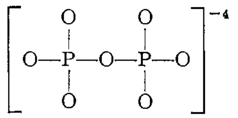
and $P_4S_4N_6(CH_3)_6$[1] are molecular, while data at present suggest that $P_2O_2N_3(CH_3)_3$[8,16] is polymeric. The possible routes leading to such imides from previous members of the condensation process are numerous and a beginning discussion must await clarification of the structure of the imide–amide class.

By analogy between the nitrogen and oxygen system of compounds, the condensation of amides, such as $PS(NHCH_3)_3$, corresponds to a formal dehydration of orthophosphoric acid according to the sequence

$$\underset{\text{orthophosphoric acid}}{H_3PO_4} \longrightarrow \underset{\text{pyrophosphoric acid}}{H_4P_2O_7} \longrightarrow \underset{\text{metaphosphoric acids}}{[HPO_2]_x} \longrightarrow \underset{\text{phosphorus pentoxide}}{P_4O_{10}}$$

Structures of salts of the oxygen acids are known[17] and follow closely the structural assignments in the amide series. Thus the phosphate ion has an analogous structure to the amide, $PS(NHCH_3)_3$; the pyrophosphate ion



$$\left[\begin{array}{c} O\quad\ O \\ O{-}\overset{|}{\underset{|}{P}}{-}O{-}\overset{|}{\underset{|}{P}}{-}O \\ O\quad\ O \end{array}\right]^{-4}$$

has a structure similar to that suggested for $[(CH_3NH)_2PS]_2NCH_3$. The tri- and tetrametaphosphates have ring structures and suggest that analogous structures should be searched for in the imide–amide class. The close structural correspondence between the imides and phosphorus pentoxide already has been referred to.

Acknowledgment.—This work was supported in part by a grant from the U. S. Army Research Office. The preparation of $PO(NH\textit{t}\text{-}C_4H_9)_3$ by Alfred G. Zielske is gratefully acknowledged as is the assistance of Constance Wright with some of the molecular weight determinations.

(17) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., pp. 486, 617, 686, and 696.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CARNEGIE INSTITUTE OF TECHNOLOGY, SCHENLEY PARK, PITTSBURGH, PENNSYLVANIA

The Systems Phosphorus Trifluoride–Trimethylamine, Phosphorus Trifluoride–Triethylamine, and Methyldichlorophosphine–Trimethylamine[1,2]

BY ROBERT R. HOLMES[3] AND RAYMOND P. WAGNER

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The binary systems PF_3–$(CH_3)_3N$, CH_3PCl_2–$(CH_3)_3N$, and PF_3–$(C_2H_5)_3N$ were studied and the solid complexes $F_3P\cdot N(CH_3)_3$ and $CH_3Cl_2P\cdot N(CH_3)_3$ characterized. Dissociation pressures were measured for each complex. Both complexes lose their existence in the vapor state. Interpretation of pressure composition data established a dissociation equilibrium for $CH_3Cl_2P\cdot N(CH_3)_3$ in the liquid state. An energy of complexing of 2.9 kcal./mole resulted. Large negative deviations were observed in the $PF_3\cdot(C_2H_5)_3N$ system, supporting association tendencies. The acceptor properties of PF_3 are discussed.

Previous work in this Laboratory established the complexes $Cl_3P\cdot N(CH_3)_3$[4] and $Br_3P\cdot N(CH_3)_3$[5] and supported the presence of a phosphorus–nitrogen linkage in each wherein phosphorus is acting as an acceptor atom. Griffiths and Burg[6] mention that PF_3 and $(CH_3)_3N$ form an unstable adduct at −78° and Parry and Bissot[7] have shown that PF_3 and $(CH_3)_3N$ react in an approximately 1:1 ratio. To define the PF_3–$(CH_3)_3N$ system precisely a more complete study was undertaken. Also to gain further information on the tendency for complex formation in this series the systems PF_3–$(C_2H_5)_3N$ and CH_3PCl_2–$(CH_3)_3N$ were investigated.

Experimental

Materials.—Trimethylamine generated from the hydrochloride (Matheson, reagent grade) was dried by passing the vapor through a barium oxide tube and then condensed at −78° on sodium chips. After being in contact overnight the amine was fractionated in the line. A tensiometrically homogeneous middle fraction was used, v.p. 681 mm. at 0.0°. A refractionated sample of triethylamine previously purified was used.[8]

Phosphorus trifluoride was prepared by the two step procedure described in *Inorganic Syntheses*,[9] the preparation of arsenic trifluoride from arsenic III oxide followed by fluorination of phosphorus trichloride. The phosphorus trifluoride was trapped at −78° as it formed and then slowly fractionated in the line using traps cooled to −78, −119, −160, and −196°. Most of the product was present in the −160° trap. This fraction was found to show a vapor pressure variation from 372 to 376 mm. at −111.7° when divided into fractions. A mass spectral analysis showed mass peaks attributed to small amounts of PF_2Cl and POF_3. The latter contaminants were readily removed by condensing a 10 mole % quantity of $(CH_3)_3N$ on the PF_3 sample at −196°, warming to −111.7° and cooling to −196°

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(1) Phosphorus Nitrogen Chemistry. VIII. Previous paper: R. R. Holmes and J. A. Forstner, *Inorg. Chem.*, **2**, 380 (1963).

(2) This paper represents part of the work submitted by Raymond P. Wagner in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

(3) Bell Telephone Laboratories, Inc., Murray Hill, N. J.

(4) R. R. Holmes, *J. Phys. Chem.*, **64**, 1295 (1960).

(5) R. R. Holmes, *J. Am. Chem. Soc.*, **82**, 5285 (1960).

(6) J. E. Griffiths and A. B. Burg, *ibid.*, **82**, 1508 (1960).

(7) R. W. Parry and T. C. Bissot, *ibid.*, **78**, 1524 (1956).

(8) R. R. Holmes and E. F. Bertaut, *ibid.*, **80**, 2980 (1958).

(9) C. J. Hoffman, *Inorg. Syn.*, **4**, 149 (1953).

several times, and transferring the excess PF_3 off at −111.7°.[10] A mass spectral analysis of the PF_3 purified in this fashion showed only mass peaks expected for PF_3 (other than background peaks). The vapor pressure of the resulting PF_3 was 372.1 mm. at −111.7°. A value calculated from Booth's and Bozarth's equation[11] gave 393.6 mm. at −111.7°.

Methyldichlorophosphine (donated by the Food Machinery and Chemicals Corporation) was purified as before.[12] Necessary vapor pressure data on methyldichlorophosphine were lacking in the literature. Consequently, measurements were made from −78 to +24°. Representative values are reported in Table I.

TABLE I

VAPOR PRESSURE OF METHYLDICHLOROPHOSPHINE

t, °C.	p, mm. obsd.	p, mm. calcd.
−44.0	1.20	1.26
−30.0	3.53	3.69
−20.0	7.08	7.37
−10.0	14.37	13.99
0.0	25.52	25.37
10.0	45.85	44.09
18.0	66.35	66.76

The equation $\log p_{\text{mm}} = -(1857/T) + 8.20245$ was calculated from the experimental points between −44 and 24°. The values of p resulting from use of this equation also are listed in the table. The equation indicated the normal boiling point as 74.8° (lit.[13] 78°) and the Trouton constant as 24.4 cal./deg. mole. The melting point of the methyldichlorophosphine was found to be −67°, using the float-method described by Sanderson.[14]

Procedure.—The apparatus and techniques are the same as those previously used.[5] All mole fractions reported in tables and figures refer to condensed state compositions. The mass spectral analysis of PF_3 was obtained with a Consolidated Electrodynamics Corporation mass spectrometer, Type 21-103C.

Results

The PF_3–$(CH_3)_3N$ System.—The PF_3–$(CH_3)_3N$ system was examined in a preliminary fashion at −78.5°. The first additions of gaseous PF_3 to liquid $(CH_3)_3N$ at −78.5° resulted in the appearance of a white solid. The vapor pressure of the system remained sensibly constant near the vapor pressure of pure $(CH_3)_3N$ at −78.5° up to the mole fraction of PF_3 of about 0.4. With further additions the pressure values were slightly higher. At a mole fraction close to 0.5 the pressure of the system rose vertically as expected for no further absorption of PF_3. Due to the limitations of the apparatus the experiment was discontinued when the pressure of the system was near 1 atm. (the vapor pressure of pure PF_3 at −78.5° is estimated[15] to be approximately 3.3 atm.).

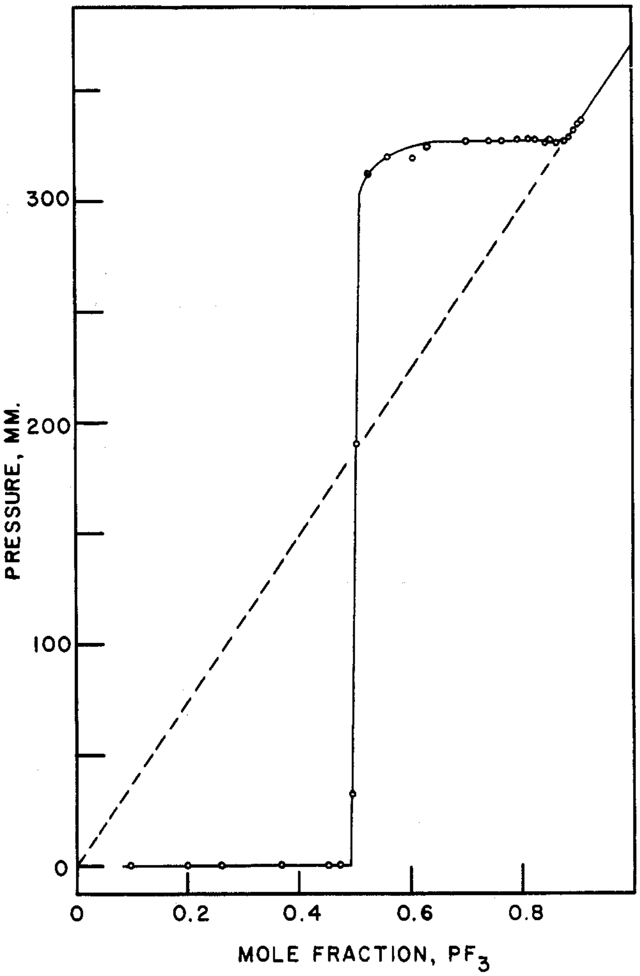

Fig. 1.—The phosphorus trifluoride–trimethylamine system at −111.7°.

By lowering the temperature to −111.7° (CS_2 slush bath), a more detailed study of the PF_3–$(CH_3)_3N$ was possible. At −111.7° the vapor pressure of pure PF_3 is low enough (372 mm.) so that the solution of the solid adduct in excess PF_3 can be followed. The data are plotted in Fig. 1.

The −111.7° diagram is of the type obtained in the PCl_3–$(CH_3)_3N$ system and has been discussed adequately.[4] The systems differ in that in this case $(CH_3)_3N$ is the less volatile component. In addition, the vapor pressure of the component $(CH_3)_3N$ is in effect zero.

The diagram clearly shows the existence of the adduct, $F_3P\cdot N(CH_3)_3$, possessing a "zero" sublimation pressure at −111.7°. It is seen to be soluble in excess PF_3, the average vapor pressure over a saturated solution of $F_3P\cdot N(CH_3)_3$ in PF_3 being 327 mm. The saturation point is reached at a mole fraction of PF_3 of 0.88. Afterward, the pressure rises linearly with increasing mole fraction of PF_3 toward the vapor pressure of pure PF_3 (372.1 mm. at −111.7°). The linearity closely follows Raoult's law (the dashed line). Removal of the excess PF_3 at −111.7° left a 1:1 adduct. A mass spectrum of a sample of the excess PF_3 removed showed no peaks assignable to $(CH_3)_3N$.

The 1:1 adduct formed at −111.7° was allowed to

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(10) Apparently $(CH_3)_3N$ preferentially complexes the impurities. This was proven by isolating the complexed impurities. They were much less volatile than $F_3P\cdot N(CH_3)_3$; consequently, separation from $F_3P\cdot N(CH_3)_3$ was readily achieved. The volatility of the complexed impurities was sufficient to allow a mass spectral determination. The latter showed the presence of $(CH_3)_3N$, POF_3, and PF_2Cl, but no PF_5.

(11) H. S. Booth and A. R. Bozarth, *J. Am. Chem. Soc.*, **61**, 2927 (1939).

(12) R. R. Holmes and R. P. Wagner, *ibid.*, **84**, 357 (1962).

(13) L. Maier, *Angew. Chem.*, **71**, 574 (1959).

(14) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, New York, N. Y., 1948.

(15) By using the equation of Booth and Bozarth[11] governing the vapor pressure of PF_3 in the range −117 to −97° and extrapolating to −78.5° a value of 2510 mm. was estimated.

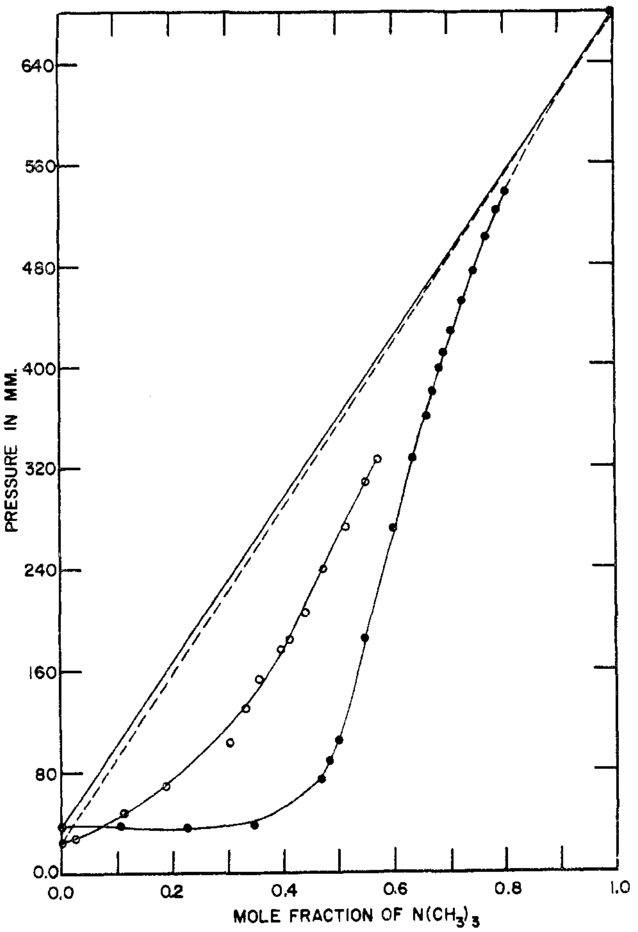

Fig. 2.—The phosphorus trichloride–trimethylamine system at 0°, -●-; the methyldichlorophosphine–trimethylamine system at 0°, -○-.

vaporize at 24.6°. Measurements of the vapor density of the resulting sample were in agreement with complete dissociation to the components.[16] Therefore, the adduct has negligible existence in this phase at room temperature.

Vapor pressures on the 1:1 solid adduct were measured as a function of temperature. The data are shown in Table II.[17] From visual observations the complex appears solid up to −80°; at −78.5° it liquefies.

The PF_3–$(C_2H_5)_3N$ System.—Additions of gaseous PF_3 to liquid $(C_2H_5)_3N$ at −78.5° failed to produce any observable reaction. Table III lists the data obtained at −78.5°. Since the vapor pressure of $(C_2H_5)_3N$ at −78.5° is close to zero it is assumed that the vapor phase contains only PF_3. If one then calculates pressure values based on Raoult's law,[15] large negative deviations from ideal liquid behavior become apparent. The latter values are included in Table III.

TABLE II

SUBLIMATION PRESSURES OF PHOSPHORUS TRIFLUORIDE–TRIMETHYLAMINE

t, °C.	−101.4	−86.4	−84.7	−83.7	−81.4	−80.2	−78.5
p, mm.	0.4	3.2	3.8	4.9	6.2	7.2	8.0

TABLE III

THE PHOSPHORUS TRIFLUORIDE–TRIETHYLAMINE SYSTEM AT −78.5°

Mole fraction[a] PF$_3$	Press., mm. obsd.	Press.,[c] mm. calcd.	Mole fraction PF$_3$	Press., mm. obsd.	Press., mm. calcd.
0.0	0.0	0	0.202	137.0	507
.024	12.3	60	.259[b]	195.9	650
.052	27.6	130	.265	194.0	665
.081	49.1	203	.289	230.9	725
.124	77.0	311	.294[b]	238.5	738
.152	105.3	382	.328	285.5	824
.168[b]	109.5	422			

[a] A sample size of 0.613 mmole of $(C_2H_5)_3N$ was used. [b] Points determined by removing PF_3; the remainder of the points were determined by adding PF_3 to the system. [c] Based on Raoult's law.

The CH_3PCl_2–$(CH_3)_3N$ System.—The first addition of $(CH_3)_3N$ to 1.65 mmoles of liquid CH_3PCl_2 at −46.0° resulted in the formation of a white solid in addition to the liquid phase present. With further additions the pressure remained relatively constant (averaging 1.5 mm.) near the vapor pressure of pure CH_3PCl_2. A sharp rise at an amine mole fraction of 0.5 to a second plateau averaging 72.5 mm. served to show the existence of the solid complex $CH_3Cl_2P \cdot N(CH_3)_3$. The complex appeared insoluble in excess $(CH_3)_3N$ since the latter plateau lies close to the vapor pressure of $(CH_3)_3N$ at −46.0° (73.6 mm.[18]).

After pumping off the excess amine at −78.5°, the sample was slowly warmed to room temperature. It was observed to change from solid to solid–liquid to all liquid. Pressure measurements as a function of temperature indicated behavior entirely analogous to that observed in the PCl_3–$(CH_3)_3N$ system, the discussion[4] of which need not be repeated here.

A more detailed study of the CH_3PCl_2–$(CH_3)_3N$ system was made in the liquid region to ascertain association tendencies of the components. Additions of $(CH_3)_3N$ to liquid CH_3PCl_2 at 0° resulted in the pressure–composition diagram plotted in Fig. 2. The data are shown in Table IV. Pressure measurements also

TABLE IV

THE METHYLDICHLOROPHOSPHINE–TRIMETHYLAMINE SYSTEM AT 0.0°

Mole fraction[a] (CH$_3$)$_3$N	Press., mm.	K	Mole fraction (CH$_3$)$_3$N	Press., mm.	K
			0.398	175.7	2.20
0.0	25.9		.409	181.4	2.27
.108	46.1	2.76	.438	204.0	2.21
.186	69.3	2.47	.478	238.8	2.06
.300	101.7	3.17	.513	270.9	1.97
.324	130.0	2.28	.551	308.5	1.75
.359	150.9	2.21	.569	325.3	1.71

[a] In this experiment 1.60 mmoles of CH_3PCl_2 was used.

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(16) To further test the lack of adduct formation in the vapor, pressure measurements of mixtures of the gaseous components were made at 26°. The results showed little deviation (negative) from Dalton's law. Measurements were made by adding $(CH_3)_3N$ to a sample of PF_3 (23.5 mm. at 26° in a volume of 262 cc.) up to a total pressure of 45.5 mm. (47.8 mm., calculated from Dalton's law).

(17) The values are approximately 1 mm. lower than those calculated from Burg's equation.[6]

(18) J. G. Aston, M. L. Sagenkahn, G. J. Szasz, G. W. Moessen, and H. F. Zuhr, *J. Am. Chem. Soc.*, **66**, 1171 (1944).

TABLE V

TEMPERATURE VARIANCE OF THE EQUILIBRIUM CONSTANT FOR THE METHYLDICHLOROPHOSPHINE–TRIMETHYLAMINE SYSTEM

Temp., °C.	mmoles of $(CH_3)_3N$	mmoles of $P(CH_3)Cl_2$	Total press., mm.	K
−10.0	1.74	2.90	102.1	2.43
−8.0	1.72	2.90	111.2	2.38
−7.0	1.71	2.90	115.7	2.35
−6.0	1.70	2.89	120.9	2.30
−5.0	1.68	2.89	125.8	2.29
−4.0	1.67	2.89	132.0	2.21
−3.0	1.65	2.89	137.4	2.17
−2.0	1.64	2.89	143.6	2.10
−1.0	1.62	2.88	149.8	2.06
0	1.61	2.88	155.7	2.03
2.0	1.58	2.88	168.7	1.95
4.0	1.54	2.87	183.1	1.85
6.0	1.51	2.86	198.0	1.75
8.1	1.47	2.85	214.2	1.68
11.0	1.42	2.84	236.3	1.61
14.0	1.37	2.83	260.3	1.57
17.0	1.34	2.81	278.3	
20.0	1.33	2.79	290.7	

were made as a function of temperature at an amine mole fraction of 0.375 (Table V).

Behavior analogous to that of the PCl_3–$(CH_3)_3N$ system[4] was obtained in the liquid region, indicating association of the components. That the association was entirely in the liquid phase was established by measuring the pressures of mixtures of the components $(CH_3)_3N$ and CH_3PCl_2 in the vapor at 26.0°. The results in Table VI show that Dalton's law is followed closely.

TABLE VI

THE METHYLDICHLOROPHOSPHINE–TRIMETHYLAMINE SYSTEM IN THE VAPOR PHASE AT 26.0°

$(CH_3)_3N$,[a] mmoles	Press., mm. calcd.[b]	Press., mm. obsd.
0	. . .	51.4
.119	59.8	58.1
.242	68.5	66.9
.360	76.9	75.3
.494	86.3	84.6
.627	95.8	94.3
.846	111.3	109.8

[a] A sample size of 0.720 mmole of CH_3PCl_2 was used. [b] Calculated values are based on Dalton's law assuming each component to individually follow ideal behavior.

An evaluation of the pressure–composition data in Tables IV and V similar to the evaluation used in the related PCl_3 system[4] led to equilibrium constants (K) for the reaction

$$CH_3PCl_2\,(\text{soln.}) + (CH_3)_3N\,(\text{soln.}) = CH_3Cl_2P\cdot N(CH_3)_3\,(\text{soln.})$$

The results are included in Tables IV and V. From the slope of a log K *vs.* $1/T$ plot an interaction energy in solution of 2.9 kcal./mole resulted for the latter reaction.

Additional pressure–composition studies of the PCl_3–$(CH_3)_3N$ system were made at −10, 0, and 20°. The resultant values of K did not differ significantly from those previously obtained.[4] The 0° data are plotted in Fig. 2 and illustrate qualitatively the greater negative deviations in this system compared to the CH_3PCl_2 system.

In all cases K remains sensibly constant up to a mole fraction near 0.5, after which the values tend to steadily decrease as the mole fraction approaches one. The reason or reasons for the latter are not apparent but most likely are a result of the decreasing validity of some of the assumptions involved in the treatment magnified by the fact that the curve is asymptotically approaching the ideal line. In this region of small deviations and large amine concentrations K is very sensitive to the resultant calculation of the mole fraction of uncomplexed phosphorus halide.

Vapor pressures of pure CH_3PCl_2 needed to perform the calculations were obtained graphically from a log p *vs.* $1/T$ plot of the experimentally determined values partially listed in Table I. Vapor pressures of pure $(CH_3)_3N$ were calculated from an equation given by Aston.[18]

Discussion

Examination of Fig. 2 shows greater negative deviations in the PCl_3 system compared to the CH_3PCl_2 system with $(CH_3)_3N$. Taking the latter to be a result of complexing of the components, treatment of the data gave a value of 2.9 kcal./mole as a measure of the energy required for the reaction

$$CH_3Cl_2P\cdot N(CH_3)_3\,(\text{soln.}) = CH_3PCl_2\,(\text{soln.}) + (CH_3)_3N\,(\text{soln.})$$

A similar calculation[4] gave a value of 6.4 kcal./mole for the corresponding reaction with PCl_3.

According to the assumptions involved in the calculations the latter values measure the energy of complexing of the components in solution. Previous work[4,5] had indicated the presence of a P–N linkage formed by electron pair donation by nitrogen to phosphorus. That this is the case is further supported by the results reported here. Substitution of a chlorine atom by a methyl group reduces the energy of complexing in line with an expected increased electron field around phosphorus.

In the PF_3–$(CH_3)_3N$ system the complex $F_3P\cdot N(CH_3)_3$ was established and is the first complex in which PF_3 presumably is acting as a Lewis acid; however, the data obtained did not allow a calculation of the stability of the complex. Previous workers[19] found no tendency for PF_3 to interact with the organic bases $(CH_3)_2SO$, $(CH_3)_2NCHO$, and C_5H_5N; however, conditions were not conducive to complexing in that relatively weak bases were used at room temperature, where dissociation would be extensive.

Using $(C_2H_5)_3N$ as a reference base the liquid system with PF_3 at −78.5° exhibited large negative deviations indicative of complexing. Since $(C_2H_5)_3N$ was shown[5] to be a weaker base than $(CH_3)_3N$ with PCl_3, qualitatively one might expect $F_3P\cdot N(CH_3)_3$ to be more stable than $F_3P\cdot N(C_2H_5)_3$, but present data do not permit one

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(19) E. L. Muetterties, T. A. Bither, M. W. Farlow, and D. D. Coffman, *J. Inorg. Nucl. Chem.*, **16**, 52 (1960).

to say definitely that PF_3 is a stronger acceptor molecule than PCl_3. Available data,[4,5] however, do permit the following ordering of acceptor ability toward $(CH_3)_3N$: $PCl_3 > PBr_3 \sim CH_3PCl_2 > (CH_3)_3P$.

Acknowledgment.—The authors wish to express their appreciation to the National Science Foundation for a grant which supported this work and to Professor G. Mains for the mass spectral analysis.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
AT THE UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON

Preparation and Properties of N,N-Difluorohydroyxlamine-O-flourosulfonate, NF_2OSO_2F

BY MAX LUSTIG AND GEORGE H. CADY

Received September 29, 1962

The preparation of the new compound, N,N-difluorohydroxylamine-O-fluorosulfonate, from tetrafluorohydrazine, N_2F_4, and peroxydisulfuryl difluoride, $S_2O_6F_2$, is reported, and some of its chemical and physical properties are given.

Introduction

Since the reported isolation of tetrafluorohydrazine by Colburn and Kennedy in 1958,[1] this compound has been a very useful free radical difluoraminating agent. The availability of $NF_2\cdot$ free radicals from tetrafluorohydrazine has been demonstrated by both ultraviolet spectrophotometric[2] and e.p.r. studies.[3] Its use as an intermediate in the preparation of NF_2 adducts with other free radicals also has been shown.[4–7]

The chemistry of peroxydisulfuryl difluoride strongly suggests that a free radical mechanism is available in its reactions. In the literature there are numerous examples of the homolytic cleavage of the oxygen–oxygen bond in the preparation of fluorosulfates by substitution[8] and addition reactions.[8–12] This information was used to predict the formation of NF_2OSO_2F from tetrafluorohydrazine and peroxydisulfuryldifluoride. The prediction has been found to be true. The chemical and physical evidence given below has confirmed the predicted structure.

Experimental

Materials.—Peroxydisulfuryl difluoride was prepared using a catalytic method of fluorinating sulfur trioxide.[12] The latter was obtained as "Sulfan B," a stabilized liquid, made by the General Chemical Division of the Allied Chemical Corp. Fluorine, obtained in a cylinder from the General Chemical Division, was passed through a flow meter and was controlled by a nickel diaphragm valve. A cylinder of tetrafluorohydrazine, obtained from E. I. du Pont de Nemours and Co., was surrounded by a protective 5/8-in. thick steel cylinder. The valve on the tank was operated from outside the steel shield by a key attached to the cylinder.

Preparation of N,N-Difluorohydroxylamine-O-fluorosulfonate.—The preparation was carried out using a Pyrex glass vacuum apparatus, the reactor being a 2-l. flask. This was filled with tetrafluorohydrazine at a pressure of 20 mm.; then an equal volume of $S_2O_6F_2$ vapor was added slowly. A mild reaction occurred at room temperature giving a gaseous product which was found by fractional codistillation[13] to be a single substance.

Chemical Analysis.—The compound was analyzed by allowing 0.273 g. (1.81 mmoles) of the gas to react at 70° in a glass flask with an excess of 0.1 *N* NaOH solution. Even at this temperature the reaction was slow. At room temperature the rate was too slow to be of practical value. The reaction occurred according to the equation

$$NF_2OSO_2F + 4OH^- \longrightarrow NO_2^- + SO_3F^- + 2H_2O + 2F^-$$

The solution was held at about 100° for 5 days to ensure complete hydrolysis of the fluorosulfate ion to sulfate. The nitrite then was determined volumetrically by titration with potassium permanganate solution using the method of Lunde. The sulfate was determined gravimetrically as $BaSO_4$ and the fluoride gravimetrically as triphenyltin fluoride.[14] *Anal.* Calcd.: N, 9.27; S, 21.18; F, 37.72. Found: N, 9.48; S, 20.9; F, 38.0. (Calcd. for the hydrolysis reaction: nitrite, 1.81 mmoles; sulfate, 1.79 mmoles; fluoride, 5.43 mmoles. Found: nitrite, 1.85 mmoles; sulfate, 1.79 mmoles; fluoride, 5.47 mmoles.)

Molecular Weight.—The average molecular weight, obtained from vapor density measurements assuming ideal gas behavior, was 150.8 g./g.m.v. (calcd. for NF_2OSO_2F, 151.1).

Melting Point.—Due to the supercooling effect of the liquid compound, the freezing point was not obtained. The liquid phase could be observed at temperatures as low as $-183°$. Prolonged exposure to this temperature resulted in freezing. The melting point was obtained by freezing the sample in a 5 mm. o.d. Pyrex glass tube. As the tube warmed at a rate of about 0.2°/min. in a pentane bath the solid was observed to melt within a 0.5° range, the last solid disappearing at $-128.8 \pm 0.5°$.

Vapor Pressure and Boiling Point.—The vapor pressures were measured in a Pyrex glass apparatus similar to that described by Kellogg and Cady.[15] In this method a sample of the liquid was boiled under a variety of constant and measured pressures while the vapor was condensed in a reflux condenser and returned to the pot as a stream of liquid. The temperature corresponding to

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[1] C. B. Colburn and A. Kennedy, *J. Am. Chem. Soc.*, **80**, 5004 (1958).

[2] F. A. Johnson and C. B. Colburn, *ibid.*, **83**, 3043 (1961).

[3] L. H. Piette, F. A. Johnson, K. A. Booman, and C. B. Colburn, *J. Chem. Phys.*, **35**, 1481 (1961).

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