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The Metal Ion Assisted Hydrolysis of Organic Fluorides

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The hydrolysis of C–F linkages in many aliphatic fluorides is accelerated in the presence of salts of Th(IV), Al(III), and other typical hard acids. Such acceleration has been noted with benzyl fluoride, fluoroacetate, benzotrifluoride, and its *ortho* hydroxy and *ortho* and *meta* amino derivatives. Two R–CF_3 compounds, trifluoroacetate and 3-nitro-4-chlorobenzo-trifluoride did not undergo hydrolysis under the conditions used. Fluorophenols were found to undergo both nitration and fluoride hydrolysis, reactions which probably proceeded through intermediate nitroso compounds. Hydrolysis of fluorophenols occurs only in the presence of nitrate salts. The product isolated from a reaction mixture containing *meta* fluorophenol and an acidic solution of thorium nitrate is 2,4,6-trinitroresorcinol. Other compounds containing a fluorine atom bonded directly to a carbon in an aromatic ring were unaffected in such reaction media.

INTRODUCTION

A previous communication reported preliminary data on accelerative effects of certain metal ions on the acid hydrolysis of benzyl fluoride (*1*). The hydrolysis of *tert*-butyl fluoride has been studied for similar effects (*2*).

The goal of the present study was to examine the effect of hard acid metal cations upon the hydrolysis of the C–F bond. To that end compounds representative of various C–F bond types have been examined to assess their response to these metal ions. The reactions studied are of the general type:

$$-\underset{|}{\overset{|}{C}}-F + H_2O + M^{+x} \longrightarrow -\underset{|}{\overset{|}{C}}-OH + H^+ + MF^{+x-1}$$

except for the fluorophenols, where nitration of the aromatic rings occurred prior to hydrolysis.

METHODS

Materials

All organic fluorine substrates were obtained commercially. The authenticity of substrates was verified by total fluoride release upon complete hydrolysis or, in the case of isomeric species, by boiling point and refractive index. In most cases, the commercial product was of adequate purity as received.

Other chemicals were of reagent quality, except for the anhydrous thorium chloride, which was purchased from Alfa Inorganics, Beverly, MA and for which no purity data were given. Unless designated to the contrary, all Al(III) solutions were prepared from $AlCl_3 \cdot 6\ H_2O$, Th(IV) from $Th(NO_3)_4 \cdot 4\ H_2O$ and Zr(IV) from either $ZrCl_4$ or $ZrOCl_2 \cdot 8\ H_2O$.

Rate Measurements

The rate of release of fluoride ion was monitored by removal of aliquots from the hydrolysis reaction media at appropriate time intervals and subsequent analysis using an Orion 92-09A Fluoride Specific Ion Electrode in conjunction with a Beckman Research Model pH Meter. Details of the analysis procedure have been described earlier (*3*). Completely aqueous reaction media were used for all substrates studied at 100°C. Media incorporating 10% or less of ethanol (V/V) were used for benzyl fluoride, *o*-hydroxy- and *o*-aminobenzotrifluoride substrates.

Substrates requiring 100°C reaction temperature were most satisfactorily studied in sealed glass ampoules containing 5 ml portions of the reaction mixture. In a typical run using 0.5 *M* Th(IV) to assist the hydrolysis of $m\text{-}H_2NC_6H_4CF_3$, a sample weight of 0.0877 g (0.545 mmole) was dissolved in 50 ml of 0.5 *M* $Th(NO_3)_4$, from which 5 ml aliquots were transferred to seven ampoules. At appropriate reaction times individual ampoules were withdrawn from the bath, cooled in ice, and emptied into 45 ml of 1:1 0.5 *M* sodium citrate: pH 5 acetate buffer (0.5 *M*). A 10 ml portion of this solution was prepared for analysis by first adding it to 15 ml of a 2:1 0.5 *M* sodium citrate: 2 *M* HCl solution before dilution to a final volume of 100 ml with 20 ml of 0.5 *M* sodium citrate and 55 ml of pH 5 acetate buffer (0.5 *M*). (A smoother complexation of the metal ion by citrate occurs if initiated in acidic solution.) This procedure gave an analysis solution having a pH of approximately 5.2, a Th(IV) concentration of 0.005 *M*, a [citrate]/[Th(IV)] ratio of approximately 35, and a maximum fluoride concentration of 3.27×10^{-4} *M* (for complete hydrolysis). Upper limits of metal ion concentration in the final analysis solution appear to be about 0.05 *M* for Al(III) and 0.01 *M* Th(IV) and Zr(IV) for best electrode performance. Mg(II) in an acetate buffer solution appears to have little adverse effect on electrode behavior.

Calibration with standard solutions of sodium fluoride was necessary for each variation in reaction conditions. These standards were made to the same composition of the analysis solutions from kinetic runs except for the omission of sample. Aging of the standards prior to analysis was made to coincide with that for samples collected during the kinetic runs as nearly as possible, as was the temperature of the solutions when analyzed.

Isolation of 2,4,6-Trinitroresorcinol from the Nitration–Hydrolysis Reaction of m-Fluorophenol

A 0.5153 g portion of *m*-fluorophenol was added to 150 ml of 0.5 *M* $Th(NO_3)_4$ that had been adjusted to pH 2.0 and the mixture was refluxed in a 300 ml flask. Total reflux time was 190 hr, during which time 1 ml aliquots were withdrawn at intervals and analyzed to determine when fluoride release stopped. The fluoride concentration at termination was 88% of the theoretical value and had not changed for the final 54 hr. The reaction mixture was acidified with 4 *M* H_2SO_4 to a pH reading of zero.

The acidified reaction mixture was extracted several times with 30 ml portions of ether, and the combined ether extracts were concentrated to a small volume. The residual liquid was allowed to evaporate slowly in air at room temperature. The yellow residue was taken up in about 5 ml of ether. Slow addition of petroleum ether caused yellow crystals to separate. The first crop of crystals was filtered off after the mixture was chilled. This material melted at 180–182°C and did not change the melting point of an authentic sample of 2,4,6-trinitroresorcinol when approximately equal portions of the two materials were mixed. A second crop of crystals obtained by adding more petroleum ether to the mother liquor melted at 179–181°C.

RESULTS

The Hydrolysis of Benzyl Fluoride

The half-life for the hydrolysis of benzyl fluoride in 10% aqueous acetone (V/V) at 50°C is about 24 days (*4*). The reaction is catalyzed by acid, and in 3.0 *M* $HClO_4$ the half-life is approximately 10 hr at 25°C. An earlier report (*1*) showed that small concentrations of Th(IV), Zr(IV), and Al(III) sharply increase the reaction rate in acid media ranging from 1 to 3 *M*. Further study has shown that larger effects from Th(IV) and Al(III) are realized when the reaction is carried out in media of low acidity (pH 2–3). Rate increases of three to four orders of magnitude are attained.

The effect of varying concentrations of Al(III) and Th(IV) on the rate can be seen from data in Table 1, together with the smaller effect from Mg(II). Sufficient excess of metal salt concentrations was used in all cases to limit any significant metal ion–fluoride interaction to the formation of MF^{n-1} species. All reactions were monitored for approximately two half-lives of the substrate. The observed reaction rates for systems involving Th(IV) and Al(III) are almost completely due to metal ion assistance. This is quite evident from a plot of the observed rate constants vs metal ion concentration extrapolated to zero metal ion as is done for the Th(IV) influenced reaction in Fig. 1.

TABLE 1
EXPERIMENTAL RATE DATA FOR THE METAL ION ASSISTED HYDROLYSIS OF BENZYL FLUORIDE[a]

Catalyst	M_{catalyst}	Temp (°C)	$k_{\text{obsd}}(10)^4$ (sec^{-1})
Th(IV)[b]	0.03	25	1.98; 1.93
	0.06	25	4.00; 4.25
	0.09	25	6.03; 6.30
	0.12	25	8.83; 9.03
	0.15	25	11.6; 10.8
	0.18	25	13.5; 14.1
Al(III)[c]	0.1	25	0.400; 0.375
	0.2	25	0.917; 0.968
	0.3	25	1.82
	0.4	25	2.78
	0.5	25	4.10
None	—	50	0.003[d]
Mg(II)[e]	0.5	50	0.0167
	1.0	50	0.0430
	1.5	50	0.0925
	2.0	50	0.197
	2.5	50	0.368

[a] The molarity of the substrate was approximately 0.004 for all runs. Samples were introduced as 2 ml aliquots of a standard solution of the substrate in ethanol to 98 ml of the previously thermostated aqueous metal salt or acid solution.

[b] The salt was $Th(NO_3)_4 \cdot 4\,H_2O$. The initial pH of the reaction media ranged from 2.3 to 2.7.

[c] The salt was $AlCl_3 \cdot 6\,H_2O$. The initial pH was adjusted to 2.5 for all runs.

[d] Reference *4*.

[e] The salt was $MgCl_2$·hydrate. No adjustments were made to either the pH or the ionic strength of the solution.

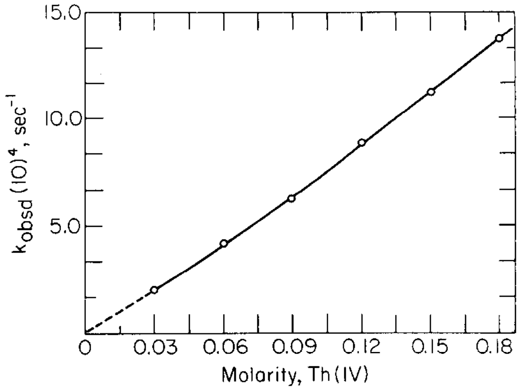


FIG. 1. An extrapolated plot of the observed rate constants for the hydrolysis of 0.0039 *M* benzyl fluoride at 25°C vs the concentration of the Th(IV) catalyst.

A temperature dependence study was made for the reaction accelerated by 0.09 *M* Th(IV). The Arrhenius plot is shown in Fig. 2. The Arrhenius energy of activation from this plot is 20.4 kcal/mole.

The Catalyzed Hydrolysis of Fluoroacetate

Hydrolysis of this substrate occurred at a significant rate only under vigorous conditions. The reaction is accelerated by acid and by salts of Al(III) and Th(IV). Both types of reactions are first order with respect to fluoroacetate concentration. Reaction media involving Th(IV) show a marked tendency to develop turbidity as

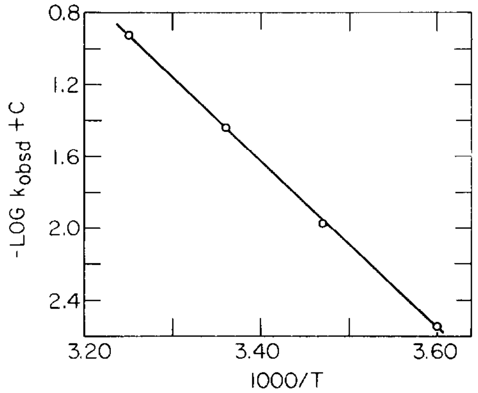


FIG. 2. An Arrhenius plot for the hydrolysis of 0.00385 *M* benzyl fluoride at 5, 15, 25 and 35°C with 0.09 *M* Th(IV).

TABLE 2
RATE DATA FOR THE HYDROLYSIS OF SODIUM FLUOROACETATE AT 100°C[a]

Added species	(M) Added species	$k_{obsd}(10)^6$ (sec^{-1})
Al(III)[b]	0.20	4.87; 4.77
	0.50	7.53; 7.02
	0.80	11.2; 10.7
Th(IV)[c]	0.02	3.70
	0.04	5.10
	0.06	6.42
	0.10	7.50
	0.15	12.1
	0.10[d]	10.4
HCl	0.01	<0.008
	0.1	0.341
	0.5	0.567
	1.0	0.795
	4.0	4.28

[a] Reaction mixtures were approximately 0.004 M in substrate which was added to 100 ml of the aqueous metal salt or acid solution at reflux.

[b–d] Initial pH of the reaction media: (b) adjusted to 2.0 with HCl; (c) adjusted to 1.0 with HCl; (d) adjusted to 1.5 with HCl.

the reaction progresses in media of pH 2–3. For this reason, media of pH 1.0 were used for most of the Th(IV) assisted reactions. Reactions with Al(III) and Th(IV) were carried out at reflux and monitored for two half-lives. Rate constants were calculated from the slopes of the first order plots. These plots remained linear through two half-lives in the case of the Al(III) reactions, but showed decreasing reaction rates beyond the 50–60% region of total reaction when Th(IV) was used.

Rate data are presented in Table 2. The acid hydrolysis data are based on reactions monitored to approximately 10% of completion.

The Effect of Al(III) and Th(IV) on the Hydrolysis of the Trifluoromethyl Group

Four of the six substrates bearing the –CF_3 group examined definitely underwent more rapid hydrolysis in the presence of Al(III) and Th(IV). These are benzotrifluoride and its *o*-hydroxy, and *o*- and *m*-amino derivatives. Two, the trifluoroacetate ion and 3-nitro-4-chlorobenzotrifluoride, showed no measurable hydrolysis. Rate data were obtained at 60 or 100°C. Even at 100°C and large metal ion concentrations, the hydrolysis of benzotrifluoride and its *m*-amino derivative proceed slowly. A precipitate occurs when 0.0324 M *m*-aminobenzotrifluoride and 2.0 M $AlCl_3 \cdot 6\,H_2O$ are mixed at room temperature. This solid readily dissolves upon heating the mixture to 100°C. Neither benzotrifluoride nor 3-nitro-4-chlorobenzotrifluoride is soluble in the aqueous metal salt media at room temperature. The former compound appears to dissolve at 100°C, but the latter does not. These two species were examined only in sealed ampoules.

Table 3 contains rate data on substrates for which rate constants could be obtained. Table 4 presents information concerning reaction conditions and extent of reaction for substrates where only one or two readings were made during the reaction period. All percentage reaction values refer to the total release of fluoride from –CF_3.

The Hydrolysis of Fluorophenols via Interaction with Nitrate Salts of Al(III) and Th(IV)

Because of the electron releasing nature of the substituent, the isomeric fluorophenols and fluoroanilines were selected for study of fluorine substituted on an aromatic ring.

All isomers of fluoroaniline were placed in 0.002–0.026 M concentrations with 1.0 M $AlCl_3$, 0.5 M $Th(NO_3)_4$, and 0.1 M HCl for 69 hr in sealed ampoules at 100°C. No detectable fluoride release (<1% reacted) was observed except in the Th(IV) reaction with *p*-fluoroaniline, where approximately 1.4% of the fluoride was released.

Extensive hydrolysis occurs with the isomeric fluorophenols at 100°C. The *meta*- and *para*-isomers react more readily than the *ortho* isomer. Hydrolysis does not occur when the chloride salts of Al(III) and Th(IV) are used under the same conditions. The use of sodium nitrate to provide comparable levels of the nitrate ion to those from Al(III) and Th(IV) nitrates does not

TABLE 3

EXPERIMENTAL RATE CONSTANTS AND REACTION CONDITIONS FOR THE METAL ION ASSISTED HYDROLYSIS OF TRIFLUOROMETHYL SUBSTRATES

Substrate	(*M*) Substrate	Metal	(*M*) Metal	Init. pH	Temp (°C)	Method[a]	$k_{obsd}(10)^6$ (sec^{-1})	% Reaction Monitored
m-$H_2NC_6H_4CF_3$[b]	0.0324	Th(IV)	1.0	1.0	100	A	1.8	41
	0.00554	Th(IV)	0.5	1.6	100	A	1.3	33
	0.00238	Th(IV)	0.15	2.1	100	A	.58	16
	0.0109	Th(IV)	0.5	1.6	100	B	1.5	50
	0.0328	Al(III)	2.0	0.8	100	A	1.7	38
	0.00284	Al(III)	1.0	2.1	100	B	.73	66
	0.00223	Al(III)	0.6	2.5	100	B	.60	57
	0.00236	HCl	0.1	—	100	B	<0.008	—
	0.00284	HCl	4.0	—	100	B	<0.008	—
o-$H_2NC_6H_4CF_3$[b]	0.00212	Th(IV)	0.1	2.60	60	C	45.6	77
	0.00212	Th(IV)	0.1	2.27	60	C	43.3	72
	0.00212	HCl	0.01	—	60	C	1.3	8
o-$HOC_6H_4CF_3$[b]	0.00205	Th(IV)	0.1	2.60	60	C	93.8	73
	0.00205	Th(IV)	.1	2.27	60	C	61.5	60
	0.00205	Th(IV)	0.05 $\mu = 0.50$	2.60	60	C	66.3	81
	0.00205	Th(IV)	0.05 $\mu = 1.00$	2.60	60	C	42.0	66
o-$HOC_6H_4CF_3$	0.00203	Al(III)	0.1	3.2	100	B	31.3	60
	0.00203	Al(III)	0.4	2.7	100	B	76.0	88
	0.00200	HCl	0.01	—	100	B	<0.5	4

[a] Reaction Methods: A—Teflon bottle as reaction vessel; B—Aliquots or reaction medium sealed in glass ampoules; C—Reaction in glass bottles closed with rubber septums.

[b] Reaction mixtures involving the m-$H_2NC_6H_4CF_3$ substrate were completely aqueous. Reaction mixtures involving the other substrates were aqueous except for a small volume of ethanol containing the substrate (not exceeding 5% of the total reaction mixture volume). See Experimental section for typical procedure. Ionic strength adjustments in reactions involving o-$HOC_6H_4CF_3$ were made with $NaNO_3$.

TABLE 4

REACTION CONDITIONS AND EXTENT OF REACTION FOR THE CATALYZED HYDROLYSIS OF TRIFLUOROMETHYL SUBSTRATES

Substrate	(*M*) Substrate[a]	Metal	(*M*) Metal	Init. pH	Temp (°C)	Method	Hours reacted	Percent reacted
$C_6H_5CF_3$	0.0234	Th(IV)	0.5	2.0	100	B	165	38.5
	0.0249	Al(III)	1.0	2.1	100	B	165	12.1
	0.0245	HCl	4.0	—	100	B	165	1.5
o-$HOC_6H_4CF_3$	0.0221	$ThCl_4$	0.5	1.5	100	B	12.5	100
	0.0195	HCl	0.1	—	100	B	12.5	1.8
o-$H_2NC_6H_4CF_3$	0.0274	$ThCl_4$	0.5	1.5	100	B	12.5	100
	0.0281	HCl	0.1	—	100	B	12.5	60
F_3CCOO^-	0.0206	Th(IV)	0.5	2.0	100	B	165	<1
	0.0214	Al(III)	1.0	2.1	100	B	165	<1
	0.0197	HCl	4.0	—	100	B	165	<1

[a] Aqueous reaction media were used for all substrates shown here. See Experimental section for details of typical procedure.

TABLE 5

Experimental Data and Reaction Conditions for the Nitration–Hydrolysis Reaction of Fluorophenols in Sealed Ampoules at 100°C

(M) Substrate[a]	Catalyst	(M) Catalyst	Init. pH	Hours reacted	% Total F^- release
		o-Fluorophenol			
0.0223	$Al(NO_3)_3$	1.0	2.2	70	68
0.0253	$Th(NO_3)_4$	0.5	1.6	69	47
0.0225	$NaNO_3$	2.0	Neut.	75	<1
0.0245	$NaNO_3$-HNO_3	2.0	2.0	68	14
0.0250	$NaNO_3$-HNO_3	2.0	1.0	68	36.4
		m-Fluorophenol			
0.0295	$Al(NO_3)_3$	1.0	2.2	70	80
0.0289	$Th(NO_3)_4$	0.5	1.6	69	95
0.0293	$NaNO_3$	2.0	Neut.	75	<1
0.0263	$NaNO_3$-HNO_3	2.0	2.0	68	11
0.0248	$NaNO_3$-HNO_3	2.0	1.0	68	55
		p-Fluorophenol			
0.0264	$Al(NO_3)_3$	1.0	2.2	70	82
0.0265	$Th(NO_3)_4$	0.5	1.6	69	93
0.0264	$NaNO_3$	2.0	Neut.	75	1.5
0.0238	$NaNO_3$-HNO_3	2.0	2.0	68	19.2
0.0255	$NaNO_3$-HNO_3	2.0	1.0	68	35.9

[a] Reactions were carried out in aqueous media exclusively. Accelerated hydrolyses were observed only when the metal salt was the nitrate.

effect fluoride release unless nitric acid is added. The extent of reaction is dependent upon the amount of added acid. Isolation of 2,4,6-trinitroresorcinol was readily accomplished from the reaction of $Th(NO_3)_4$ and m-fluorophenol. The initial release of fluoride is very rapid, but the rate diminishes as the reaction progresses. The rate is faster in sealed ampoules than under reflux. In all cases the reaction media become intensely colored (red to reddish-brown) upon heating and progress to a lemon yellow as the reaction proceeds. Noticeable pressure develops in sealed ampoules.

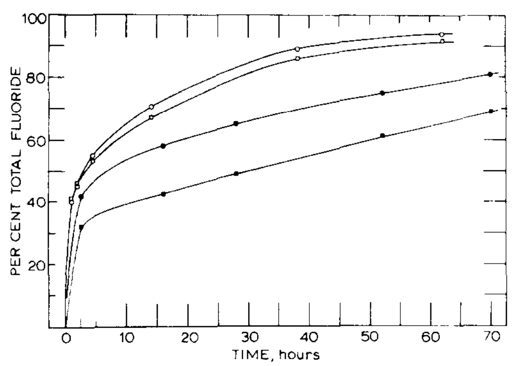


Fig. 3. Fluorophenol (FP) hydrolysis at 100°C with 0.5 M Th(IV) as nitrate. Open circles and squares: sealed tube reaction of m-FP at pH 1.58 and 2.00, respectively. Solid circles: reaction of m-FP at reflux at pH 2.00. Solid squares: reaction of p-FP at reflux, pH 2.00.

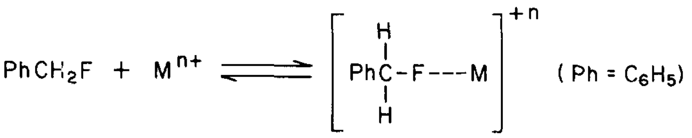
Table 5 contains data obtained on these systems. Figure 3 presents data on the reactions of m- and p-fluorophenol in the presence of $Th(NO_3)_4$.

Discussion

The Effect of M^{n+} on the Hydrolysis of the Fluoromethyl Group

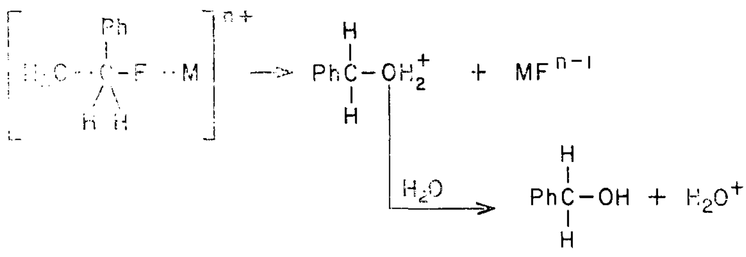
The results indicate that many organic fluorine compounds undergo accelerated hydrolysis in the presence of hard acid cations. The accelerative effects of Al(III) and Th(IV) in the hydrolysis of benzyl fluoride and fluoroacetate indicate that these and similar hard acids activate the $-CH_2F$ group for hydrolysis.

It appears that the hydrolysis involves a rapid equilibration in which M^{n+} is weakly coordinated to the substrate.

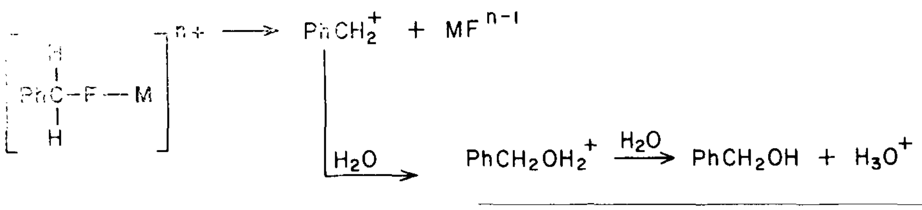


$$PhCH_2F + M^{n+} \rightleftharpoons \left[Ph\overset{H}{\underset{H}{C}}-F---M \right]^{+n} \quad (Ph = C_6H_5)$$

Coordination confers positive character to the substrate, leading to the expulsion of MF^{n-1}, either by a bimolecular process involving prior aquation to produce a five-coordinate intermediate



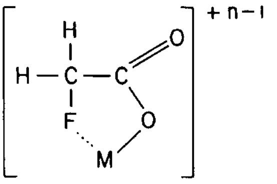
or by a unimolecular process which generates a carbanium ion



Some preference for the bimolecular route arises from consideration of the mechanism proposed for the acid-catalyzed reaction (*4*) and the analogy that exists between the two processes.

The availability of the lone pairs of the fluorine atom on fluoroacetate is diminished because of their nearness to the carboxyl group. Coordination with M^{n+} is further hindered by competition from the hard base, hydroxylic oxygen. There are two possibilities for interaction with M^{n+} to account for the observed accelerative effect. One of these is the chelate shown as structure I. The second involves weak coordination of M^{n+} to an unionized fluoroacetic acid molecule, as illustrated by structure II. The latter form of interaction should be favored by media of higher acid concentration, but this was not observed. Although the initial accelerative effect of Al(III) and Th(IV) is enhanced by low acidity, interference from precipitate formation in reactions with Th(IV) quickly cancels this advantage. Since the interference is not manifested until the reaction is well advanced, it is likely that it results from interaction of the glycolate ion or its oxidation product, the oxalate ion, with Th(IV).

The chelate is in competition with the more probable monodentate complex $M(OOCCH_2F)_n$. The positive character of M^{n+} is more uniformly dispersed in structure I than if coordination occurred through only the fluorine atom, hence the susceptibility of the fluoromethyl carbon to nucleo-



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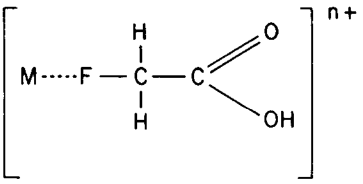

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philic attack is reduced. The data presented in Table 2 for fluoroacetate demonstrate that its hydrolysis is acid-catalyzed.

The Effect of M^{n+} on the Hydrolysis of the Trifluoromethyl Group

Metal ion assisted displacement of fluoride from the $-CF_3$ group bound to an aromatic carbon is influenced by the other substituents. Electron withdrawing substituents suppress the effect while donor groups enhance it. Reaction rates are greatest when substituents of the latter type are located *ortho* to the carbon bearing the $-CF_3$ group. No substrates having *para* substituents were studied.

Exposure of *m*-aminobenzotrifluoride to 4 M HCl at 100°C for more than 17 days produced no detectable hydrolysis. This is attributable to protonation of the $-NH_2$ group which causes less positive character to be conferred upon the *meta* carbons than upon those which are *ortho* and *para* to NH_3^+. Further reason to associate the absence of acid catalysis with $-NH_3^+$ arises from the fact that unsubstituted benzotrifluoride readily hydrolyzes in warm concentrated sulfuric acid (*5*). The accelerative effects shown by Al(III) and Th(IV) on the hydrolysis of *m*-aminobenzotrifluoride mark the only observed occurrence of metal ion catalysis for a substrate whose hydrolysis is apparently not catalyzed by acid.

Despite the unfavorable orientation of the $-NH_2$ group in *m*-aminobenzotrifluoride from an inductive standpoint, this group does have a positive effect on the Al(III) and Th(IV) assisted hydrolysis reaction, since this substrate hydrolyzes more rapidly than does benzotrifluoride under the same conditions. The solubilizing effect of the $-NH_2$ group is one contributor to the enhancement. Another possibility is that substrate coordination with the metal ion occurs through this group. As has been previously noted, a precipitate does form when this substrate is added to 1 M or 2 M $AlCl_3 \cdot 6\ H_2O$ at room temperature but dissolves upon heating. Coordination of M^{n+} in this manner does not favor hydrolysis. It is more reasonable to associate the accelerative effect with M^{n+} interaction through the $-CF_3$ group, which competes with $-NH_2$ for the metal ion. The hydrolysis of *o*-hydroxybenzotrifluoride probably proceeds primarily via coordination of the metal ion to the phenolic oxygen atom. Two features of the data in Table 3 are cited in this connection. First, the hydrolysis with 0.10 M Th(IV) proceeds about 50% more rapidly when the initial pH is raised from 2.27 to 2.60. This sharp increase in rate with decreased acidity can be readily associated with increased concentration of the Th(IV)–phenol complex at the higher pH. If interaction with the $-CF_3$ group were exclusively responsible for the acceleration, this small change in pH should have little effect on rate, as is apparent in Table 3 for the hydrolysis of *o*-aminobenzotrifluoride under the same conditions, and an earlier study of the catalyzed hydrolysis of BF_4^- (*3*). Further evidence is seen in the unusually large margin of rate enhancement by Th(IV) over that by Al(III). The hydrolysis of o-$HOC_6H_4CF_3$ with 0.10 M Th(IV) at pH 2.6 at 60°C proceeds more rapidly than in the presence of 0.4 M Al(III) at 100°C. By comparison, the hydrolysis of $C_6H_5CF_3$ with 0.5 M Th(IV) occurs only about 3 times more rapidly than with 1.0 M Al(III) under identical conditions. This latter margin of effectiveness for Th(IV) over Al(III) is typical of the behavior noted with m-$H_2NC_6H_4CF_3$ and other substrates. The extremely large difference noted in the case of *o*-$HOC_6H_4CF_3$ can only be explained through a more effective interaction between Th(IV) and the phenolic oxygen than occurs with Al(III).

The substantial decrease in the rate of hydrolysis of *o*-$HOC_6H_4CF_3$ assisted by 0.05 *M* Th(IV) when the ionic strength is increased to 1.0 *M* by the addition of $NaNO_3$ shows that the nitrate ion does not contribute to the effect here.

The Hydrolysis of Fluorophenols Induced by Nitrates of Al(III) and Th(IV)

The extensive release of fluoride from fluorophenols at 100°C in solutions containing the nitrate of Al(III) or Th(IV) is effected by action of both the cation and anion of the metal salt. Data in Table 5 indicate that some acidity is essential. There is strong evidence that fluoride release is preceded by nitration of these substrates. The predominant final product when *m*-fluorophenol is involved is 2,4,6-trinitroresorcinol.

Okon and Alama (*6*) have obtained high yields of *o*-nitrophenol simply by refluxing a 1:1 equivalent ratio of phenol and the hydrated nitrates of Be(II), Al(II), Mn(II), Fe(III), and Bi(III) for 6 hr.

The mildly acidic conditions at which the reactions were carried out (pH 1.5–2.0) suggest that the nitration–hydrolysis process is complex. Clearly the nitration does not arise from NO_2^+ at this low acidity. DeLaMare and Ridd (*7*) describe a nitration mechanism for the more reactive aromatic substrates which is independent of NO_2^+. The process is initiated by a trace of HNO_2 and is autocatalytic in the presence of HNO_3 to oxidize the nitroso intermediate.

Our results with *m*-fluorophenol conform to the following mechanism:

1. Generation of trace HNO_2 through a redox side reaction, one possibility being

$$2\,FC_6H_4OH + H_3O^+ + NO_3^- \rightarrow HNO_2 + 2\,H_2O + 2\,FC_6H_4O\cdot$$

$$2\,FC_6H_4O\cdot \rightarrow \text{other products.}$$

2. Nitrosation of fluorophenol

$$FC_6H_4OH + HNO_2 \rightarrow \underset{\text{(colored)}}{ONC_6H_3F(OH)} + H_2O.$$

3. Oxidation of nitrosofluorophenol

$$ONC_6H_3F(OH) + HNO_3 \rightarrow O_2NC_6H_3F(OH) + HNO_2$$

4. Nucleophilic displacement of fluorine

$$O_2NC_6H_3F(OH) + H_2O \rightarrow O_2NC_6H_3(OH)_2 + HF$$

5. Nitrosation of nitroresorcinol and subsequent oxidation

$$O_2NC_6H_3(OH)_2 \xrightarrow{(1)\,2\,HNO_2} O_2N(ON)_2C_6H(OH)_2 + 2\,H_2O$$

$$\xrightarrow{(2)\,2\,HNO_3} (O_2N)_3C_6H(OH)_2 + 2\,HNO_2$$

The sequence results in a depletion of acidity from conversion of HNO_3 to HNO_2. The Al(III) or Th(IV) helps to maintain the acidity for continuing the process. This can occur in three ways: (1) displacement of phenolic hydrogen through complex formation; (2) complexation of fluoride formed from the hydrolysis reaction; and (3) hydrolysis of the aquated catalyst ion. Experiments using $NaNO_3$ and varying levels of HNO_3 (Table 5) clearly demonstrate that acid is consumed by the overall reaction.

The decreasing rate of fluoride release with time (Fig. 3) may be attributed to a diversion of available HNO_2 from step 2 of the proposed mechanism to step 5 as the mononitroresorcinol forms via hydrolysis. The slower reaction at reflux, in which case NO_2 is visibly liberated, can be explained by a depletion of HNO_2 concentration via an equilibrium of the form

$$2\,HNO_2 \rightleftharpoons NO_2 + NO + H_2O.$$

The forward reaction is obviously inhibited by a closed system.

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