the data on quadrupole coupling. A positive e^2qQ corresponds to an excess of 5p electrons along the threefold symmetry axis (z axis) in $(C_6H_5)_3Sb$.[9] The fact that the sign of e^2qQ remains positive upon complexing indicates no large increase in 5p population along the x and y axes. A π back-donation from Fe would primarily increase p_x and p_y densities. If this were a major interaction, the sign of e^2qQ should become negative. However, the reduction in magnitude (from +17 to about +10 mm/sec) *is* consistent with a σ donation along the z axis from a hybrid orbital with some p character.

The parameters δ_{Sb} and e^2qQ change somewhat more upon complexing for $(C_6H_5)_3SbFe(CO)_4$ than for $((C_6H_5)_3Sb)_2Fe(CO)_3$. The infrared spectrum of the latter indicates both $(C_6H_5)_3Sb$ groups are in axial positions.[14] It is expected that a σ interaction along the Sb–Fe–Sb axis would be weakened at either Sb nucleus due to the presence of the other. The monosubstituted compound should have a stronger effect at Sb since no other important σ interaction occurs along the Sb–Fe bond axis. Again, these differences are not easily explained by a π interaction.

The ^{57}Fe results are reported in Table II. Two obvious effects are the second-order Doppler shift in δ_{Fe} of ~0.06 mm/sec and the reduced intensities upon raising the temperature. The features of particular interest involve trends in δ_{Fe} and Δ_{Fe} at a given temperature. First, there is a large increase in Δ_{Fe} on changing from a monosubstituted to a disubstituted compound, and for $(C_6H_5)_3As$ and $(C_6H_5)_3Sb$, an increase in δ_{Fe} as well. In the monosubstituted series both δ_{Fe} and Δ_{Fe} are about equal for $(C_6H_5)_3As$ and $(C_6H_5)_3Sb$ and somewhat smaller for $(C_6H_5)_3P$. In the disubstituted case the trend in Δ_{Fe} is the same: $(C_6H_5)_3Sb \approx (C_6H_5)_3As > (C_6H_5)_3P$, while δ_{Fe} varies through the series $(C_6H_5)_3Sb > (C_6H_5)_3As > (C_6H_5)_3P$. The splittings for $((C_6H_5)_3Sb)_2Fe(CO)_3$ and $((C_6H_5)_3As)_2Fe(CO)_3$ are among the largest observed for low-spin iron complexes. Since the geometry of these compounds is similar, D_{3h} for the disubstituted[12-14] and probably C_{3v} for the monosubstituted,[14] the above trends should reflect the relative changes in the Fe–M bond as M is varied. It is not feasible to isolate all the possible effects from the limited data. However, if the Fe–M bond is primarily σ, as the ^{121}Sb results indicate for those compounds, and since increasing δ_{Fe} corresponds to decreasing the 4s electron density at Fe, the trend in δ_{Fe} would indicate $(C_6H_5)_3Sb$ is the weakest σ donor and $(C_6H_5)_3P$ the strongest in the series[19] (the latter donating more electron density to the 4s orbitals of Fe). The increase in δ_{Fe} upon disubstitution of a weak σ donor ($(C_6H_5)_3Sb$ or $(C_6H_5)_3As$) for a strong π acceptor (CO) could then be explained simply by increased d shielding at Fe.

TABLE II

^{57}Fe MÖSSBAUER PARAMETERS[a]

Compound	Temp, °K	δ_{Fe},[b] mm/sec	Δ_{Fe}, mm/sec
$(C_6H_5)_3PFe(CO)_4$[c]	80	0.07	2.40
	295	0.12	2.47
$(C_6H_5)_3AsFe(CO)_4$[d]	80	0.10	2.71
	295	0.15	2.68
$(C_6H_5)_3SbFe(CO)_4$[d]	80	0.10	2.67
	295	0.15	2.63
$((C_6H_5)_3P)_2Fe(CO)_3$[e]	80	0.06	2.62
	295	0.12	2.68
$((C_6H_5)_3As)_2Fe(CO)_3$	80	0.16	3.24
	295	0.20	3.17
$((C_6H_5)_3Sb)_2Fe(CO)_3$	80	0.19	3.16
	295	0.27	3.16

[a] Samples contained 5–10 mg of Fe/cm^2 and gave intensities of 5–12% at 80°K and 1–3% at 295°K. Errors are estimated as ±0.01 mm/sec at 80°K and ±0.03 at 295°. [b] Relative to $Na_2Fe(CN)_5NO \cdot 2H_2O$ at 295°K. [c] Values reported in the literature, on the same scale (δ, Δ): 0.14, 2.42;[3,5] 0.17, 2.54;[1] 0.08, 2.53 mm/sec.[19] [d] These samples upon standing developed an impurity with $\delta_{Fe} \cong 0.6$ and $\Delta_{Fe} \cong 0.9$ mm/sec. [e] Values reported in the literature (δ, Δ): 0.16, 2.76;[2] 0.13, 2.71 mm/sec.[19]

The large variations in Δ_{Fe} reflect variations in V_{zz}, the component of the field gradient tensor along the axial symmetry axis, since $\eta = 0$ for either D_{3h} or C_{3v} symmetry. For Fe(0), V_{zz} will depend primarily on the population distribution in the 3d orbitals. It appears reasonable that V_{zz} should change markedly as $(C_6H_5)_3Sb$ or $(C_6H_5)_3As$ is substituted for CO due to the change in overall 3d population, as indicated above. The fact that in a series the $(C_6H_5)_3P$ compounds have the smallest Δ_{Fe} (and $|V_{zz}|$) cannot be as readily explained. However, the similarity of δ_{Fe} and Δ_{Fe} for $(C_6H_5)_3PFe(CO)_4$ and $Fe(CO)_5$[20] indicates either similar bonding for the two ligands or, more likely, compensating effects on these parameters by distinctly different types of bonding, such a case corresponding to $(C_6H_5)_3P$ as a strong σ donor.

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The Deuterolysis of Monofluorophosphate

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The kinetics and equilibria of the hydrolysis of the difluoro- and monofluorophosphates have been studied[1,2] as a function of pH. Herein we report the kinetics observed for the deuterolysis of PO_3F^{2-} as a function of pD and temperature. A kinetic isotope effect of 2.1 is observed.

Experimental Section

Materials.—Sodium monofluorophosphate was obtained from the Ozark-Mahoning Co., Tulsa, Okla. Ionic fluoride was present to the extent of less than 0.18% by weight. Deuterium oxide (99.7% D_2O) and deuterium chloride solution (99% DCl) in D_2O were purchased from Merck & Co., Inc., St. Louis, Mo. Other chemicals used in this study were of reagent quality and were used without further purification.

Rate Measurements.—A solution of Na_2PO_3F in D_2O was made just prior to use for each kinetic study. Na_2PO_3F was deter-

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TABLE I

EXPERIMENTAL RATE CONSTANTS FOR THE DEUTEROLYSIS OF 0.048 F $Na_2PO_3F^a$

	15°		25°		40°	
$[D^+]$, M	10^3k_{obsd}, min^{-1}	10^2k	10^3k_{obsd}, min^{-1}	10^2k	10^3k_{obsd}, min^{-1}	10^2k
0.200	0.974	2.66	2.70	7.38	10.21	27.93
0.400	4.24	2.84	11.44	7.68	42.68	28.66
0.670	9.76	2.79	24.28	6.92	99.49	28.34
		Av 2.76		Av 7.33		Av 28.31

[a] $k = (k_{obsd})([D^+] + k_1)/[D^+]^2$.

mined to be stable toward deuterolysis in neutral D_2O solutions. Typically, 10 ml of the Na_2PO_3F solution, 0.096 M, was added to 10 ml of thermostated DCl solution in a plastic bottle with a screw-cap top. At intervals during the reaction, 2 ml of this solution was withdrawn and discharged into a plastic dish containing 10 ml of a buffer solution. The buffer solution was composed of 3.78 M ammonium chloride and sufficient ammonium hydroxide to give a total ammonium ion concentration of *ca.* 4 M. Each sample collected was analyzed for fluoride by reading the emf *vs.* sce with the Orion Model 94-09 fluoride electrode. Emf measurements were made with a Beckman Research Model pH meter. A calibration curve was prepared by reading potentials developed from standard solutions containing sodium fluoride, Na_2PO_3F, and DCl. These materials were added to an ammonium chloride–ammonium hydroxide buffer solution so as to give solutions which would be similar to those analyzed from the kinetic studies. The sampling technique and analyses were checked by determining a k_{obsd} for the hydrolysis of Na_2PO_3F in water at 40°. In H_2O k_{obsd} (this work) was determined to be 69.3×10^{-3} min^{-1} *vs.* $k_{calcd} = 66.8 \times 10^{-3}$ min^{-1} obtained from ref 1.

Results and Discussion

The observed rate constants for the D_2O–D^+–PO_3F^{2-} system are reported in Table I. Kinetic runs were made in which the fluoride was monitored to 70–80% of the deuterolysis of PO_3F^{2-}. Rate constants (k_{obsd}) were calculated from the linear plots of log ($[F^-]_\infty - [F^-]_t$) *vs.* time. The k_{obsd} values were calculated from least-squares slopes all of which involved more than 15 data points and are based on reaction times corresponding to 40–50% reaction. The rate data were treated as before[1] by assuming that $[D^+]$ is equal to the difference between the deuteriochloric acid concentration and the monofluorophosphate ion concentration. The primary ionization constant for H_2PO_3F, K_1, had been assumed to be equal to 0.8 by Devonshire and Rowley[1] for a satisfactory treatment of their kinetic data while Clark and Jones[2] used $K_1 = 0.3$, the reported value of K_1,[3] for the treatment of their kinetic data. In order to achieve the greatest constancy for k (in the D_2O system), a value of K for D_2PO_3F was determined to be 0.48. From a plot of log k *vs.* $1000/T(°K)$, the apparent Arrhenius energy of activation for the deuterolysis of PO_3F^{2-} is estimated to be 16.7 ± 0.3 kcal/mol as compared with 16.9 ± 0.8 kcal/mol reported[2] for the hydrolysis reaction. At 25° with similar concentrations of acid and PO_3F^{2-}, the observed rate constant ratio k_{obsd}(in H_2O)/k_{obsd}(in D_2O) is found to be equal to 2.1. This observation is consistent with the proposed mechanism for the hydrolysis reaction in which a proton transfer occurs in the rate-determining step. A mechanism for the deuterolysis reaction is thus postulated to be

$$D_2PO_3F + D^+ \rightleftharpoons D_3PO_3F^+$$

$$D_3PO_3F^+ + D_2O \longrightarrow D_3PO_4 + DF + D^+$$

which is consistent with the observed kinetics.

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Antiferromagnetic Interactions in Diamminecopper(II) Carbonate

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From an X-ray diffraction study, Hanic[2,3] determined that the structure of the complex $Cu(NH_3)_2CO_3$ consisted of chains of copper(II) ions. As shown in Figure 1, two ammine groups and two oxygen atoms from the bidentate carbonate ion define a plane which contains the copper ion, and the third oxygen from a carbonate ligand of an adjacent unit occupies the fifth coordination position of a tetragonal pyramid at a distance of 2.55 Å. Tomlinson and Hathaway[4] have concluded from the results of an electron paramagnetic resonance investigation on this compound that the presence of exchange coupling between nonequivalent copper(II) ions is likely. In order to document the magnetic properties of $Cu(NH_3)_2CO_3$, we have measured the magnetic susceptibility of a powdered sample over the temperature range 4.2–295°K. Here we report the results of our study.

Experimental Section

Preparation of the Complex.—Diamminecopper(II) carbonate was prepared in the manner suggested by Tomlinson and Hathaway.[4] Basic copper carbonate was dissolved in ammonium hydroxide and undissolved residue was filtered away. To the dark blue solution was added several milliliters of 95% ethanol. The resulting greenish blue precipitate which formed was filtered off, and the remaining blue solution was allowed to stand until very dark blue crystals formed. These were collected and washed with ethanol. *Anal.* Calcd for $Cu(NH_3)_2CO_3$: C, 7.62; H, 3.84; N, 17.78. Found: C, 7.58; H, 3.90; N, 17.61.

Magnetic Measurements.—At 77, 195, and 295°K, the magnetic susceptibility of a powdered sample was determined using the Faraday technique.[5] Measurements in the temperature range 4.2–60.7°K were made using a Foner-type vibrating-sample magnetometer,[6] which was operated at field strengths of 10.0,

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