tensive work was not done to determine whether there was a peak in yield at some pH near 8.6, so it is premature to postulate whether the F^- or OH^- is most effective in aqueous solution.

Experimental

Preparation of Difluorodiazine. Method I.—In a typical experiment an ampoule containing potassium fluoride (1.25 g., 21.5 mmoles) was evacuated and heated intermittently to about 300° until no more gases were evolved. A measured gas volume of difluoramine (50.5 cc., 2.25 mmoles) was then condensed into the ampoule and the contents were allowed to remain in contact at ambient temperature for 17 hr. The gases were separated quantitatively by fractional condensation in a high vacuum line and identified both by vapor pressure and by infrared spectra. The results of similar experiments are summarized in Table I.

TABLE I

PREPARATION OF N_2F_2

$$MF + HNF_2 \longrightarrow MF\cdot HF + {}^1/_2N_2F_2$$

Metal fluoride	Time, hr.	% HNF_2 reacted	% yield N_2F_2
K	2.5	26.2	100
K	17.0	45.4	100
K	24.0	100.0	100
Rb	16.0	35.0	84
Cs	0.5	27.0	84

Because of the explosive nature of the $CsF-HNF_2$ complex a variation of the above technique was employed to effect the conversion of HNF_2 to N_2F_2 with CsF. Gaseous difluoramine (~0.5 mmole) was introduced into an evacuated ampoule containing CsF at ambient temperature. Even under these conditions, deflagrations often occurred, particularly when larger quantities of difluoramine were used.

Method II.—A reactor was constructed from a 50-cm. length of 12-mm. Pyrex tubing and packed with RbF. The RbF was heated for several hours in a tube furnace at 300–400° with pumping and then the reactor temperature was lowered to the desired level. With pumping maintained, HNF_2 was submitted from a 2-l. bulb to the reactor. The gases were slowly passed through the reactor to a 25-cm. section of 1-mm. capillary tubing and then to two traps maintained at -142 and $-196°$, respectively. The unreacted difluoramine, if any, was found in the first trap and the difluorodiazine in the second. In a typical run, with the reactor maintained at 120°, 14 cc. of HNF_2 was converted to 6.1 cc. of N_2F_2 with 1.9 cc. of HNF_2 recovered. This corresponds to an 87% conversion with 100% yield.

Difluoramine–Alkali Fluoride Addition Compounds.—Alkali fluorides (0.2–2 g.) were placed in a Pyrex ampoule which had large indentations on the bottom to provide a maximum surface exposed to the salt. The salts were heated *in vacuo* as in the preparation of difluorodiazine, after which gaseous difluoramine (20–40 cc.) was condensed therein. At least 45 min. was allowed for temperature equilibration at each temperature. A mercury manometer, with the mercury protected by Fluorolube, was used for the pressure measurements. Pressures were read with a cathetometer and all points were reproduced on other samples.

Potassium Fluoride–Difluoramine.—The dissociation pressures of $KF\cdot HNF_2$ measured as a function of temperature are (given as t (°C.), P (mm.)): -81.8, 1.2; -71.4, 4.6; -58.8, 7.9; and -46.6, 20.2. This temperature dependence is correlated by the equation $\log K_p = -1467/T + 7.784$, which corresponds to $\Delta H = 6.7$ kcal./mole for $KF\cdot HNF_2(s) = KF(s) + HNF_2(g)$.

Rubidium Fluoride–Difluoramine.—The dissociation pressures of $RbF\cdot HNF_2$ measured as a function of temperature are (t (°C.), P (mm.)): -81.6, 0.0; -72.0, 0.0; -65.0, 0.8; -57.8, 1.9; -45.8, 6.5; and -31.6, 23.5. This temperature dependence is correlated by the equation $\log K_p = -2166/T + 10.338$, which corresponds to $\Delta H = 9.9$ kcal./mole for $RbF\cdot HNF_2(s) = RbF(s) + HNF_2(g)$.

Cesium Fluoride–Difluoramine.—In a typical experiment, HNF_2 (19.7 cc., 0.88 mmole) was condensed over a sample of dried CsF (1.1233 g., 7.47 mmoles) contained in a Pyrex ampoule similar to that used in the above experiments. The equilibrium dissociation pressure at $-64.2°$ was 1.5 mm. and bleeding off small portions of the vapor resulted in no decrease in pressure until 9.2 cc. of gas was removed when the pressure dropped to essentially zero. Even pumping did not remove additional difluoramine. In all three experiments run, the ampoule was allowed to warm up and the contents exploded before reaching room temperature.

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Donor–Acceptor Function in Organofluorophosphoranes

BY E. L. MUETTERTIES AND W. MAHLER

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Phosphorus pentafluoride forms moderately stable complexes with a variety of organic donor molecules[1,2] but appears inactive toward strong acceptors. We have further assayed the acceptor and donor functions in phosphorus(V) fluorides by examining the interaction of alkyl and aryl derivatives of PF_5 with representative donor and acceptor molecules.

Acceptor Behavior.—Phenyl tetrafluorophosphorane possesses sufficient acceptor strength to yield isolable complexes with strong donors such as dimethylformamide and pyridine. These complexes in solution display a simple doublet F^{19} spectrum in which the splitting arises from FP spin–spin coupling.[3] The doublet sharpens with decreasing temperatures and shifts slightly to higher fields, but no significant change in the doublet separation occurs. Apparently the complexes are dissociated to some extent in solution

$$C_6H_5PF_4\cdot\text{donor} \rightleftharpoons C_6H_5PF_4 + \text{donor}$$

and the rate constants are sufficiently large that the n.m.r. spectra represent an averaged FP environment. Estimated lifetimes for fluorine atoms in the complex are of the order of 10^{-4} sec. For solutions of $C_6H_5PF_4$ in donor solvents of lower base strength like acetonitrile or highly hindered donor solvents like triethylamine, the F^{19} spectrum is the same as for pure $C_6H_5PF_4$; no change occurs in the FP coupling constant. Thus there is no significant complex formation in these solvents.

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(1) S. Johnson, Ph.D. Thesis, Purdue University, 1953.

(2) E. L. Muetterties, T. A. Bither, M. W. Farlow, and D. D. Coffman, *J. Inorg. Nucl. Chem.*, **16**, 62 (1962).

(3) The J_{PF} values fall in the range 840–880 c.p.s. These compare with 900–1000 c.p.s. for RPF_4 species and ~740 c.p.s. for $F_5P\cdot$base complexes.

Alkyl tetrafluorophosphoranes react exothermally with amides and other strong organic bases but the complexes are too highly dissociated for conventional isolation techniques at 25°. The n.m.r. spectral behavior of solutions of CH_3PF_4 and $C_2H_5PF_4$ in organic bases parallels that of $C_6H_5PF_4$. Acceptor strength is too severely depressed in R_2PF_3 and R_3PF_2 (R is alkyl or aryl) for detectable interaction between these derivatives and strong donor molecules, *e.g.*, dimethyl sulfoxide, down to $-78°$ (n.m.r. criterion).

The gross reduction in acceptor strength in the series $PF_5 > ArPF_4 > AlkPF_4 \gg R_2PF_3$ and R_3PF_2 reflects the expected decrease in nuclear charge on phosphorus with substitution of electropositive groups for fluorine. In addition, steric repulsion must play an important role in the reduction of acceptor properties in this series; models clearly indicate significant steric interactions for the octahedral complexes.

Formation of RPF_5^-.—Dimethyl sulfoxide complexes of aryl tetrafluorophosphoranes are not stable but decompose irreversibly in solution at 25° with attendant increase in conductivity of the solutions. Initially, simple ionization of the complex was presumed

$$2RPF_4 \cdot OS(CH_3)_2 \rightleftharpoons RPF_3[OS(CH_3)_2]^+ + RPF_5^-$$

since the n.m.r. data clearly indicated the presence of the novel RPF_5^- anion. However, no phosphorus-containing cation was identified, and $RPOF_2$ was formed in company with RPF_5^-. The decomposition of $RPF_4 \cdot OS(CH_3)_2$ appears to comprise oxygen abstraction and the formation of $RPOF_2$, H^+, and RPF_5^-.[4] The behavior of the alkyl tetrafluorophosphoranes toward the sulfoxide was similar although decomposition of the initial complex was extremely rapid. The n.m.r. characterization of these systems is described in the following paragraphs.

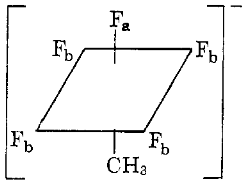
The F^{19} spectrum of a freshly prepared solution of $C_6H_5PF_4$ in $(CH_3)_2SO$ consists of two broad peaks with a separation of about 866 c.p.s. at 56.4 Mc. The two peaks broaden with decreasing temperature; freezing of the solution precluded spectral examination below $-100°$. In a fresh solution, the following equilibrium exists

$$C_6H_5PF_4 + (CH_3)_2SO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_6H_5PF_4 \cdot OS(CH_3)_2$$

and k_1 and k_2 are sufficiently large to yield spectroscopic equivalence of fluorine atoms and an averaged FP coupling constant. On standing at 20°, the two peaks in the F^{19} spectrum of $C_6H_5PF_4$ in $(CH_3)_2SO$ disappear at a measurable rate at 20° (and more rapidly at 80–90°), and a number of new lines appear. There is a doublet with 1102 c.p.s. separation which is due to $C_6H_5POF_2$ and a somewhat broad doublet with 866 c.p.s. separation due to unreacted $C_6H_5PF_4 \cdot OS(CH_3)_2$. The remaining lines comprise a pair of doublets and a pair of quintuplets; the multiplets are somewhat distorted because J_{FF} is of the same order of magnitude as the FF chemical shift. The pairs arise from PF coupling and the doublet–quintuplet fine structure establishes C_{4v} symmetry for the set of fluorine atoms. The n.m.r. parameters are $\delta_{\mathrm{FF}} \cong 3.7$ p.p.m., $J_{\mathrm{FF}} \cong 41$ c.p.s., $J_{\mathrm{PF}_4} \cong 830$ c.p.s., and $J_{\mathrm{PF}} \cong 680$ c.p.s. These values are approximate; no attempt was made to analyze the spectra precisely. The relatively low J_{PF} values suggest an octahedral structure.[2] The only species consistent with these observations is $C_6H_5PF_5^-$. In the alkyl derivatives discussed below, FH coupling is observed, and these data definitively establish the presence of the RPF_5^- ion in these sulfoxide solutions.

The fate of the dimethyl sulfoxide reactant was not established. Proton n.m.r. spectra of the $C_6H_5PF_4$–$(CH_3)_2SO$ reaction mixture show a number of new CH resonances ranging from 2.1 to 5.5 p.p.m. to the low-field side of tetramethylsilane.

Monoalkyl derivatives of PF_5 react exothermally and irreversibly with dimethyl sulfoxide. The F^{19} spectrum of a solution of CH_3PF_4 in dimethyl sulfoxide at $-30°$ contains the following resonances. There is a doublet of 1103 c.p.s. separation which is not affected by temperature changes and is due to CH_3POF_2 (CH_3POF_2 was isolated from these solutions and characterized by mass spectrographic and infrared analyses). The remaining peaks comprise a pair of doublets and a pair of quintuplets, which data again establish C_{4v} symmetry for the set of five fluorine atoms. The doublets have superimposed quadruplet fine structure which arises from HF coupling between the three protons of the methyl group and the four coplanar fluorine atoms. There is no detectable coupling between the apical fluorine atom and the methyl group. All these data rigorously establish the structure as **1**.



1

The n.m.r. parameters for $CH_3PF_5^-$ are $\delta_{\mathrm{FF}} = 10.3$ p.p.m., $J_{\mathrm{FF}} \cong 39$ c.p.s., $J_{\mathrm{PF}} \cong 691$ c.p.s., $J_{\mathrm{PF}_4} \cong 830$ c.p.s., $J_{\mathrm{H-F}_4} = 8$ c.p.s.

The part of the F^{19} spectrum arising from $CH_3PF_5^-$ is temperature dependent and undergoes the typical broadening and collapse of systems that exchange. Since this effect is reversible and since the part of the F^{19} spectrum due to CH_3POF_2 and the proton spectrum of the solution are essentially temperature independent, we ascribe this effect to a fluoride ion exchange. Since protons are present in these solutions, the process may be best described as a hydrogen fluoride catalyzed exchange. Analysis[5] of the exchange broadening sets an approximate value of 20 kcal. for the activation energy for fluoride ion exchange in this particular sys-

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[4] A similar behavior was observed with NbF_6 and dimethylformamide: K. J. Packer and E. L. Muetterties, *J. Am. Chem. Soc.*, **85**, 3035 (1963).

[5] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., p. 224.

tem. Estimates of the exchange barrier for $C_6H_5PF_5^-$ and for $C_2H_5PF_5^-$ in these sulfoxide solutions are >25 and <12 kcal., respectively. The significant difference here between $CH_3PF_5^-$ and $C_2H_5PF_5^-$ must be steric in origin, whereas the greater stability of $C_6H_5PF_5^-$ may reflect the higher effective nuclear charge on phosphorus in the aryl derivatives and the resultant greater stability of aryl pentafluorophosphate anions.

Donor Behavior.—A pentacoordinate phosphorus compound may function as a donor either (1) through ionization

$$PX_5 \rightleftharpoons PX_4^+ + X^-$$

as established for phosphorus(V) chloride and bromides or (2) through nonbonding electron pairs on the ligands. There is no evidence of such behavior for phosphorus pentafluoride but all of the mono-, di-, and trialkyl and -aryl derivatives of PF_5 give evidence of donor activity, although our data do not distinguish between mechanisms (1) and (2).

Strong acceptor molecules such as BF_3, SbF_5, and PF_5 form crystalline, colorless 1:1 complexes with the various types of alkyl and aryl phosphorus fluorides. The dialkyl derivatives form more stable complexes than the monoalkyl derivatives. For example, the dissociation pressure of $(CH_3)_2PF_3 \cdot PF_5$ is <1 mm. at 25°, whereas the dissociation pressure of $CH_3PF_4 \cdot PF_5$ is 10 mm. at −61°. Boron trifluoride forms a relatively stable complex with $(CH_3)_2PF_3$ but is immiscible with CH_3PF_4 at −120°. The aryl phosphoranes consistently form less stable complexes with SbF_5 and PF_5 than do the analogous alkyl phosphoranes.

It is tempting to conclude that these fluoride complexes consist, at least in the solid state, of RPF_3^+ or $R_2PF_2^+$ and MF_x^- aggregates. However, we have no evidence to support this formulation nor to exclude an alternative scheme based on fluorine bridge bonding.

Experimental

Reagents.—Purification of the phosphoranes was effected by distillation from sodium fluoride. All organic solvents were rigorously dried by standard procedures. Special procedures were necessary for dimethyl sulfoxide. Commercial samples were distilled and then dried further with a molecular sieve. This yielded material free of absorption in the OH infrared stretching region and free of proton n.m.r. resonance in the water region[6]; however, the conductivity was greater after molecular sieve treatment. A final distillation under reduced pressure, *ca.* 300 mm., gave sulfoxide free of water and with minimal conductivity. Commercial boron trifluoride was used without purification. Arsenic trifluoride, sulfur tetrafluoride, antimony pentafluoride, and phosphorus pentafluoride were purified by distillation.

Reactions with Donor Molecules.—Dimethylformamide (100 mmoles) was added to a solution of $C_6H_5PF_4$ (50 mmoles) in 60 ml. of ethyl ether. Considerable heat was evolved, and the solution on cooling yielded colorless crystals. *Anal.* Calcd. for $C_6H_5PF_4 \cdot OCHN(CH_3)_2$: C, 42.0; H, 4.67; F, 29.6. Found: C, 41.9; H, 5.37; F, 28.6. A similar procedure was followed with pyridine and $C_6H_5PF_4$ to give colorless crystals. *Anal.* Calcd. for $C_6H_5PF_4 \cdot NC_5H_5$: C, 50.2; H, 3.82; F, 28.9. Found: C, 50.2; H, 4.41; F, 29.1. These stoichiometries were also confirmed tensimetrically in a vacuum system; dissociation pressures of the crystalline solids were 1 mm. or less at 25°.

Reactions with Acceptor Molecules.—In a vacuum system, gaseous $(CH_3)_2PF_3$ was introduced into a reaction vessel containing 0.5 g. of SbF_5. When no further absorption occurred as evidenced by a static pressure reading, the vessel was evacuated. The product was a colorless crystalline solid. *Anal.* Calcd. for $(CH_3)_2PF_3SbF_5$: C, 6.11; P, 9.27; Sb, 36.4. Found: C, 7.17; P, 9.31; Sb, 36.1. A similar procedure was employed to make $C_2H_5PF_4 \cdot SbF_5$. *Anal.* Calcd. for $C_2H_5PF_4 \cdot SbF_5$: P, 8.78; Sb, 34.5. Found: P, 7.69; Sb, 33.4. The $BF_3 \cdot (CH_3)_2PF_3$ complex was prepared in a vacuum system by reaction of liquid $(CH_3)_2PF_3$ with gaseous BF_3 at ∼−30°; the dissociation pressure was ∼1 mm. at 25° and may account for the high phosphorus and carbon analysis. *Anal.* Calcd. for $(CH_3)_2PF_3 \cdot BF_3$: C, 12.4; B, 5.83; P, 16.7. Found: C, 14.1; B, 5.64; P, 18.54. Stoichiometries of other systems, *e.g.*, RPF_4 and R_2PF_3 with PF_5, were determined tensimetrically in a vacuum system. The dissociation pressure of $CH_3PF_4 \cdot PF_5(c)$ conformed to the equation $\log p_{mm} = 9.89 - 1882/T$ over the temperature range −78 to −20°.

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[6] This region was identified by adding water to the dimethyl sulfoxide.

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Kinetics and Mechanisms of Reactions of Iron(II) and Acidopentaamminecobalt(III) Ions[1]

BY JAMES H. ESPENSON

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Dominating current work on oxidation–reduction reactions of metal complexes in solution is the question of the mechanism by which the over-all electronic change occurs. Such systems involving one-equivalent changes have been studied extensively in the past decade.[2–5]

Reactions proving particularly useful for learning about mechanisms of electron transfer have been those of divalent metal ions with monoacido complexes of pentaamminecobalt(III), and of pentaaquo- and pentaamminechromium(III). The metal ions studied as reducing agents have included especially chromium(II), and also vanadium(II), europium(II), as well as complexed forms of these. Recent work[6] reported on the reducing agent $Co(CN)_5^{3-}$. In the present study some analogous reactions of iron(II) are considered.

$$Co(NH_3)_5X^{2+} + Fe^{2+} + 5H^+ = Co^{2+} + Fe^{3+} + X^- + 5NH_4^+ \quad (1)$$

Two related reactions have been studied previously: the reaction of iron(II) with trisoxalatocobalate(III)

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

[3] D. L. Ball and E. L. King, *ibid.*, **80**, 1091 (1958).

[4] J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86**, 1019 (1964).

[5] H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

[6] J. P. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc* **85**, 2517 (1963).