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The Acid and Metal Salt Catalyzed Hydrolyses of $PO_2F_2^-$ and PO_3F^{2-}

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A general catalytic effect is shown by Th(IV), Zr(IV), and Al(III) toward the removal of one fluoride ligand from $PO_2F_2^-$ in dilute acidic media. Release of fluoride from PO_3F^{2-} is accelerated by Th(IV) in media having a pH above 1.5; inhibition occurs under more acidic conditions. The acid hydrolysis of $PO_2F_2^-$ conforms to a series first-order rate law in which the second step proceeds approximately 1.8 times more rapidly than the first. Data were obtained for the acid-catalyzed reaction at 15, 25, and 35° in solutions ranging from 0.25 to 3.0 *M* HCl. A suitable rate expression for these concentrations is

$$\frac{-dC}{dt} = \left[\frac{a_{HCl} + K}{(a_{HCl})^2}\right]C$$

where $C = [PO_2F_2^-] + [HPO_2F_2]$ and $K = 0.45$, the apparent ionization constant of HPO_2F_2. The behavior of these fluorophosphates suggests that metal ion catalyzed fluoride release is suppressed as the oxygen:fluorine ligand ratio increases about a central atom whereas acid catalysis is facilitated. Alternative hard-base coordination sites and the chelating tendency of M^{n+} (in contrast to H^+) are used in rationalizing this trend.

Introduction

Work in this laboratory has recently shown that hard acid metal cations, such as Zr(IV), Th(IV), Al(III), and Be(II), exert a general accelerative effect upon the hydrolytic displacement of fluoride from certain polyfluoro complex anions, including the hexafluorophosphate(V) anion.[1] While the rate of initial fluoride release from PF_6^- is sharply increased by the metal ions mentioned, some instances were noted wherein the rate decreased significantly in the later stages of reactions in the presence of excess catalyst at low acidity (pH ~2). This suggested that the final oxygenated intermediate, the monofluorophosphate species, might behave quite differently toward metal ion catalysis from the starting PF_6^- complex. Since both PO_3F^{2-} and $PO_2F_2^-$ are isolable intermediates from the aquation of PF_6^-,[2] an investigation of their hydrolytic behavior in the presence of hard acids seemed necessary to clarify this point. Furthermore, there is a likelihood that the behavior of these fluorophosphates may typify that of other fluoro complexes in which oxygen ligands are also present.

The absence of rate data for the acid hydrolysis of $PO_2F_2^-$ in the literature required their collection in the present study in order to make comparisons between normal hydrolysis data in acid media and similar reactions influenced by metal ions. In addition, such data were desired to conclude the study of the acid hydrolysis behavior of the fluorophosphate anionic sequence $PF_6^- \rightarrow PO_2F_2^- \rightarrow PO_3F^{2-}$.[3,4]

Neutral and alkaline hydrolyses of $PO_2F_2^-$ proceed stepwise[5,6]

$$PO_2F_2^- + 2OH^- \longrightarrow PO_3F^{2-} + H_2O + F^-$$

$$PO_3F^{2-} + 2OH^- \longrightarrow PO_4^{3-} + H_2O + F^-$$

Under these conditions the first step proceeds much more readily. Data reported in this paper show that this order of rates does not hold in acidic media.

Experimental Section

Materials.—Potassium difluorophosphate and sodium fluorophosphate were purchased from the Ozark-Mahoning Co., Tulsa, Okla. Analysis of these materials as received revealed that 1.3 and 8.2% respectively, of the total fluoride was present in the ionic state. A fractional crystallization of KPO_2F_2 from 1:1 isopropyl alcohol–water using the procedure of Tul'chinskii, *et al.*, as a guide[7] produced second and third crops of crystals containing only 0.4% free fluoride. This material was used for all kinetic runs. Efforts to reduce the free fluoride content of Na_2PO_3F by recrystallization were not successful as this salt tends to separate from its saturated aqueous solution as a syrupy layer upon slow addition of alcohol or other precipitating solvent. Crystallization could only be induced by rapid addition of a large excess of alcohol. Material recovered in this manner showed no reduction in free fluoride. Analyses of completely hydrolyzed solutions of the commercial product consistently gave total fluoride values of more than 98% of theory for Na_2PO_3F, which indicated that the sodium fluoride impurity was accompanied by a stoichiometric amount of sodium trimetaphosphate. Such a condition is quite probable, since a commmon preparation of Na_2PO_3F involves the fusion of these two reagents.[3,8] Corrections for ionic fluoride were applied in the treatment of rate data throughout this study.

Other chemicals used in the study were of reagent quality and were used without further purification. Hydrochloric acid solutions used for hydrolysis media were standardized against standard sodium hydroxide. Catalyst ion stock solutions were prepared from the chloride or nitrate salts of the metals.

Rate Measurements (Metal Ions Absent).—A portion of the solid complex (approximately 0.4 mmol for Na_2PO_3F and 0.2 mmol for KPO_2F_2), weighed to 0.01 mg, was added to 100 ml of thermostated acid solution contained in a wide-mouth Nalgene bottle with a screw-type top. A timer was started and the bottle was shaken briefly to dissolve the sample. At intervals during the reaction 5-ml aliquots of the hydrolysate were withdrawn and immediately discharged into plastic bottles containing sufficient 1.0 *M* sodium acetate solution to provide 4 mol for each mole of acid present in the aliquot. The volume was subse-

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TABLE I

EXPERIMENTAL RATE CONSTANTS FOR THE HYDROLYSIS OF KPO_2F_2[a] (k_1) AND Na_2PO_3F[a] (k_2)

	15°			25°			35°		
[HCl], *M*	10^4k_1, sec^{-1}	10^4k_2, sec^{-1}	10^4k	10^4k_1, sec^{-1}	10^4k_2, sec^{-1}	10^4k	10^4k_1, sec^{-1}	10^4k_2, sec^{-1}	10^4k
0.247	0.122	0.230, 0.233	2.08	0.330	0.665, 0.681	5.65	0.883	1.85, 1.85	15.1
0.493	0.359	0.696, 0.703	2.08	0.956	0.193, 0.195	5.55	2.45	5.16, 5.13	14.2
0.995	1.07	2.10, 2.07	2.05	3.25	6.01, 5.96	5.58	7.11	14.4, 14.3	13.6
1.495	2.23	3.83, 3.85	2.18	5.91	9.83, 9.93	5.65	14.2	24.1, 23.6	13.8
1.99	3.53	5.55, 5.70	2.10	9.83	14.7, 15.3	5.85	23.8[b]	36.6[b]	14.1
2.50	...	...	...	13.9	20.1, 20.0	5.61	34.1[b]	47.8[b]	13.8
2.98	8.03	10.1, 10.2	2.23	21.1	26.5, 26.1	5.88	...	...	...
		Av	2.15		Av	5.71		Av	14.1

[a] The initial concentration was approximately 0.002 *M* for KPO_2F_2 and 0.004 *M* for Na_2PO_3F in each run. [b] Rate constants estimated by the Powell plot method: A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 169.

quently adjusted to 100 ml with water or, for reactions run in acid solutions less than 1.0 *M*, with 0.25 *M* acetate buffer (pH 5). After collecting all samples for a run, each was analyzed for fluoride by reading the potential developed by an Orion Model 94-09 fluoride electrode *vs.* sce using a Beckman Research Model pH meter. A calibration curve was simultaneously developed by reading the potentials from standard solutions of sodium fluoride (ranging from 0.25 to 2.0 × 10^{-4} *M*) having identical composition except for the sample being studied and brought to the same temperature (±0.5°) as the solutions to be analyzed from the run.

Rate Measurements (Catalyst Ions Present).—All runs of this type involved 0.1-mmol samples except those with KPO_2F_2 and Na_2PO_3F in which relatively large metal ion concentrations ($[M^{n+}]_{total}/[F^-]_{total} > 10$) were used and for which 0.2- and 0.4-mmol samples, respectively, were used. Aside from these runs, aliquots of hydrolysate were initially added to 20 ml of 0.5 *M* sodium citrate solution and later diluted to 100 ml with 0.25 *M* acetate buffer (pH 5). Where larger metal ion concentrations were used, the amount of sodium citrate was adjusted to provide at least 10 mol for each mole of metal ion present in the aliquot (approximately 30 mol when Th(IV) was the catalyst). It was preferable in these cases to add the sample aliquot initially to 10 ml of 0.5 *M* sodium citrate and 5 ml of hydrochloric acid, then dilute with the remaining citrate and water to 100 ml. The concentration of hydrochloric acid used was such to give the final solution a pH of approximately 5.

Separate calibration curves are necessary for each variation in composition of the hydrolysis medium.

Results

Acid-Catalyzed Hydrolysis of $PO_2F_2^-$.—The hydrolysis of $PO_2F_2^-$ was studied in HCl solutions varying from 0.25 to 3.0 *M*. The reaction proceeds to completion over this range of acidity but does not conform to a pseudo-first-order rate law as do PF_6^-[4] and PO_3F^{2-}.[3] Trial plots of this type revealed that the rate of hydrolysis of $PO_2F_2^-$ increases at an intermediate stage of the reaction. Subsequent investigation showed that a series first-order rate law is applicable. A log plot of the observed rate constants determined in this manner for the hydrolysis of $PO_2F_2^-$ *vs.* activities of the HCl reaction media exhibits a slight decrease in slope with increasing acid concentration but has an overall slope of nearly 2. This feature suggests a rate expression of the form

$$\frac{-\mathrm{d}C}{\mathrm{d}t} = [H^+][HPO_2F_2]k$$

where $C = [PO_2F_2^-] + [HPO_2F_2]$ at a designated time. A similar expression has been reported for the acid hydrolysis of PO_3F^{2-} by Devonshire and Rowley.[3] The derivation described by these investigators, which by analogy incorporates substitution in the above expression for $[HPO_2F_2]$ in terms of C and the ionization constant K for HPO_2F_2, leads to a more functional rate expression

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = \left[\frac{k[H^+]^2}{[H^+] + K}\right]C = k_1C$$

The constant k is readily defined, in terms of activities, as the quantity $(a_{HCl} + K)k_1/(a_{HCl})^2$, where k_1 is the observed rate constant for the initial stage of the series reaction as presented in the reaction sequence outlining the proposed mechanism

$$HPO_2F_2 + H_2O \overset{K}{\rightleftharpoons} PO_2F_2^- + H_3O^+$$

$$HPO_2F_2 + H_3O^+ \rightleftharpoons H_2PO_2F_2^+ + H_2O$$

$$H_2PO_2F^+ + H_2O \xrightarrow{k_1} H_3PO_3F^+ + HF$$

$$H_3PO_3F^+ + 2H_2O \xrightarrow{k_2} H_3PO_4 + HF + H_3O^+$$

All rate data collected for both $PO_2F_2^-$ and PO_3F^{2-} are presented in Table I as a function of acid concentration and temperature. The suitability of the proposed rate expression is recognizable by the constancy of k values included therein. Rate data for PO_3F^{2-} were collected for evaluation of k_2 preparatory to the determination of k_1. Kinetic runs with PO_3F^{2-} were made in duplicate, and the appearance of fluoride was monitored for at least 2 half-lives. Rate constants (k_2) were calculated from the slopes of the linear plots of log $([F^-]_\infty - [F^-]_t)$ *vs.* time. These values, together with fluoride release data from the overall hydrolysis of $PO_2F_2^-$ monitored to 80–85% of completion, were used to evaluate k_1, such that experimentally measured fluoride concentrations were in agreement with those calculated from the integrated expressions[9]

$$[HPO_2F_2]_t = [HPO_2F_2]_0e^{-k_1t}$$

$$[H_2PO_3F]_t = \frac{[HPO_2F_2]_0}{k_2 - k_1}k_1(e^{-k_1t} - e^{-k_2t})$$

$$[H_3PO_4]_t = [HPO_2F_2]_0 - [HPO_2F_2]_t - [H_2PO_3F]_t$$

$$[F^-]_t = [H_2PO_3F]_t + 2[H_3PO_4]_t$$

Initial calculations for k_1 were made using reaction times corresponding to 40–50% reaction. Values of k_1 giving close agreement between experimental and cal-

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(9) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed., Wiley, New York, N. Y., 1961, p 166.

culated [F$^-$] at this point were then used for other reaction times covering approximately the 10–80% region of total reaction. Adjustments were made as needed to assign a k_1 value giving the best overall fit to the experimental results. Typically, experimental and calculated fluoride values disagreed by not more than 3% at any point within the above region.

Temperature dependence curves for both $PO_2F_2^-$ and PO_3F^{2-} are shown in Figure 1. Curve A represents all data for the hydrolysis of $PO_2F_2^-$ in 0.25–3.0 M HCl, for which values of k were calculated from the expression $k = (a_{HCl} + K)k_1/(a_{HCl})^2$. A value for K, the ionization constant of HPO_2F_2, of 0.45 was required to achieve constancy for k in treating all the data.[10] No experimental value for K has been reported, and it is difficult to evaluate because of the formation of HF from hydrolysis. Curve B represents a similar treatment of data obtained from PO_3F^{2-}, using a value of 0.3 for K_1, the reported value for the first ionization constant of H_2PO_3F in terms of activity. Values of k from the latter calculations exhibit greatest constancy for reactions in solutions 2 M or less in acid.

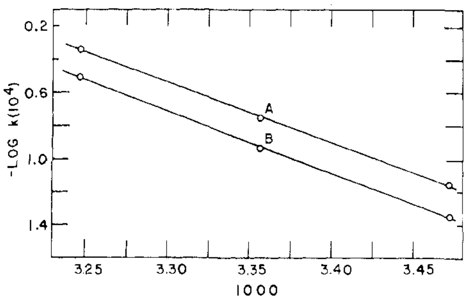

Figure 1.—Arrhenius plots of the composite rate data for the acid-catalyzed hydrolysis of KPO_2F_2 (curve A) and Na_2PO_3F (curve B).

Apparent Arrhenius energies of activation estimated from the slopes of curves A and B in Figure 1 are 16.7 ± 0.6 and 16.9 ± 0.8 kcal/mol, respectively. The latter value compares favorably with 16.3 ± 1 kcal/mol reported earlier for the acid hydrolysis of PO_3F^{2-}.[3]

Hydrolysis of $PO_2F_2^-$ in the Presence of Hard Acid Metal Cations.—In all observed instances where the rate of hydrolysis of $PO_2F_2^-$ is influenced by metal ions, the loss of the first fluoride ligand is rendered more rapid. This contrasts with the acid-catalyzed hydrolysis, for which loss of the first ligand is the slower of the two-step reaction. Furthermore, under most conditions used in this study the release of the second fluoride is inhibited by the same ions most active in promoting the displacement of the first, notably Zr(IV) and Th(IV). With the latter ion in weakly acidic media, however, it has been found that the hydrolytic removal of both ligands is promoted. Some evidence for the same behavior with Zr(IV) has been noted. Metal ion catalyzed displacement of fluoride from difluorophosphate species is strongly influenced by the acidity of the reaction media. This influence is considerably greater than previously observed for the parent PF_6^- species.[1] The catalytic effect of metal ions is enhanced by low acidity in both $PO_2F_2^-$ and PF_6^-, but the enhancement is significantly greater with $PO_2F_2^-$. For example, small concentrations of Th(IV) promote the hydrolysis of PF_6^- in 1.0 M HCl but show no significant effect on $PO_2F_2^-$ in the same media. Similarly, small amounts of Be(II), Al(III), or Fe(III) do not alter the rate of $PO_2F_2^-$ hydrolysis in 1.0 M HCl. In contrast, Zr(IV) in low concentration does catalyze the removal of the first ligand at this acidity, again emphasizing the stronger affinity of Zr(IV) for F$^-$ in strong acid.

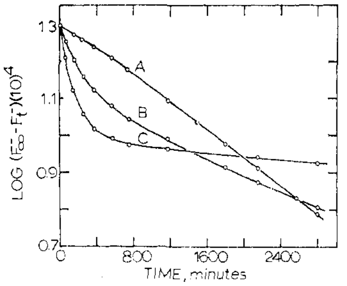

Figure 2.—First-order plots of fluoride release from 0.001 M KPO_2F_2 at 25°. The reaction medium was 0.1 M HCl in each run. Curve A represents the reaction with no Th(IV) present, curve B with 0.002 M Th(IV), and curve C with 0.005 M Th(IV).

Figure 2 presents simple first-order representations of fluoride release with time for the hydrolysis of $PO_2F_2^-$ in the presence of Th(IV) in 0.1 M HCl. These clearly show that the loss of the first fluoride ligand is catalyzed by Th(IV) which simultaneously inhibits displacement of the second. Similar data, not shown here, were obtained by use of different levels of Zr(IV) for the hydrolysis in 1.0 M HCl.

The data for Figure 2 seemed to warrant a prediction that the second step of the $PO_2F_2^-$ hydrolysis can be completely suppressed by excess catalyst at low acidity. Accordingly, runs were made using varying levels of excess Al(III) and Th(IV) (the only catalyst ions which remain in solution at pH >1 without a complexing agent) with the initial acidity of the reaction media adjusted to pH ~2. Data from reactions with Al(III) showed rate enhancement, though less than anticipated, for the removal of the first ligand and an almost imperceptible rate for the second. The rate data were satisfactorily treated as a first-order loss (with respect to [$PO_2F_2^-$] of one fluoride from $PO_2F_2^-$. Experimental rate constants estimated in this manner are presented in Table II. Evidence available at this time indicates

TABLE II

OBSERVED RATES FOR THE CATALYZED LOSS OF ONE FLUORIDE LIGAND FROM $PO_2F_2^-$ AT 25°

[Al(III)],[a] M	10^7k_{obsd}, sec^{-1}	[Al(III)],[a] M	10^7k_{obsd}, sec^{-1}	[Al(III)],[a] M	10^7k_{obsd}, sec^{-1}
None	2[b]	0.4	28	0.8	53
0.2	11	0.6	37	1.0	65

[a] The initial concentration of KPO_2F_2 was 0.002 M; the ionic strength of the reaction media was adjusted to 6.0 with $NaNO_3$; the initial pH was approximately 2. [b] Estimated from extrapolation to zero [Al(III)] with data shown.

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[10] G. M. Barrow, "Physical Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1966, p 706.

that the catalytic effect of Al(III) on the hydrolysis of $PO_2F_2^-$ is predominantly, if not completely, confined to the loss of the first ligand. This is not the case with Th(IV), however, since a catalytic effect for both steps of the hydrolysis is shown by data from the runs mentioned above. Table III presents fractional reaction times for the different levels of Th(IV) used which suffice to show the catalytic trends. The lack of smoothness in these trends may be largely attributed to the extreme sensitivity of each hydrolytic step to pH and to the varying effect on this property from adding the same amount of KPO_2F_2 to different dilutions of Th(IV). Although not feasible because of the initially fast reaction rate, more uniform data would be expected from adjusting the reaction media to a constant pH immediately after charging the sample rather than before as was done here.

TABLE III

FRACTIONAL REACTION TIMES FOR THE Th(IV)-CATALYZED HYDROLYSIS OF $PO_2F_2^-$ AT 25°

[Th(IV)],[a] *M*	Time for % of complete fluoride release, sec 50%	75%	87.5%
0.02	8400	97,200	. . .
0.04	4800	63,000	. . .
0.06	3300	39,600	93,000
0.08	1800	24,600	58,800
0.10	780	7,200	17,400

[a] The initial concentration of KPO_2F_2 was approximately 0.002 *M;* the ionic strength was adjusted to 1.0 with $NaNO_3$; the initial acidity of the reaction media was pH 2.30 (prior to addition of the sample).

Hydrolysis of PO_3F^{2-} in the Presence of Hard Acid Metal Cations.—For a time during this study it was believed that metal ions acted only to stabilize PO_3F^{2-} against hydrolysis. While definite evidence for inhibitive action is cited in Table IV, the previously described hydrolysis of $PO_2F_2^-$ in the presence of Th(IV) (Table III) shows that under proper conditions of acidity, catalytic action can be realized, at least with Th(IV) as catalyst. For this system the change from inhibition to catalysis occurs between pH 1.0 and pH 2.3. Figure 3 is a plot of the observed rate constants as a function of pH for several reactions initiated between these pH limits. The extreme pH dependence of the Th(IV) influenced hydrolysis of PO_3F^{2-} is most apparent, and, considering the rate constant for the reaction in 0.1 *M* HCl, 1.44 × 10^{-5} sec^{-1}, the turning point from inhibition to catalysis must be approximately pH 1.5 under these conditions.

TABLE IV

RATE DATA FOR THE HYDROLYSIS OF PO_3F^{2-} IN THE PRESENCE OF Zr(IV) AND Th(IV)[a]

M^{n+}	$[M^{n+}]$, *M*	Medium HCl, *M*	Temp, °C	10^4k_{obsd}, sec^{-1}
None	. . .	1.0	25	6.0
Zr(IV)	0.005	1.0	25	0.68
None	. . .	0.50	25	1.95
Zr(IV)	0.005	0.50	25	0.48
Th(IV)	0.002	0.50	25	1.01
Th(IV)	0.005	0.50	25	0.43
None	. . .	0.10	35	0.38
Th(IV)	0.0005	0.10	35	0.29
Th(IV)	0.002	0.10	35	0.068
Th(IV)	0.005	0.10	35	0.046

[a] The initial concentration of Na_2PO_3F was approximately 0.001 *M* for all runs with metal ions.

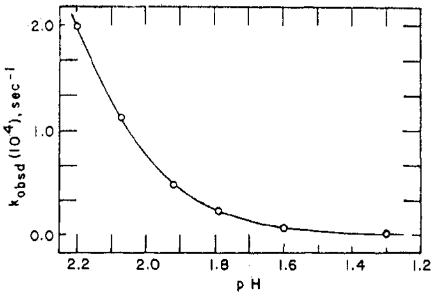


Figure 3.—A plot of the observed rate constants *vs.* pH of the reaction media for the hydrolysis of 0.004 *M* Na_2PO_3F in 0.06 *M* $Th(NO_3)_4 \cdot 4H_2O$. The acidity was adjusted with HNO_3. The pH plotted is that measured immediately after charging the sample. Samples were introduced as 5-ml portions of a *freshly* prepared solution of Na_2PO_3F. Rate constants were calculated from the integrated rate expression and the average value over 1 half-life plotted.

Discussion

Acid Hydrolysis of $PO_2F_2^-$.—The acid hydrolysis behavior of $PO_2F_2^-$ has definite similarities to that of PO_3F^{2-}. The latter hydrolyzes only slightly faster at all conditions used in this study, and an examination of the experimental rate constants in Table I reveals that the margin becomes progressively smaller as acid concentration is increased. Activation energies, which are substantially higher for PO_3F^{2-} in the alkaline hydrolyses of the two species,[11,12] do not show a significant difference for the reaction in acid. Log plots of observed rate constants for both species *vs.* activities of the HCl reaction media show only nominal differences in overall slope, reflecting a similar rate dependence upon acid concentration. Both plots show slight downward curvature with increasing acid concentration but possess general slopes approaching 2. These similarities argue that both reactions occur by the same mechanism and conform to similar rate expressions.

The small difference in reaction rates found for the acid hydrolysis of $PO_2F_2^-$ and PO_3F^{2-} may be associated with an acid–base preequilibrium step of the mechanism commonly invoked for reactions similar to this.[3,13–15] The quantity of protonated material available for the rate-determining nucleophilic attack by water clearly relates to the acceptor behavior of the central phosphorus atom in the neutral species. For HPO_2F_2, the presence of an additional fluorine atom renders phosphorus less suited for accepting a positive charge. The increased rate at which $HAsF_5(OH)$

[11] I. G. Ryss and V. B. Tul'chinskii, *Zh. Neorg. Khim.*, **8**, 1060 (1963).

[12] I. G. Ryss and V. B. Tul'chinskii, *ibid.*, **9**, 831 (1964).

[13] F. Basolo, W. R. Matoush, and R. G. Pearson, *J. Amer. Chem. Soc.*, **78**, 4883 (1956).

[14] W. A. Waters and C. G. M. deWorms, *J. Chem. Soc.*, 926 (1949).

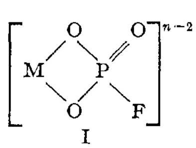
[15] M. L. Kilpatrick and M. J. Kilpatrick, *J. Phys. Colloid Chem.*, **53**, 1371, 1385 (1949).

undergoes acid hydrolysis in comparison to $HAsF_6$ bears analogy here.[16,17]

A plot of log k_{obsd} for $PO_2F_2^-$ at 25° *vs.* the Hammett acidity function H_0 approximates two linear segments which change slope very near the point for 1.0 *M* HCl. The segment pertaining to the higher acid concentrations has essentially unit slope, which denotes that the rate-determining step is dominated by a protonated form.[18] Since tetracoordinated phosphorus is involved, conceivably the loss of HF could occur either from unimolecular decomposition of the protonated intermediate or from prior attack by H_2O. The graph segment corresponding to acidities of 1.0 *M* and lower has a slope of approximately 1.5, thereby indicating a rate contribution from another path toward aquation, possibly attack by H_2O on HPO_2F_2. There is evidence that the three possible species $PO_2F_2^-$, HPO_2F_2, and $H_2PO_2F_2^+$ have ascending reactivity toward hydrolysis in the order shown. Apparent Arrhenius activation energies calculated for increasing acid concentrations show small but unidirectional changes toward smaller values with increasing acidity: 17.46, 16.96, 16.69, and 16.55 kcal/mol, respectively, for reactions in 0.25, 0.50, 1.0, and 1.5 *M* HCl.

Hydrolysis of $PO_2F_2^-$ and PO_3F^{2-} in the Presence of Some Hard Acid Metal Cations.—Experimental results for this part of the study are summarized by two observations apparently linked to a change in the oxygen:fluorine ligand ratio in the substrate. First, metal ion catalysis of fluoride removal from PO_3F^{2-} is suppressed from that of $PO_2F_2^-$, where the O:F ratio is smaller. Second, metal ion catalysis is distinctly more selective and more sensitive to pH in the more heavily oxygenated species. Since both oxygen and fluorine ligands possess hard-base character and compete for metal ion coordination, it is likely that this type of rate effect will be observed in the hydrolysis of structurally similar fluoro species.

Metal ion catalytic effects, as well as that from acids, may be attributed to initial electrophilic attack so as to confer partial positive character upon the central atom. Metal ions, under favorable conditions, produce the more dramatic increases in reaction rate because more units of positive charge are introduced into the substrate. While hydronium ion coordination is restricted to one coordination site, metal ions may coordinate through other available hard-base sites, in ways that do not favor the release of fluoride. Two forms of chelation of M^{n+} with the mono- and difluorophosphates are possible, as represented here for PO_3F^{2-}



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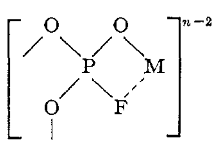

II

With respect to inductive effects, chelate structure I appears unfavorable for promoting fluoride displacement since a general drift of electrons toward the electrophilic M^{n+} ($n = 3, 4$) is expected, thereby strengthening the P–F bond and simultaneously rendering the fluorine atom less susceptible to attack by uncoordinated M^{n+}. Only coordination involving the fluoride ligand, the chelated form of which is shown in structure II, can reasonably be expected to accelerate fluoride release. In this form the electron drift is away from phosphorus which increases the possibility for P–F bond severance from nucleophilic attack by H_2O. Similar structures have been proposed by Martell, *et al.*,[19] and Fowkes, *et al.*,[20] for the metal chelate catalyzed displacement of fluoride from isopropyl methylphosphonofluoridate (Sarin) and diisopropyl fluorophosphate, respectively.

The fraction of total monofluorophosphate concentration coordinated in the manner of structure II may be quite small considering available evidence for the preferred linkage being through the two hydroxylic oxygens. When aqueous 0.1 *M* $Th(NO_3)_4$ (pH ~2.3) is added to freshly dissolved Na_2PO_3F (pH ~6.5), the pH of the mixture immediately drops to a value below that of 0.1 *M* Th(IV). The same behavior is observed upon adding Th(IV) solution to one containing $H_2PO_4^-$. Both increases in acidity result from displacement of weak acid protons on the phosphate species through coordination with Th(IV). Without coordination, addition of PO_3F^{2-} to a weakly acidic solution would consume H^+ in the formation of HPO_3F^- ($K_2 = 1.6 \times 10^{-5}$).[3] The fact that the proton concentration actually increases when Th(IV) is present indicates coordination through the hydroxylic oxygen. If, prior to mixing, the solution of Na_2PO_3F is quickly acidified to the pH of the Th(IV) solution, the increase in $[H^+]$ following mixing is in approximately a 1:1 relationship to the molarity of added PO_3F^{2-} after adjusting for dilution. This points to HPO_3F^- being the reactive species under the pH conditions of mixing (pH ~2.3), which is reasonable since H_2PO_3F is not formed in quantity at this acidity ($K_1 = 0.3$).[3]

Both Al(III) and Th(IV) yield precipitates with PO_3F^{2-} upon decreasing the acidity of the solution containing the reactants. The affinity of Al(III) for PO_3F^{2-} is apparently much less than that of Th(IV), for only a slight increase in $[H^+]$ results from mixing neutral Na_2PO_3F solution with aqueous 0.2 *M* $AlCl_3$ (pH ~2.8). No evidence for a catalytic effect by Al(III) on fluoride release from PO_3F^{2-} was observed for reaction conditions studied. This is interpreted to mean that coordination occurs only through oxygen linkages under pH conditions used.

The general catalytic effect of metal ions toward the removal of one fluoride ligand from $PO_2F_2^-$ implies that coordination to this species occurs through a fluorine and the hydroxylic oxygen. The latter is protonated

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only in strongly acidic media, based on the indicated value for the ionization constant being 0.45. This type of coordination is favored both from statistical and electrostatic considerations. Upon acquisition of a second hydroxylic oxygen following hydrolysis of one fluoride ligand, the coordinating link apparently forms *via* the two acid groups as proposed for PO_3F^{2-}.

Coordination of the metal ion to individual oxygen or fluorine ligands is conceivable for both the $PO_2F_2^-$ and PO_3F^{2-} substrates. This type of interaction is considered less prevalent than chelation as proposed, however. This conclusion arises from the restricted catalytic effect by Th(IV) on the hydrolysis of PO_3F^{2-} and the absence of such an effect by Al(III). In addition, the pH drop observed upon adding Th(IV) to HPO_3F^- suggests that both acid groups participate in the coordination.

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The Reaction of Tetrasulfur Tetranitride with Sulfuric Acid

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The stable products of the reaction of tetrasulfur tetranitride with 100% sulfuric acid are sulfur dioxide, sulfamic acid, bisulfate ion, disulfate ion, ammonium ion, and an unidentified cation which probably contains an S–N bond and which has an intense uv and a complex visible absorption spectrum. The approximate stoichiometry of the overall reaction has been determined by a combination of analytical techniques.

Introduction

The chemistry of tetrasulfur tetranitride (S_4N_4) dates back to 1835, when Gregory[1] obtained the compound by the reaction of disulfur dichloride with ammonia. Since then, many researchers have studied this compound and its large family of derivatives.[2] In this paper, we report the results of our study of the reaction of S_4N_4 with 100% sulfuric acid. Two related studies have been described by other workers.

Goehring and her coworkers[3] have reported the preparation of sulfur trioxide adducts of S_4N_4. Depending on the ratio of reactants, either $S_4N_4\cdot 2SO_8$ or $S_4N_4\cdot 4SO_3$ can be formed. When excess sulfur trioxide is used, the sulfur nitride complex is oxidized to $S_3N_2O_5$ and sulfur dioxide is evolved. Subsequent hydrolysis yields more sulfur dioxide as well as ammonia, sulfuric acid, and sulfamic acid. The hydrolysis of S_4N_4 in acidic dioxane–water solutions has been studied by Nair and Murthy.[4] They showed that the principal products are ammonium ion, sulfur dioxide, hydrogen sulfide, and elemental sulfur.

Even before we began our study, it was known that the products of the reaction of S_4N_4 with 100% sulfuric acid were not just a combination of those of the two aforementioned reactions, *i.e.*, the reactions of S_4N_4 with SO_3 and with aqueous acid. Several investigators[5–7] have reported the formation, in freshly prepared "solutions" of S_4N_4 in concentrated sulfuric acid, of a radical which has recently been identified as $S_2N_2^+$. The purpose of this study was to characterize the stable products of the reaction (*i.e.*, those present after the decay of intermediate species such as $S_2N_2^+$) and, if possible, to establish the stoichiometry of the overall reaction.

In order to systematically investigate the reaction, 100% sulfuric acid was used as the solvent instead of ordinary concentrated (95%) sulfuric acid; thus more methods of analysis were applicable. The analytical procedures employed successfully included esr, nmr, electrical conductivity, cryoscopy, uv–visible spectroscopy, and classical chemical analysis.

Experimental Section

General Information.—The 100% sulfuric acid (hereafter designated as H_2SO_4 unless otherwise specified) was prepared by mixing Baker and Adamson reagent grade concentrated H_2SO_4 (95%) and Baker and Adamson reagent grade 15% fuming H_2SO_4. The solution was first adjusted to the point where fuming just stops by the "fair and foggy" method.[8] Exactly 100% acid was obtained by a readjustment with either slightly aqueous or slightly fuming H_2SO_4 until the maximum freezing point was

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