stance B, the molar concentrations a_r, b_r, respectively, being related by

$$a_r = k_r a_1 \quad (r = 1, 2, \ldots, i) \tag{1}$$

$$b_r = l_r b_1 \; (r = 1, 2, \ldots, j) \tag{2}$$

These different forms of A and B, combined, give n complexes, the molar concentrations of which are related by

$$c_r = m_r c_1 \quad (r = 1, 2, \ldots, n) \tag{3}$$

The linear relation (eq 3) assumed to exist between the concentrations of the various complexes imposes a restriction on the composition of the complexes considered.

K_m is defined by the relation

$$K_m = \frac{\sum\limits_n c_n}{\sum\limits_i a_i \sum\limits_j b_j} \tag{4}$$

Using eq 1, 2, and 3 with 4 gives

$$K_m = \frac{c_1}{a_1 b_1} \frac{\sum\limits_{r=1}^{n} m_r}{\sum\limits_{r=1}^{i} k_r \sum\limits_{r=1}^{j} l_r} \tag{5}$$

In eq 5 c_1/a_1b_1 is the inverse of the instability constant of complex c_1; the remaining terms on the right side are generally functions of the instability constants of the various complexes and also of various experimental parameters such as hydrogen ion concentration, ionic strength, etc. These experimental parameters remain constant during the determination of the equilibrium constants by the modified method of continuous variations.[24] The maximum or minimum of an additive property of the system, such as the absorbance, corresponds to the maximum or minimum of the concentration of each of the complexes at the given conditions and hence of their sum, also. This is a direct consequence of the assumed linear relations (eq 3) between the concentrations of the complexes. Moreover, with the assumptions made, there is a one to one correspondence between the sum of the concentrations of the complexes and the measured property, *i.e.*, two points having the same value of the property must also correspond to the same value of the sum of the concentrations of the complexes. K_m (eq 4) can, therefore, be determined by the method of Sakellaridis; it is the measured equilibrium constant. Determining K_m as a function of the experimental parameters mentioned above, numerical coefficients directly related to the equilibria between complexes can be found.

In order to apply these general considerations to the case of V_{aq}^{2+} + maleic acid we examine the dependence of K_m on one parameter only, namely the hydrogen ion concentration, the other parameters assumed to remain constant. Then in the case of the two complexes of eq I and II, from eq 5

$$K_m\left(1 + \frac{K_a}{[H^+]}\right) = K_1 + K_a K_2 \frac{1}{[H^+]} \tag{6}$$

Ligand Substitution Catalysis *via* Hard Acid–Hard Base Interaction

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Abstract: Spectrophotometric and potentiometric methods have been used to obtain quantitative rate data which show that certain cations accelerate the hydrolytic displacement of fluoride from a variety of anionic fluoro complexes. Typical hard acids, such as Be(II), Al(III), Zr(IV), and Th(IV), catalyze the hydrolysis of $AsF_5(OH)^-$, PF_6^-, BF_4^-, and AsF_6^-. The extent of catalysis varies with the catalyst: total fluoride ratio, the pH of the hydrolysis media, and the stability of the catalyst ion–fluoro complex. Catalyzed hydrolyses are first order in substrate only when the ratio of catalyst to substrate is large. Direct interaction between bound fluoride and the catalyst ion rather than promotion of an acid catalyzed reaction is shown by the extensive hydrolysis of PF_6^- and AsF_6^- under conditions of acidity (pH 2) where the uncatalyzed hydrolysis has a half-life of several months. These results show that the hard and soft acid–base theory can be used to select catalysts for replacement of ligands by basing the selection on the hard or soft nature of the ligand to be replaced.

The hard and soft acid–base theory[1] has contributed significantly to the understanding of acid–base interactions and has become a useful tool for predicting the acid–base behavior of species in many types of reaction. Previously[2] it has been shown that soft acids can catalyze the replacement of soft bases present as ligands within the coordination sphere of a metal. The objective of the present study was to determine the validity of the generalization of this phenomenon to systems of hard acids and hard bases. Specifically the authors wished to determine if hard acids *in general* were able to catalyze the hydrolytic displacement of complexed fluoride. The hydrogen ion catalysis of

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[1] R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

[2] (a) C. Bifano and R. G. Linck, *Inorg. Chem.*, 7, 908 (1968), and references therein; (b) S. P. Tanner and W. C. E. Higginson, *J. Chem. Soc., A*, 1164 (1969).

such reactions is now well documented[3] and is found both in reactions of the sort

$$[Co(NH_3)_5F]^{2+} + H_2O + H^+ \longrightarrow [Co(NH_3)_5(H_2O)]^{3+} + HF$$

and with fluoro anions as in

$$PF_6^- + H^+ + 4H_2O \longrightarrow H_3PO_4 + 6HF$$

The small body of published work on metal chelate catalyzed fluoride hydrolysis gives some indication of a general interaction between chelate derivatives of hard acid cations and complexed fluoride. The acid hydrolysis of $AsF_5(OH)^-$ has been shown to be catalyzed by a number of iron(III) complexes.[4,5] Furthermore, the hydrolysis of the P–F bond in diisopropyl fluorophosphate[6] and isopropyl methylphosphonofluoridate (Sarin)[7] is catalyzed by chelates of copper(II), zirconium(IV), thorium(IV), and uranium(VI), all in nearly neutral media. Because of interest in chelated and unchelated metal ions, both have been examined as catalysts. When chelates are used, their decolorization by released fluoride can be used to follow the course of the reaction. When aquo ions are used as catalysts, a potentiometric method, adapted from that recently used in this laboratory for studying the acid hydrolysis of PF_6^-,[3b] was used. This method was used in all studies on the metal ion catalyzed hydrolysis of PF_6^- and BF_4^-. This technique offers considerable flexibility in the choice of experimental conditions.

Experimental Section

Materials. $KAsF_5(OH)$ was prepared by literature procedures[8,9] and analyzed for arsenic by an iodimetric procedure following complete alkaline hydrolysis of the complex.[8] *Anal.* Calcd for $KAsF_5(OH)$: As, 33.14. Found: As, 33.26.

KPF_6 and $KAsF_6$ were purchased from the Ozark-Mahoning Co. of Tulsa, Okla. These products were recrystallized from aqueous potassium hydroxide and washed, following suction filtration, with portions of ice water, ethanol, and ether in that order. The purified samples were dried at 100° for 2 hr and stored in a desiccator. Neither material gave evidence of ionic fluoride prior to hydrolysis.

$NaBF_4$ was purchased from Alfa Inorganics, Inc., Beverly, Mass., and was purified by addition of ethanol to a small volume of cold saturated aqueous solution until a slight turbidity appeared, whereupon it was quickly chilled until a considerable quantity of solid precipitated. After collection on a filter the solid was redissolved in the minimum volume of cold water and the precipitation and chilling steps repeated. The filtered solid from the second precipitation was washed successively with portions of ethanol and ether and dried at 100° for 2 hr before storing in a desiccator. The recrystallized material still contained 0.8% of the total fluoride in the ionic condition, for which a correction was made in treating rate data.

The samples were analyzed after ten or more half-lives to ascertain total fluoride release in most cases. Recoveries ranged from 98 to 102% of theoretical fluoride for all systems except as noted.

Chelating dyes used in the spectrophotometric study of the $AsF_5(OH)^-$ ion were obtained commercially and used throughout the study. Concentrations of acids used as hydrolysis media were checked by titration against standard sodium hydroxide.

Stock indicator solutions, except in instances where rate comparisons were sought from varying the metal:indicator ratio, contained equimolar quantities of the dye and metal ion (usually 10^{-3} *M* in each) dissolved in the same medium to be used for the hydrolysis reaction. Aliquots supplying the desired indicator concentration were then diluted to volume (100 ml) prior to a kinetic run. All metal–indicator solutions were stable as evidenced by a negligible change in absorbance upon aging several days.

Rate Measurements. Spectrophotometric. The procedure used was basically that described in ref 4. The present metal–indicator systems have higher molar absorptivities and are more sensitive to fluoride than is the Fe(III)–Ferron chelate previously used.[4] The amount of solid complex per run was reduced to 0.01–0.02 mmol and was weighed on a microbalance.

Calibration with standard sodium fluoride was necessary for each level of indicator concentration used, as the absorbance of none of the systems follows Beer's law with respect to fluoride. Absorbance readings were made with the Beckman Model B spectrophotometer zeroed on a solution containing an equimolar concentration of the indicator dye in the absence of metal ions. The wavelengths (mμ) used are as follows: Al(III)–Alizarin Red S, 490; Be(II)–Eriochrome Cyanine R, 550; and Zr(IV)–Xylenol Orange, 590 (a shoulder wavelength, the use of which was necessary to obtain an adequate fluoride capacity for study due to the high molar absorptivity of this complex).

Potentiometric. All kinetic runs were made in wide-mouth plastic bottles with plastic screw-type caps. A weighed sample (0.1 mmol) of the fluoro complex salt was added to a previously thermostated bottle containing 100 ml of the hydrochloric acid–metal ion solution selected for the hydrolysis reaction medium. A timer was started and the bottle shaken briefly. At intervals, 5-ml aliquots were withdrawn and immediately discharged into 20 ml of 0.5 *M* sodium citrate to quench the reaction and to partially displace the fluoride coordinated by the catalyst ion. The resulting solution was then diluted to 100 ml with an acetate buffer containing 0.5 *M* sodium acetate and 0.5 *M* acetic acid in such proportion to establish the pH of the final solution at 5.00 ± 0.1. The diluent was 1.1 *M* sodium acetate for the runs in 6 *M* hydrochloric acid. The diluted solutions were analyzed by measuring the potential attained by the fluoride electrode *vs.* the sce and comparison with a calibration curve. The fluoride electrode used was an Orion Model 94-09 in conjunction with a Beckman Research Model pH meter, which allowed measurement of potential to ±0.1 mV.

Separate calibration data were required for each change in acid and/or catalyst concentration. Shifts toward higher potential occurred as metal ion concentration was increased. These calibration curves were constructed on single cycle semilog paper from potentials attained by the fluoride electrode in solutions of known fluoride concentration. Calibration solutions were identical in composition and pH with the analysis solutions from the pertinent kinetic run except for substitution of a quantity of standard sodium fluoride solution for the sample.

For runs in low acid and high catalyst ion concentrations, *i.e.* for data to construct Figure 1, the 5-ml aliquots of hydrolysate were initially discharged into 10 ml of 0.5 *M* sodium citrate containing 5 ml of hydrochloric acid, since complexation of the catalyst ion was more rapid and repeatable if initiated in acidic solution. Additional 0.5 *M* sodium citrate was then added to produce a [citrate]:[metal ion] ratio of approximately 10 in the case of Al(III) and 30 with Th(IV). The concentration of hydrochloric acid was chosen so as to yield an analysis solution having a pH near 5.0 when all other components were added and the volume adjusted to 100 ml with water. For example, in runs using 0.12 *M* Th(IV) the hydrolysate aliquots were initially added to 10 ml of 0.5 *M* sodium citrate and 5 ml of 3.0 *M* HCl, then 30 ml of 0.5 *M* sodium citrate and 50 ml of water were added to give 100 ml of solution having a pH of 5.0.

Response time for the fluoride electrode in media containing large concentrations of catalyst ion and citrate (relative to fluoride) is much longer than in media without these interferences. Several minutes were sometimes required for the meter to attain a stable null reading, particularly when a solution was being analyzed that had lower fluoride than the one just preceding. Daily calibration checks were required for runs of long duration when large catalyst concentrations were being used.

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(3) See, for example: (a) M. Anbar and S. Guttmann, *J. Phys. Chem.*, **64**, 1896 (1960); (b) A. E. Gebala and M. M. Jones, *J. Inorg. Nucl. Chem.*, 31, 771 (1969); (c) L. N. Devonshire and H. H. Rowley, *Inorg. Chem.*, **1**, 680 (1962).

(4) W. L. Johnson and M. M. Jones, *ibid.*, **5**, 1345 (1966).

(5) G. Slate and M. M. Jones, unpublished results.

(6) T. Wagner-Jauregg, B. E. Hackley, Jr., T. A. Lies, O. O. Owens, and R. Proper, *J. Amer. Chem. Soc.*, 77, 922 (1955).

(7) R. C. Courtney, R. L. Gustafson, S. J. Westerback, H. Hytiainen, S. C. Chaberek, Jr., and A. E. Martell, *ibid.*, **79**, 3030 (1957).

(8) H. M. Dess and R. W. Parry, *ibid.*, **79**, 1589 (1957).

(9) L. Kolditz and W. Rohnsch, *Z. Anorg. Allg. Chem.*, **293**, 168 (1957).

The potentiometric method is particularly applicable to the study of fluoro species whose hydrolysis reactions are quenched by buffering in the pH 5 region. Substances which continue to react at this pH, *e.g.*, $AsF_5(OH)^-$, require some procedural modifications even in the absence of catalyst ions and can only be studied with catalyst if the electrode potential stabilizes rapidly, *i.e.*, rapid equilibration between citrate and the catalyst species. Electrode potential readings must be taken as quickly as good mixing is achieved and the meter has attained initial equilibrium. Higher fluoride concentrations (*e.g.*, 10^{-4}–10^{-3} *M*) expedite rapid electrode equilibration. The more active catalyst ions (*e.g.*, Zr(IV)) apparently do not release coordinated fluoride instantly in the presence of excess citrate, thereby causing a delayed electrode response which in turn restricts the value of rate data for metal ion catalyzed hydrolyses of substances which have significant reaction rates in weakly acidic media.

Results

The conditions for, and rate data from, a typical kinetic run are summarized in Table I, together with the relevant calibration points.

Table I. The Al(III) Catalyzed Hydrolysis of BF_4^- [a]

Time, min	mV	$[F^-] \times 10^3$ (sample basis) Total	Net	$[(F_\infty - F_t) \times 10^3]$
0				3.978
1.0	120.8	0.520	0.487	3.491
2.0	106.1	0.960	0.927	3.051
3.0	98.0	1.346	1.313	2.665
5.0	89.1	1.952	1.919	2.059
7.0	84.1	2.44	2.407	1.571
10.0	79.8	2.94	2.907	1.071
14.0	76.6	3.40	3.367	0.611
∞	72.5	4.06	4.027	

Calibration

$[F^-] \times 10^4$	mV
0.25	121.8
0.50	104.9
1.0	88.5
2.0	72.9

[a] $[H^+] = 0.1$, $[Al(III)] = 0.04$, $[NaBF_4] = 1.003 \times 10^{-3}$ *M*.

In this run the tetrafluoroborate sample contained 4.011×10^{-3} *M* total fluoride of which 0.033×10^{-3} *M* was initially free and 3.978×10^{-3} *M* present in BF_4^-. For analysis 5-ml aliquots were added to 20-ml portions of 0.5 *M* sodium citrate and diluted to 100 ml with a solution containing equal volumes of 0.5 *M* sodium acetate and 0.5 *M* acetic acid. The pH of this solution was 5.02 and the fluoride electrode readings were obtained on it.

$K[AsF_5(OH)]$. The hydrolysis of this complex is catalyzed by each of the following or complexes thereof: Be(II), Al(III), Zr(IV), and Ti(IV). The first three were studied as colored chelates with Eriochrome Cyanine R (ECR), Alizarin Red S (ARS), and Xylenol Orange (XO), respectively. No colored complex was found for Ti(IV), which would equilibrate rapidly with free fluoride, an essential for the metal–indicator method. Fortunately the equilibration between citrate ion and Ti(IV) from an aliquot of hydrolysate is sufficiently rapid to permit use of the potentiometric method to measure the catalytic effect of Ti(IV).

The hydrolysis of the $AsF_5(OH)^-$ ion in the absence of the metal ion catalyst and at constant acidity conforms to a first-order rate law with respect to the complex.[10] When the catalytic effect from metal ions is large, as was the case for all ions studied except Be(II), the reaction is no longer simple first order, but shows decreasing rates as the reaction progresses. This behavior was general for all anionic fluoro species studied when the catalyst concentration was of similar magnitude to that of the fluoro complex.

For the catalytic reactions of $AsF_5(OH)^-$, rate constants valid for 50% or more of the reaction could be obtained only in the case of mild catalysis by the Be(II)–ECR complex. However, a comparison of typical times required to release half of the total fluoride reflects the magnitude of catalysis among the various systems. Such a comparison is summarized in Table II.

The rates of hydrolysis of the $AsF_5(OH)^-$ ion in 0.10 and 1.0 *M* HCl as shown in Table II suggest that acid catalysis is operative. This is in agreement with the complete acid hydrolysis pattern for this complex recently resolved in this laboratory.[10]

Half-life data shown in Table II for the Al(III)–ARS system doped with fluoride ion demonstrate that catalytic activity decreases sharply with consumption of fluoride ion by the catalyst.

KPF_6. The hydrolysis of the PF_6^- ion in 1.0 *M* HCl is markedly catalyzed by Th(IV) and Zr(IV). The activity of the latter persists even in 6.0 *M* HCl. Considerably less catalytic effect is shown by Al(III) and Be(II). The reactions are first order with respect to PF_6^- only when a large excess of the catalyst ion is used, *i.e.*, pseudo-first-order catalyst concentrations. Under these conditions only the MF^{n-1} species can form in significant amount.

Typical half-life data for the uncatalyzed hydrolysis and metal ion catalyzed hydrolyses under nonpseudo-first-order conditions are shown in Table III. Table IV presents kinetic data collected using psuedo-first-order catalyst concentrations.

Precipitate formation in the hydrolysate during late stages was observed for Zr(IV)-catalyzed reactions when excess catalyst was used. This was most likely a phosphate salt, since calibration solutions of the same composition except for PF_6^- showed no tendency to give a precipitate. No precipitate was noted for either Th(IV)- or Al(III)-catalyzed reactions. An attempt to use zirconium(IV) sulfate as catalyst resulted in early precipitate formation. Solutions of 0.1 *M* zirconium(IV) sulfate in 1.0 *M* HCl exhibited considerable aging just from standing several days at room temperature.

Data reported in Tables III and IV came from media having hydronium ion concentration in great excess over that of the catalyst ion. There was some question as to whether the catalyst ions were interacting directly with bound fluoride or were merely assisting in the acid hydrolysis by facilitating removal of hydrogen fluoride. Accordingly, the hydrolysis of the PF_6^- ion was run in the presence of varying excess amounts of Al(III) and Th(IV) with the acidity adjusted to approximately 0.01 *M*. At this acidity the rate contribution from acid catalysis could not be significant. A measurable rate under these conditions together with an increase in rate

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(10) A. E. Gebala and M. M. Jones, *J. Inorg. Nucl. Chem.*, in press.

Table II. Comparison of Half-Lives for the Hydrolysis of Hydroxopentafluoroarsenate(V) at 25°

Catalyst	[Catalyst]/ [total fluoride]	Reaction medium	$t_{1/2}$, min
None		Acetate buffer^{e} pH 4.0	101^{f}
Be(II)-ECR (1:1)	0.350^{a}	Acetate buffer^{e} pH 4.0	80
	0.212^{a}	Acetate buffer^{e} pH 4.0	87.5
Be(II)-ECR (2:1)	0.418^{a}	Acetate buffer^{e} pH 4.0	69.0
	0.346^{a}	Acetate buffer^{e} pH 4.0	72.5
Al(III)-ARS (1:1)	0.500^{b}	Acetate buffer^{e} pH 4.0	5.2
	0.247^{b}	Acetate buffer^{e} pH 4.0	10.7
Al(III)-ARS (2:1)	0.555^{b}	Acetate buffer^{e} pH 4.0	3.6
	0.313^{b}	Acetate buffer^{e} pH 4.0	6.8
Al(III)-F$^-$-ARS (2:2:1)	0.492^{b}	Acetate buffer^{e} pH 4.0	6.7
	0.290^{b}	Acetate buffer^{e} pH 4.0	17.1
None		1.0 *M* HCl	84
Zr(IV)-XO (1:1)	0.450^{c}	1.0 *M* HCl	5.2
	0.385^{c}	1.0 *M* HCl	6.4
	0.300^{c}	1.0 *M* HCl	9.2
	0.227^{c}	1.0 *M* HCl	13.6
None		0.10 *M* HCl	198
Ti(IV)^{g}	0.50^{d}	0.10 *M* HCl	50
	0.30^{d}	0.10 *M* HCl	80

[a] Initial [$KAsF_5(OH)$] (10^4), 1.1–1.2. [b] Initial [$KAsF_5(OH)$] (10^4), 1.6–1.8. [c] Initial [$KAsF_5(OH)$] (10^4), 1.25–1.35. [d] Initial [$KAsF_5(OH)$] (10^4), 20. [e] Prepared by adding 0.5 *M* $NaC_2H_3O_2$ to 0.5 *M* $HC_2H_3O_2$ to a reading of 4.0 on a pH meter. [f] Calculated from the extrapolated value: $k_0 = 6.84 \times 10^{-3}$ min^{-1}. This value was obtained from a plot of k_{obsd} *vs.* [catalyst] for the Be(II)–ECR (1:1) system using five [catalyst] values ranging from 0.00006 to 0.0002 *M*. [g] Potentiometric method used with fluoride electrode potentials read rapidly in a pH 4.0 buffer.

Table III. Comparison of Half-Lives for the Catalyzed and Uncatalyzed Hydrolysis of Hexafluorophosphate(V) at 25°

Catalyst	[Metal ion] total/ [fluoride] total^{a}	Reaction medium, *M* HCl	$t_{1/2}$
None		1.0	1565 hr
Zr(IV)	0.25	1.0	718 hr
	0.50		180 hr
	1.0		78 hr
Th(IV)	0.50	1.0	676 hr
	1.0		524 hr
	1.5		213 hr
Al(III)	0.50	1.0	1290 hr
	2.0		767 hr
Be(II)	0.50	1.0	1370 hr
	1.5		1050 hr
None		6.0	1135 min^{b}
Zr(IV)	0.50	6.0	298 min
	1.0		118 min
	3.0		44 min

[a] Initial molarity of KPF_6 was 0.001 in all cases. [b] Reference 3b.

as the catalyst concentration increased would point convincingly to a direct interaction between catalyst species and the fluoro complex. That this indeed occurs is apparent from the results of these runs shown in Figure 1.

Table IV. Experimental Rate Constants from the Metal Ion Catalyzed Hydrolysis of Hexafluorophosphate(V) at 25°

Catalyst^{a}	Reaction medium, *M* HCl	10^4k_{obsd}, min^{-1}	$k_{cat}{}^{b}/k_0$
None	1.0	0.0764	
	2.0	0.214^{c}	
	4.0	1.03^{c}	
	6.0	6.10	
Zr(IV)	1.0	3.98	51.1
	2.0	16.1	74.3
	4.0	85.8	82.4
	6.0	410	66.2
Th(IV)	1.0	3.19	40.8
	2.0	3.92	17.3
	4.0	8.84	7.6
Al(III)	1.0	0.451	4.9
	2.0	0.745	2.5

[a] The mole ratio of catalyst to total fluoride was 10:1 for all catalysts used; initial molarity of KPF_6 was 0.001 in each case. [b] $k_{cat} = k_{obsd} - k_0$. [c] Reference 3b.

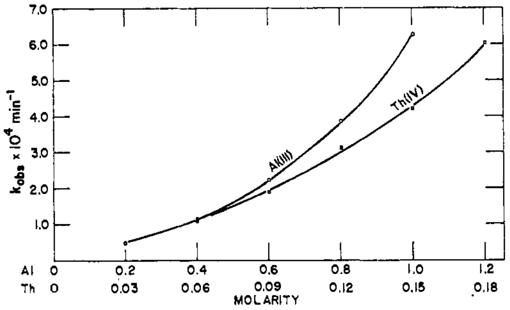

Figure 1. A plot of observed rate constants *vs.* molar concentration of catalyst for the catalyzed hydrolysis of PF_6^-. The upper abscissa represents the concentration of $AlCl_3 \cdot 6H_2O$ and the lower abscissa represents that of $Th(NO_3)_4 \cdot 4H_2O$. Ionic strength was maintained at 6.0 *M* for all runs with Al(III) and at 2.0 *M* for those with Th(IV). The initial pH was 2.0 for all runs. The k_{obsd} values plotted are valid only for approximately the first half-life (see Discussion section).

$NaBF_4$. Table V summarizes the data for the effect of metal cations on the rate of acid hydrolysis of the BF_4^- ion. Significant rate increases are apparent for all the hard acid cations examined, but that of Th(IV) exceeds all others. Pseudo-first-order conditions with respect to catalyst were used in all cases. At constant acidity the rate law is

$$-d[BF_4^-]/dt = k_{obsd}[BF_4^-]$$

Rate constants reported in Table V were evaluated by the slope of the first-order plots. Such plots were typically linear through three half-lives. In some cases the reaction was quite rapid, and although good agreement was consistently observed for replicate runs, the rate constants are shown as approximate because of inherent effects on accuracy due to the rapid rate.

$KAsF_6$. Displacement of fluoride from the As–F bond in this complex was accomplished only by use of high catalyst concentration and reflux temperature. As such, a quantitative rate study was not feasible. Significant, however, is the fact that the hydrolysis is catalyzed by hard acid cations. After refluxing a 0.001

Table V. Experimental Rate Constants for the Metal Ion Catalyzed Hydrolysis of Tetrafluoroborate at 25°

Catalyst[a]	Reaction medium, $[H^+]$	10^3k_{obsd}, min^{-1}	k_{cat}/k_0
None	1.0	7.17[b]	
	0.1	0.830[b]	
	0.01	0.013[b]	
Th(IV)	1.0	~1000	~140
	0.1	~1300	~1,600
	0.01	~1500	$\sim 1.15 \times 10^5$
Zr(IV)	1.0	800	111
	0.1	160	192
	0.01	5.77[c]	445
Al(III)	1.0	95	12.2
	0.1	133	159
	0.01	157	12,100
Ti(IV)	1.0	39.6	4.52
	0.1	32.0[d]	37.5
Be(II)	1.0	57.6	7.02
	0.1	63.0	75.0
	0.01	71.0	5,460
Al(III)	0.1[e]	124	149
	0.01[e]	114	8,780
	0.001[e]	110	

[a] The mole ratio of catalyst to total fluoride was 10:1 in each case; initial molarity of $NaBF_4$ was 0.001. [b] Experimentally determined using identical conditions for fluoride analysis in runs with catalyst except for omission of catalyst. Reference 3a gives $t_{1/2}$ = 98 min for 1.0 *M* HCl and 850 min for 0.1 *M* HCl. Above values correspond to 96.5 min for 1 *M* HCl and 830 min for 0.1 *M* HCl. [c] A NaOAc–HCl buffer was used to keep the Zr(IV) in solution. Complexation of Zr(IV) by OAc^- decreased the catalytic activity. [d] Freshly diluted from a more concentrated Ti(IV) solution in 1 *M* HCl. Aging rapidly decreased catalytic activity due to hydrolysis of Ti(IV). [e] NaCl added to adjust ionic strength to 0.26.

M solution of the complex in 1.0 *M* Al(III) at pH 2 for 80 hr, the hydrolysis was 40% complete. A similar experiment using 0.18 *M* Th(IV) yielded 29% hydrolysis after 98 hr. Refluxing the same amount of complex for 80 hr in 1.0 *M* Cd(II) at identical pH produced no detectable hydrolysis, thus indicating that the catalyst role demands a hard acid.

Discussion

Data presented in Tables II–V apparently represent the first reported quantitative evidence for interaction between hard acid metal cations and fluoride ion bound in stable anionic complexes in strongly acidic media. In addition, these data are probably the first involving metal ions functioning as catalysts for fluoride displacement in the absence of seriously competing ligands. Certainly one of the most significant aspects of the study has been the development of a simple experimental technique for the production of quantitative data on fluoride systems that appear to be well within the usual limitations of kinetic precision and accuracy. While no data are available for comparison for the catalyzed reactions, a comparison of our uncatalyzed rate data for tetrafluoroborate using the fluoride electrode and that of Anbar and Guttmann[3a] using a counting technique shows agreement within approximately 2%. Acceptable agreement has been established in a related study with acid hydrolysis rate constants of benzyl fluoride determined by Swain and Spalding[11] using a steam distillation for fluoride separation followed by a titrimetric analysis. Still another favorable comparison has been established with certain rate constants for the acid hydrolysis of monofluorophosphate reported by Devonshire and Rowley.[3c]

The fluoride electrode technique as described herein has limitations which restrict its generality. One has been stated previously in that the uncatalyzed hydrolysis rate must be negligible in the pH 5 region, which is nearly optimum for measuring the electrode potential. This difficulty can usually be circumvented in the study of hydrolysis uncatalyzed by metal ions but in general cannot be managed otherwise. A second limitation seems likely in dealing with fluorometalate complexes and the necessity for using a large excess of an auxiliary complexing agent (such as the citrate ion) to generate free fluoride ion, the only form to which the electrode responds. Interaction between the auxiliary agent and the fluorometalate species could possibly lead to erroneous potentials. Systems of this type have not been examined from a metal ion catalyzed standpoint in this laboratory.

From an examination of the results given here it appears probable that *hard acid–hard base interaction will generally accelerate fluoride displacement.* This work has demonstrated a reasonable generality for catalyzed displacement of fluoride from the As–F, P–F, and B–F linkages. Another study in progress indicates that certain C–F bonds readily yield to metal ion catalysis. Exceptions are foreseeable for metal ion catalysis as have been noted for acid catalysis, and the two processes will not necessarily parallel. Chelates can arise in these reactions which stabilize, rather than accelerate, the hydrolysis of the species.

Possible inhibitive behavior from catalyst ions was noted in collecting the data shown in Figure 1, particularly for Al(III). Plots of log $[PF_6^-]$ *vs.* time for these systems remain linear only for approximately one half-life. Beyond this point the rate diminishes and becomes extremely slow after 80–85% of reaction. This indicates that the final oxygenated intermediate, the PO_3F^{2-} ion, resists hydrolysis under these conditions and that the rate decrease is caused by a buildup of the PO_3F^{2-} species. Gustafson and Martell[12] have proposed a four-membered chelate intermediate for the hydrolysis of Sarin, and Courtney, *et al.*,[7] have done likewise for the hydrolysis of diisopropylfluorophosphate. Comparison of structural features of these compounds with those of the PO_3F^{2-} ion suggest an even greater possibility of chelation for the latter. Separate experiments have shown that Al(III) and Th(IV), as well as other ions, *inhibit* the hydrolysis of the PO_3F^{2-} ion in solutions with $[H^+]$ in the 0.1 *M* region. High acidity affords an acid-catalyzed route for the hydrolysis,[3c] which counteracts the inhibitive effect from metal ions. This accounts for rate decreases not being observed early in the reactions leading to data presented in Table IV.

The extent of catalysis is at least qualitatively related to the catalyst species employed and the acidity of the hydrolysis media. The change in greatest catalytic efficacy from Zr(IV) for the PF_6^- ion to Th(IV) for the

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(12) R. L. Gustafson and A. E. Martell, *ibid.*, 84, 2309 (1962).

BF_4^- ion suggests that relative fluoride affinity[13] may be an imperfect criterion for predicting catalytic effectiveness. Obviously the catalysis is not restricted completely to metal ion–fluoride interaction but may be influenced by metal ion interaction with the oxygenated hydrolysis product as well. This could be a factor in the efficiency of Zr(IV) for accelerating fluoride displacement from the PF_6^- ion. The results of this study have clearly confirmed that catalytic activity of a given hard acid is greatest in the absence of competing ligands. In addition, there is a definite link between catalytic activity and hydrolytic properties of the catalyst ion on the one hand and the stability of the fluoro complex resulting from catalytic action on the other. It is probable that all fluoro species involving the catalyst are collectively subject to acid hydrolysis. On that assumption, the range of acidity wherein a catalyst ion is active is broadly defined by the most basic environment in which its electrophilic nature has not been significantly diminished by hydroxyl ion attack and the other extreme as the most acidic environment in which the various fluoro complex species escape disruption *via* production of HF.

There is marked variation among the catalyst ions considered in this work with respect to the activity limits just elaborated. For instance, Zr(IV) is seen from Tables III and IV to be most active in rather acidic media, peaking in the 2–4 *M* acid region in the case of PF_6^-. On the other hand, Al(III) shows greater activity with decreasing acidity, both with the PF_6^- ion (Table IV and Figure 1) and the BF_4^- ion (Table V) hydrolyses. The activity of Ti(IV) is apparently confined to a narrow range of acidity. No acceleration of the rate of the $AsF_5(OH)^-$ ion hydrolysis was observed on adding Ti(IV) to a 1 *M* HCl hydrolysis medium, whereas its use in 0.1 *M* HCl resulted in a significant increase in rate as shown in Table II.

The complexity of kinetic behavior arising from the use of catalyst concentrations of the same order of magnitude as those of the total fluoride may be rationalized by assigning a diminishing catalytic efficiency of catalyst species as fluoride is coordinated. In this manner, the observed first-order rate may be represented as the uncatalyzed rate plus a summation of catalytic contributions to the rate from various fluoro complexes of the catalyst, namely

$$k_{\text{obsd}} = k_0 + \sum_{n=0}^{n=N} k_n[\mathrm{MF}_n]^{y-n}$$

where an active catalyst ion, M^{y+}, having a maximum coordination number *N*, has a greater catalytic effect than the MF^{y-1} species, which in turn is more active than the MF_2^{y-2} species, etc. The reasonableness of this rationale arises from the experimentally observed decreasing rates in all cases involving [catalyst]:[total fluoride] ratios of near unity when treated by first-order kinetics. Furthermore, it is evident from Table II, where the catalyst was introduced as equimolar amounts of Al(III) and fluoride, that sharply diminished catalysis is found in the presence of fluoride. A final piece of evidence may be cited from hydrolyses using pseudo-first-order catalyst concentrations. By using a tenfold excess of catalyst, both the PF_6^- and BF_4^- systems yielded linear first-order plots for at least two half-lives, thus indicating a constancy of rate only when the MF^{y-1} species is the exclusive product in significant amount.

Displacement of fluoride from the As–F bond in the AsF_6^- ion proceeds at a measurable rate only when excess catalyst concentration and reflux temperature are used. This correlates with the extreme resistance of this complex to acid hydrolysis.[14]

The hydrolytic susceptibility of the As–F bond in $AsF_5(OH)^-$ compared to that in AsF_6^- is not fully understood. One of the more plausible rationales is that of Kolditz and Rohnsch,[9] who suggest that the $AsF_5(OH)^-$ ion probably has octahedral asymmetry arising from the As–O bond being longer than the As–F bond, thereby facilitating electrophilic attack on the fluoride opposite the hydroxo group. The extra fluorine, together with the increased symmetry, makes $HAsF_6$ a much stronger acid than $HAsF_5(OH)$, thereby facilitating protonation in the latter case.

The clarification of the mechanistic role of metal ions in fluoride displacement was not an immediate objective of this work; however, the results obtained do provide information on this. Most of the data have been derived from systems wherein the hydronium ion concentration greatly exceeded that of the metal ion catalyst. This was done, first of all, for comparisons of catalyzed *vs.* uncatalyzed rates and, secondly, to exclude basic hydrolysis of the catalyst species. The role of the catalyst under these conditions might be construed to exclude direct interaction with the fluoro species and be limited to assistance in the expulsion of HF from the protonated intermediate. The results with the AsF_6^- ion, the data for the PF_6^- ion shown in Figure 1, and the final pieces of data for the BF_4^- ion in Table V prove conclusively that direct coordination is operative. All of these runs involved acid concentrations too small to contribute significantly to the rate. Only the catalyst ions functioning independently of acid hydrolysis could have brought about the large rate increases observed.

A simple interpretation of the process would thus incorporate coordination of the aquated catalyst ion to one or more fluorine atoms, thereby creating a species susceptible to nucleophilic attack, presumably by a water molecule. Indeed, the metal ion interaction must parallel that of hydronium ion to some degree. Multiple coordination is possible, however, from a single metal ion, and the electrophilic nature of the intermediate is apparently much greater than from protonation. This presumption becomes more reasonable when one considers the relative catalytic efficacy of 1.0 *M* HCl with that of 1.0 *M* $AlCl_3$. In the latter solution the initial decomposition of the PF_6^- ion is more than 80 times faster than the first; it has an accelerative effect almost identical with that of 6.0 *M* HCl on the rate of fluoride release from the PF_6^- ion. The greater polarizing effect of Th(IV) over Al(III) on the incipient fluoride ion is manifested in the fact that 0.18 *M* Th(IV) is essentially equivalent in accelerative effect to 1.0 *M*

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Al(III). Other investigations into the scope and mechanistic aspects of metal ion catalyzed hydrolysis of fluorine-containing species are in progress. Presently there is optimism regarding application to certain C–F linkages. This type of interaction has practical consequence in addition to the theoretical application of the hard and soft acid–base theory to metal-catalyzed substitutions in a number of organic reactions.

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Catalatic Activity of Metal Chelates and Mixed-Ligand Complexes in the Neutral pH Region. II. Copper–Histidine

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Abstract: The catalytic decomposition of hydrogen peroxide by Cu–histidine complexes has been investigated in the pH range 6–8 in phosphate buffer (0.013 *M*) by a differential manometric technique. The kinetic data on the initial rates of O_2 evolution are explained by a second-order rate equation, first order with respect to the 1:1 Cu–histidine chelate, and first order with respect to the HOO^- anion. Chemical and spectrophotometric studies indicated that the reaction mechanism involves a cupric–cuprous couple. The mechanism of the catalatic activity agrees with previous studies in which it was deduced that the peroxide anion acts as a bidentate ligand occupying two adjacent free sites in the complex. The greater bond angle in the Cu(I) complex facilitates rupture of the peroxidic oxygen bond. The presence of an anionic group, COO^-, on the coordinating molecule considerably reduces the catalytic activity of its copper chelate. The esr spectra of Cu(II)–histidine–H_2O_2 solutions were obtained but did not provide positive evidence regarding the participation by free radicals or radical intermediates in the reaction mechanism. However, as expected from the steady state approximation in the kinetic treatment of the system, the concentration of these radicals would be too small to be detected by esr.

The complex compounds of copper and iron provide relatively simple models for investigating the mechanisms of action of vitally important types of enzymes. They catalyze the decomposition of hydrogen peroxide, and, in general, promote the oxidation of hydrogen donors such as alcohols, phenols, and amines. However, in the neutral pH region, relatively few quantitative studies of catalatic reactions of copper complexes from which reaction mechanisms can be deduced have been reported. The reasons for the scarcity of data are due to the complexity of the equilibria at neutral pH, *e.g.*, hydrolytic reaction, mixed ligand complexes, etc.[1] It was concluded[2,3] from previous investigations in this laboratory that the reaction mechanism involved a cupric–cuprous couple and that the catalytically active complex species possessed two nitrogen atoms coordinated to the central metal ion, leaving two adjacent sites free on the metal ion. The chelating ligands presently studied had only nitrogen atoms available for coordination. Now, the catalytic reactions involving copper–histidine complexes, which possess a carboxylic group as well as donor nitrogen atoms, have been examined. In addition to the kinetics of O_2 evolution, the esr spectra of Cu–histidine–H_2O_2 solutions have been studied to ascertain if the reaction involves free radical species as was postulated by Barb, *et al.*,[4,5] for Fe(III)–H_2O_2 systems. The results reported here indicate that the catalytically active species is the 1:1 copper(II)–histidine complex and the hydrogen peroxide anion, HOO^-. The esr spectra did not provide evidence for the participation of free radical species in the reaction mechanism.

In addition to the catalytic reaction between Cu–histidine and hydrogen peroxide, it is well known that histidine undergoes metal-catalyzed decarboxylation. However, at room temperature in aqueous solutions, the decarboxylation reaction can be ignored.[6] Histidine is also known to form an H_2O_2–histidine adduct.[7] As the equilibrium constant for the formation of this adduct is not known, no correction could be made for its concentration. To minimize the effect of these side

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