. gas cell with NaCl windows.

Reaction Procedure.—In general, P_3N_5 powder (coarse and fine) was packed snugly into a small volume of a one-inch i.d. nickel tube (0.065″ wall). A short tube furnace about 4″ long heated the portion of the tube in which the P_3N_5 was packed. The tube was adapted so that the gaseous reagents could be run from a small containing cylinder into the reaction vessel. Flow rates were controlled with a needle valve and measured with a capillary flow meter. Products were collected in cold traps protected from the moisture in the air by drying tubes. The procedure was to purge the system with dried nitrogen until all the air was replaced. Then the system was heated to a predetermined reaction temperature under a positive N_2 flow. The N_2 was shut off and gaseous reagent was slowly let into the system at some predetermined rate. When the run was completed nitrogen again was passed through the system to purge it of products, which were collected.

Reactions.—Numerous trials were made to find some optimum reaction condition. In an initial run at 850°, 30 g. of CF_3SF_5 was passed over excess P_3N_5 at the rate of 10 g./hr. The liquid air condensate was found to contain SF_4, C_2F_6 and other low boiling gases which were acidic. Six grams of material boiling between 54 and 86° remained behind when the low boiling fraction was removed. It had a mol. wt. of from 259 to 297 and hydrolyzed in water. The

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[1] This work was supported by the Chemistry Branch, Office of Naval Research. Part or all of this paper may be reproduced for purposes of the United States Government.

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[3] O. Schmitz-Dumont and H. Kulens, *Z. anorg. allgem. Chem.*, **238**, 189 (1938).

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[5] H. Moureau and P. Rocquet, *Bull. soc. chim.*, [V], **3**, 1801 (1936).

[6] E. O. Hoffman, *et al.*, THIS JOURNAL, **76**, 6239 (1954); H. Moureau, B. Rosen and G. Wetroff, *Compt. rend.*, **209**, 207 (1939).

[7] A. F. Clifford, H. K. El-Shamy, H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 2372 (1953); R. D. Dresdner, THIS JOURNAL, **77**, 6633 (1955).

[8] J. H. Simons and co-workers, *J. Electrochem. Soc.*, **95**, 47 (1949).

aqueous solution gave positive tests for F^- and $PO_4^{\equiv}$ but did not evolve NH_3 until it was made basic.

At 450°, the amount of any reaction was vanishingly small, while at 550°, of 47 g. of CF_3SF_5 reacted, only 4.5 g. of product appeared which boiled above $-20°$. This boiled from 45 to 90°. However, this material decomposed slowly while stored in a desiccator, forming a yellow precipitate.

Finally a trial was run at 710° in which 35 g. of CF_3SF_5 was passed through 15 g. of P_3N_5 at the rate of 9.6 g./hr. The calculated contact time was between 15 and 30 seconds. Thirty-six and a half g. of product was trapped. The products were fractionated. The overhead from the column (Dry Ice–acetone cooled head) was a mixture which appeared to be C_2F_6, SF_4 and PF_3 and amounted to 7.5 grams. At $-40°$, a fraction amounting to 5.0 g. with a mol. wt. of 106–109 was isolated. SF_4 boils at $-38°$ and has a mol. wt. of 108. During the fractionation a solid accumulated on the head. It was trapped out *in vacuo* after the pot was removed from the column. It had a mol. wt. of 101 to 111 (mostly 102) and contained phosphorus and fluorine. The residual 16 g. boiled well above room temperature. Fractionation of this yielded two narrow boiling fractions, *viz.*, (1) 50.0 to 50.8° amounting to 6 grams and (2) 88.8 to 89.2° amounting to four grams. The intercuts were 1.5 g., b. 50.8° to 52° and 3.5 g., b. 83–88° with only a few drops between these ranges. The two narrow boiling fractions 1 and 2 were investigated sufficiently to assure that they were the phosphonitrilic fluorides reported by Seel and Langer.

Properties of $(PNF_2)_3$.—This had a m.p. of 26.0 ± 1.0° and a mol. wt. of 250 (theo. 249) determined by gas density. Its purity was checked chromatographically using stationary phases of both hexadecane and the ethyl ester of Kel-F Acid 8114 with the same results—essentially a pure substance. Seel and Langer reported a b.p. of 51.8° and a triple point of 27.1. The $(PNF_2)_3$ has an approximate density of 1.7. The $n^{30}D$ was 1.3178.

Anal. Calcd. for $P_3N_3F_6$: F, 45.71; N, 16.87. Found: F, 45.29; N, 16.96, 16.76.

The gas phase infrared spectrum was extremely simple. The only absorption peaks in microns were 7.66(vs), 10.25(vs), 11.23(m) 11.60(vs) 13.00(w). These were determined using a pressure of 20 mm.

Properties of $(PNF_2)_4$.—This had a gas density mol. wt. of 328 (theo. 332) and a m.p. of 28.0–29.0°. Its purity did not exceed 99% by weight as established chromatographically on the same stationary phases as before. Seel and Langer reported a b.p. of 89.7 and a triple point of 30.4. The approximate density of the liquid was again 1.7 while the $n^{30}D$ was 1.3345.

Anal. Calcd. for $P_4N_4F_8$: F, 45.71; N, 16.87. Found: F, 45.47, 45.71; N, 16.75, 16.91.

The infrared spectrum of the tetramer was also simple. The assignments in microns were 6.92(vs), 10.25(vs) and 13.00(vs). This spectrum was also run at 20 mm. It will be noted that the spectra of the two substances have the 10.25 and 13.00 lines in common.

Solubility tests on both substances showed them to be quite soluble in hydrocarbons such as C_6H_{14}, C_7H_{16} and C_6H_6 and a fluorocarbon such as N-43 (commercial grade $(C_4F_9)_3$-N—Minnesota Mining).

Reaction of P_3N_5 with NF_3.—Nine g. of NF_3 was passed through 15 g. of P_3N_5 at 710° at the rate of 1.8 g./hr. The calculated contact time was not less than 30 seconds or more than 45 seconds. There was infrared evidence that not all of the NF_3 was decomposed. Nine grams of product was obtained in the cold trap. There was about three grams of the subliming solid mol. wt. 102–106 reported previously and 3 grams of high boiling material. It was not enough to separate conveniently into its components so it was analyzed by gas chromatography. For a given developer gas flow rate, operational temperature, stationary phase and attenuation, appearance times were determined for 0.01-cc. quantities of trimer and tetramer. Then the appearance times for the mixture were measured under exactly the same conditions. They were essentially the same within 1% of the respective times involved. Even the shapes of the chromatographic curves were the same. Finally an infrared spectrum of the mixture was made at 20 mm. pressure. A comparison of the absorptions in Table I led rather conclusively to the fact that the mixture contained only $(PNF_2)_3$ and $(PNF_2)_4$.

TABLE I

INFRARED ABSORPTION PEAKS OF TRIMERS AND TETRAMERS WAVE LENGTHS IN MICRONS

Pure trimer	Pure tetramer	Mixture
...	6.92	6.92
7.66	...	7.66
10.25	10.25	10.25
11.25	...	11.25
11.58	...	11.58
13.00	13.00	13.00

Discussion of the Results

This work with CF_3SF_5 was performed with other ends in mind. It has been shown that under thermal condition CF_3SF_5 can eliminate SF_4 leaving the transitory free radicals $CF_3\cdot$ and $F\cdot$.[9] With this fact and the added information that PN can exist as a vapor at elevated temperatures, the attempt was to make materials having a $CF_3\cdot$ group(s) and $F\cdot$ incorporated in the structure. This materialized only to the extent that PN reacted with some of the available fluorine. There seemed to be no doubt that PN was actually formed as the red and yellow forms were always deposited in the lines and on the walls of the traps.

Incidentally, since both C_2F_6 and SF_4 were detected in the reaction products, it appeared that the concentration of PN in the vapor phase was probably too low to react readily with $CF_3\cdot$ free radical, which coupled to form C_2F_6 preferentially. Accordingly, higher reaction temperatures were favored to increase the PN partial pressure in the reaction environment. However, in the 710° trial with CF_3SF_5 the amount of F required to make 16 grams of PNF_2-mers was in excess of that which would normally appear in a free radical form from the decomposition of 35 g. of CF_3SF_5 by a factor of 2. As neither a theoretical amount of C_2F_6 or SF_4 was recovered, it must be concluded that other fluorine than free radical F was involved. In retrospect this is not strange, considering the high temperatures involved. Accordingly, the work with NF_3 was instituted to find out if a relatively inert inorganic fluoride would act similarly. From reactions carried out in this Laboratory, it has been shown that under non-catalytic condition NF_3 acts as a fluorinating agent, at elevated temperatures with a fluorocarbon olefin.[10] Again, in this work the NF_3 acted as a source of fluorine and a small quantity of (PNF_2)-mers were produced.

The implication of this work seems to be that any source of PN and any source of fluorine in diluted concentrations will tend to lead to the preparation of $(PNF_2)_3$ and $(PNF_2)_4$ at elevated temperatures.

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