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Kinetics and Mechanism of Trimethylamine–Fluoroborane Hydrolysis

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Hydrolysis of trimethylamine–fluoroborane occurs via acid-independent and acid-catalyzed pathways each of which is first order in substrate. Below 0.5 M HCl, the acid-catalyzed reaction is first order in a_{H^+}. The logarithm of the observed rate constant, which is linear with pH from about 0.1 to 0.5 M HCl, continues linear with the Hammett acidity function, H_0 (slope = 1.1 at 25 °C), in concentrated acid solutions up to 6 M H_2SO_4. Thus, the rate is described by the expression $-d[Me_3N{\cdot}BH_2F]/dt = [Me_3N{\cdot}BH_2F][k_1 + k_2h_0]$. Rates are about 30% faster in water than in deuterium oxide over a range of acidity from 0.1 M HCl to 3 M H_2SO_4. It is suggested that the uncatalyzed reaction may proceed via the rate-limiting loss of F^- from the coordination sphere of boron analogous to the previously proposed mechanism for hydrolysis of iodo-, bromo- and chloroborane–amines. An A-1 mechanism is suggested for the acid-catalyzed pathway involving the preequilibrium protonation of substrate at fluorine with subsequent rate-determining loss of HF via dissociative activation. This susceptibility of the fluoro derivative to acid-catalyzed hydrolysis bears analogy to the aquation chemistry of cobalt(III) complexes containing highly electronegative coordinated ligands.

Introduction

Effects of iodide, bromide, chloride, and, more recently, cyanide ion as boron-bonded substituents on the kinetics and mechanism of hydrolysis of borane–amine addition compounds have been subjects of previous investigation.[1,2] A study of the particular effect of fluoride was precluded due to the unavailability of the appropriate substrate. In a more recent period, however, VanPaasschen and Geanangel[3] have succeeded in preparing and characterizing both the mono- and difluoroborane adducts of trimethylamine and this has prompted us to extend the investigation of such substituent effects by exploring the hydrolysis behavior of the monofluoro derivative, $Me_3N{\cdot}BH_2F$. Further incentive for such a study was based upon previously noted similarities in the apparent mechanisms of hydrolysis of substituted amine–boranes with those of selected transition metal complexes,[1,2] e.g., of Co(III), where, unlike that of the higher halo derivatives, the aquation of certain fluoroammine complexes has been found to be highly susceptible to acid catalysis.[4,5] It was, therefore, of interest to examine the possibility of an analogous divergent influence of fluoride on the mechanism of hydrolytic decomposition of amine–haloboranes.

Experimental Section

Materials. Trimethylamine–fluoroborane, prepared via the reaction of HF with trimethylamine–borane in benzene and displaying the previously reported analytical and spectral properties,[3] was supplied by Dr. R. A. Geanangel and co-workers (University of Houston). All reagents were of analytical grade and supplied by Baker, Matheson Coleman and Bell, or Allied Chemical Co. Vitex starch was obtained from G. F. Smith Co. Deuterium oxide (99.8% isotopic purity) and 98% D_2SO_4 in D_2O were obtained from Diaprep Inc. of Aldrich Chemical Co. Deuterium chloride was prepared from D_2O and benzoyl chloride by the method of Brown and Groot.[6] Aqueous solutions of sulfuric acid and hydrochloric acid were prepared using deionized water and analytical concentrations of all acid solutions were determined by routine titration with solutions of NaOH which had been standardized with potassium hydrogen phthalate.

Kinetic Studies. In a typical run, a 0.05–0.10-g (0.55–1.1-mmol) sample of trimethylamine–fluoroborane was weighed in an iodine flask and suspended in a constant-temperature bath for about 5 min. To this sample was added about 100 ml of the desired acid solution which had been brought to temperature equilibrium in the same bath. The time of mixing was taken as t_0, and complete solution was obtained usually in about 0.5 min. At various time intervals, 10-ml portions of solution were withdrawn and added to previously prepared solutions containing KIO_3 and KI. The hydride content was determined iodometrically using 0.02 N $Na_2S_2O_3$ as previously described for comparable studies of the hydrolysis of amine–boranes.[7] The temperature was controlled to ±0.1 °C using a Sargent Thermonitor or Freas Precision constant-temperature bath. The rate of decomposition of substrate was studied in various media including water, dichloroacetate buffer solutions, aqueous HCl (0.05–3.0 M), aqueous HCl containing KCl as added electrolyte, aqueous sulfuric acid (1.5–6.0 M), DCl in D_2O, D_2SO_4 in D_2O, and aqueous sodium hydrogen sulfate. Values of H_0 of concentrated acid solutions (>0.5 M HCl; >1.0 M H_2SO_4) containing no added electrolyte were obtained by interpolation using the data of O'Connor.[8] The D_0 values for selected solutions of D_2SO_4 in D_2O and H_0 values for various solutions at different temperatures were obtained from Rochester.[9] Three solutions containing respectively 0.60, 1.2, and 1.8 M HCl were adjusted to constant ionic strength (μ = 3.0) by the addition of potassium chloride. Values of H_0 for such solutions were obtained by spectrophotometric measurements using a Cary 15 recording spectrophotometer and employing the indicators *p*-nitroaniline (mp 147–147.5 °C) and *o*-nitroaniline (mp 71 °C). Both indicators had been recrystallized from H_2O and their concentrations ranged from 1.4 to 1.7 mM in these determinations.

In a separate study, a 0.28-g sample of $(CH_3)_3N{\cdot}BH_2F$ was dissolved in 100 ml of 0.46 M DCl in D_2O at 25 °C. After 15 h, corresponding to about 1 half-life for hydrolysis of the substrate, the unreacted fluoroborane was extracted with four 25-ml portions of Et_2O. The solution was then dried over anhydrous $MgSO_4$, the liquid decanted from the solid residue, and ether removed by evaporation

Table I. Rates of Hydrolysis of Trimethylamine–Fluoroborane

Medium	[Acid],[a] M	$-H_0$[b]	10^3k_{obsd},[c] s^{-1}
		45.1 °C	
H_2O			0.003 4
Buffer[d]	0.0174[e]	−1.76	0.007 01
Buffer[f]	0.0263[g]	−1.58	0.010 7
Buffer[f]	0.0339[g]	−1.47	0.012 0
HCl	0.0494	−1.31	0.009 56
HCl	0.0494[h]	−1.31	0.009 56
HCl	0.0988	−1.01	0.017 9
HCl	0.0461	−0.336	0.088 1
HCl	0.505	−0.297	0.098 3
HCl	1.01	0.135	0.290
HCl	1.51	0.370	0.565
HCl	2.02	0.605	1.05
		25.0 °C	
H_2O			0.000 2
DCl	0.0981	−1.01	0.000 95
HCl	0.0988	−1.01	0.001 22
HSO_4^-	0.5	−0.68	0.002 1
HSO_4^-	0.75	−0.52	0.003 2
HCl	0.340	−0.468	0.004 70
HSO_4^-	1.0	−0.36	0.007 1
DCl	0.456	−0.341	0.005 02
HCl	0.461	−0.336	0.006 85
DCl	0.75	0.03	0.010 2
HCl	0.75	0.03	0.013 6
HCl	0.605[i]	0.297[j]	0.026 2
HCl	1.5	0.47	0.048 7
H_2SO_4	1.5	0.55	0.057 5
HCl	1.21	0.620[j]	0.063 5
HCl	1.82	0.823[j]	0.125
DCl	3.0	1.05	0.188
HCl	3.0	1.05	0.281
H_2SO_4	3.0	1.37	0.524
D_2SO_4	3.06	1.4	0.394
H_2SO_4	4.9	2.25	4.9
H_2SO_4	6.0	2.75	10.4
		14.9 °C	
H_2SO_4	4.0	1.85	0.555
H_2SO_4	5.0	2.30	1.53
H_2SO_4	6.0	2.72	4.11

[a] Stoichiometric acid concentration. [b] $-\log h_0$. H_0 = pH for [acid] < 0.8 M. [c] $k_{\mathrm{obsd}} \equiv -\mathrm{d}\ln[\mathrm{Me_3N{\cdot}BH_2F}]/\mathrm{d}t$. [d] $Cl_2CHCOOD$, Cl_2CHCOO^-. [e] D_3O^+. [f] $Cl_2CHCOOH$, Cl_2CHCOO^-. [g] H_3O^+. [h] 0.1 N KCl. [i] KCl added to give $\mu = 3.0$ M. [j] Determined spectrophotometrically.

in a stream of N_2. An infrared spectrum of the solid (KBr wafer) using a Beckman IR-10 spectrophotometer showed strong absorption in the B–H stretching region (2260–2360 cm^{-1}) and no significant absorption in the B–D stretching region (1600–1700 cm^{-1}).

Results

The stoichiometry of trimethylamine–fluoroborane hydrolysis in aqueous acid solution is depicted in eq 1. In water,

$$(CH_3)_3N{\cdot}BH_2F + 3H_2O + H^+ \rightarrow (CH_3)_3NH^+ + B(OH)_3 + HF + 2H_2 \qquad (1)$$

buffered solutions, or aqueous acid solution where the concentration of hydronium ion is *at least* tenfold greater than substrate concentration, the rate of disappearance of fluoroborane is described by eq 2 with k_{obsd} displaying a pro-

$$-\mathrm{d}[(CH_3)_3N{\cdot}BH_2F]/\mathrm{d}t = k_{\mathrm{obsd}}[(CH_3)_3N{\cdot}BH_2F] \qquad (2)$$

nounced dependence on acidity at pH <1.5 (Table I). In the region 0.1 to about 0.5 M HCl, at 25 °C, the rate is first order in the stoichiometric concentration of acid, C_A. At higher acid concentrations, a departure of linearity between k_{obsd} and C_A is evident, and a correlation of log k_{obsd} with the Hammett acidity function,[10] H_0, is obtained. In Figure 1, the results of this correlation are shown at 14.9, 25.0, and 45.1 °C. At each temperature, nearly unit slopes are observed. These were obtained by linear regression analysis of data excluding those studies in deuterated solvent and employing at 45.1 °C only those data for $H_0 \leq 1$. As can be seen from the data at 25 °C, the linear relationship is maintained from acid solutions as concentrated as 6 M H_2SO_4 to the low concentration region $H_0 > 0$, where $h_0 \simeq a_{H^+}$ and H_0 is identified with pH. Attempts to extend the correlation to regions of higher acid concentration were unsuccessful due to the high rate of decomposition above 6 M H_2SO_4, even at 14.9 °C.

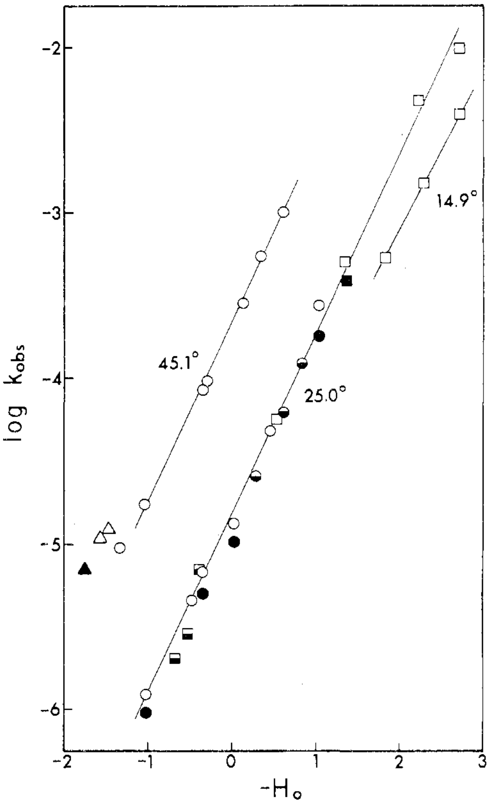

Figure 1. Correlation of hydrolysis rate with acidity at 14.9, 25.0, and 45.1 °C; $k_{\mathrm{obsd}} \equiv -\mathrm{d}\ln[(CH_3)_3NBH_2F]/\mathrm{d}t$: $H_0 = -\log h_0$; ○, HCl; ◐, HCl (KCl added to give $\mu = 3.0$); ●, DCl; □, H_2SO_4; ⬓, HSO_4^-; ■, D_2SO_4; △, $Cl_2CHCOOH$ buffer; ▲, $Cl_2CHCOOD$ buffer. Slopes: 1.00 at 14.9 °C; 1.09 at 25.0 °C; 1.10 at 45.1 °C.

In preliminary investigations, the effect of added inert electrolyte was explored through a comparison of rates in HCl with and without added KCl. As shown in Table I, the addition of 0.1 M KCl has no effect in dilute acid solution (0.049 M H^+ at 45 °C) where its presence causes no change in the activity of hydrogen ion; however, in concentrated acid its addition results in rate enhancement; e.g., the rate is about 30% higher in 1.2 M HCl at $\mu = 3.0$ than in 1.5 M HCl in the absence of added salt. In an attempt to elucidate this effect, h_0 values for three HCl solutions containing potassium chloride were determined spectrophotometrically, and as can be seen from data of Table I and Figure 1, the kinetic effect of added salt in concentrated acid appears to be due to a consequent increase in h_0. Thus, the influence of salt is apparently one of increasing the proton-donating capacity of the medium, rather than a "primary" salt[11] effect. The influence of hydrogen sulfate ion at 25 °C ($pK_a = 1.9$) also seems to reflect its contribution to h_0, with no evidence for general acid catalysis up to solutions 1 M in HSO_4^-.

A small residual rate of hydride decomposition is found in water alone ($k_{\mathrm{obsd}} = 2 \times 10^{-7}\ \mathrm{s}^{-1}$ at 25 °C; $3.4 \times 10^{-6}\ \mathrm{s}^{-1}$ at 45 °C). If it is assumed that k_{obsd}(from eq 2) = $k'h_0$ where k' denotes a second-order rate constant assuming a single-pathway reaction which is first order in substrate with rate

Table II. Relative Rates of Uncatalyzed Hydrolysis of $(CH_3)_3N{\cdot}BH_2X$ at 25 °C

X	10^3k_1,[a] s^{-1}	Solvent
I	4.1	67% dioxane-33% H_2O
Br	0.51	67% dioxane-33% H_2O
Cl	0.0013	67% dioxane-33% H_2O
F	0.0002	H_2O

[a] $k_1 \equiv -d \ln [Me_3N{\cdot}BH_2X]/dt$.

proportional to h_0, a value of $k' = 4 \times 10^{-4}\ M^{-1}\ s^{-1}$ is calculated at 45 °C from the results in concentrated acid where log k_{obsd} is linear with $-H_0$. This leads to a calculated value of k_{obsd} (10^{-10}–$10^{-9}\ s^{-1}$) in CO_2-saturated water which is smaller than the observed rate by a factor of about 10^4, strongly suggesting the existence of an uncatalyzed or acid-independent pathway which is masked by the acid-catalyzed path in concentrated acid. On this basis, it is suggested that eq 3 represents a more complete description of the rate law

$$-d[(CH_3)_3N{\cdot}BH_2F]/dt = [(CH_3)_3N{\cdot}BH_2F][k_1 + k_2h_0] \quad (3)$$

for hydrolysis of the substrate.

A measurable influence of the uncatalyzed pathway at 45 °C is found at pH >1. Some departure from linearity of log k_{obsd} with $-H_0$ (–pH in this region) is apparent in 0.05 M HCl and again in dichloroacetate buffer. In the latter solution at $[H^+] = 0.026$ M, assuming $k_1 = k_{obsd}$ in water alone, a value of $k_2 = 2.8 \times 10^{-4}\ M^{-1}\ s^{-1}$ is obtained from eq 3. This is in fair agreement with k', which is essentially equal to k_2 in regions of high acid concentration.

Rates observed in D_2O solutions of about 0.1, 0.46, 0.75, and 3.0 M DCl also are presented in Table I and lead to calculated $k_{obsd(H_2O)}/k_{obsd(D_2O)}$ values of $\simeq$1.3, 1.4, 1.3, and 1.5 at the respective concentrations at 25 °C. In 3 M D_2SO_4, a concentration within the range where $D_0 = H_0$, i.e., where the D_0 and H_0 functions are identical for 0.6 M < $C_{L_2SO_4}$ < 12 M (L = H or D),[9] $k_{H_2SO_4}/k_{D_2SO_4} = 1.2$. Some of the implications of such a small normal-isotope effect are considered below.

Variations of k_2 and k_1 at 25.0 and 45.1 °C lead respectively to $\Delta H_2^{\ddagger} = 24$ kcal/mol, $\Delta S_2^{\ddagger} = +0.3$ eu, $\Delta H_1^{\ddagger} = 26$ kcal/mol, and $\Delta S_1^{\ddagger} = 2.5$ eu. Since these values are based on data only at two temperatures, there is considerable uncertainty particularly in the entropy terms.

Discussion

In a previous study,[1] the rates of hydrolysis in aqueous dioxane of the iodo-, bromo-, and chloroborane adducts of trimethylamine were found to be independent of hydrogen ion concentration in solutions ranging from 0.3 M HCl to 0.1 M OH^-. From these and other kinetic data, a dissociative mechanism was proposed involving the rate-limiting loss of halide ion from the coordination sphere of boron, analogous to the unimolecular dissociative pathway proposed for solvolysis of alkyl halides[12] and the suggested mechanism for the aquation of selected haloammine complexes of transition metal ions such as Co(III).[4] It seems reasonable to presume such a mechanism for the acid-independent hydrolytic decomposition (in water alone) of the fluoro analogue, trimethylamine–fluoroborane. The value of k_1 at 25 °C for $Me_3N{\cdot}BH_2F$ is considerably lower than analogous first-order rate constants for hydrolysis of other haloborane adducts of trimethylamine in aqueous dioxane (Table II)[13] and the observed trend is consistent with what is presently accepted as the relative leaving-group tendencies of halide ions in a variety of nucleophilic substitution and aquation reactions. Of particular interest is the qualitative way in which the relative hydrolysis rates parallel those of aquation of the halopentaamminecobalt(III) ion $Co(NH_3)_5X^{2+}$ where X = I, Br, Cl, or F.[4,14]

Also similar to the aquation chemistry of the transition metal complex is the tendency of the fluoro derivative to hydrolyze at accelerated rates in (acid) solutions which do not affect the aquation of the higher halides. On the basis of the observed dependence of rate on the H_0 parameter, a stoichiometric mechanism involving rapid reversible protonation of substrate followed by a dissociative rate-determining step is proposed (eq 4, 5). This scheme is analogous to the A-1 mechanistic

$$(CH_3)_3N{\cdot}BH_2F + H^+ \rightleftharpoons (CH_3)_3NBH_2FH^+ \quad \text{(fast)} \quad (4)$$

$$(CH_3)_3NBH_2FH^+ \xrightarrow{k_r} \text{products} \quad \text{(slow)} \quad (5)$$

classification for reactions of a variety of organic substrates[15-17] and to the suggested mechanism for acid-catalyzed aquation of selected metal complexes containing highly electronegative coordinated ligands, e.g., $Co(NH_3)_5F^{2+}$, $Co(en)_2F_2^+$, and $Co(en)_2(N_3)_2^+$.[4,18] Though no implication is intended with regard to generalizing the overall diagnostic value of correlations of rates with specific acidity functions, it appears reasonable to consider such a stoichiometric mechanism (eq 4, 5) to be consistent, within the framework of the Zucker–Hammett hypothesis,[19] with the view that the activated complex differs from substrate by the addition of a proton. It is suggested, therefore, that protonation (4) occurs probably at the highly electronegative fluorine center and that the dissociative process (5) involves loss of fluorine, as HF, from the coordination sphere of boron. The mechanistic nature of the acid-catalyzed route, therefore, is viewed in terms of the tendency of HF to serve as a better leaving group than F^- in a process involving dissociative activation.

Assuming the scheme depicted in (4) and (5), k_2(from eq 3) = k_r/K_a where K_a is the acid dissociation constant of substrate conjugate acid. Thus, the observed isotope effect, measured by k_2 values, should be considered in terms of effects on both the preequilibrium and the subsequent rate-limiting step. For many A-1 reactions, an inverse solvent isotope effect is observed.[15] This is usually interpreted in terms of the effect of isotopic composition of the acid medium on the preequilibrium where, for comparable acid concentrations, higher concentrations of substrate conjugate acid are expected in the deuterated solvent. In such cases, there is presumably no compensating kinetic isotope effect associated with the rate-determining step. Many cases of such inverse solvent isotope effects have been documented for reactions in which protonation is thought to occur at carbon or oxygen.[15] Although comparable studies on fluorinated substrates are rare, the inverse isotope effect observed for the acid-catalyzed hydrolysis of $Co(en)_2F_2^+$ also has been interpreted in this manner.[5]

Studies of the theory of the origin of isotope effects for equilibria, however, show that for many Bronsted acids, HA, an increase in acidity, reflected by an increase in the acid dissociation constant, K_{HA}, is accompanied by a decrease in the magnitude of the primary isotope effect for dissociation, measured by the ratio K_{HA}/K_{DA}.[20] It is evident that by usual standards, $(CH_3)_3NBH_2FH^+$ may be regarded as a strong Bronsted acid. In decomposition of the fluoroborane–amine adduct, log k_{obsd} is linear with H_0 up to 6 M H_2SO_4 ($H_0 = -2.7$) at 25 °C. There is no indication of approach to a plateau region where the rate would no longer be dependent on h_0 which, within the framework of an A-1 mechanism, would be interpreted as the point of stoichiometric conversion of substrate to conjugate acid with a limiting rate defined by (5) with $k_{obsd} = k_r$. Clearly, at 25 °C, k_r must be greater than 0.01 s^{-1}, which is the value of k_{obsd} for $H_0 = -2.7$, and since $K_a = k_r/k_2 = k_rh_0/k_{obsd}$, p$K_a < -2.7$. Thus, at 25 °C, K_a for the substrate conjugate acid must be greater than 500. Insufficient data are available to draw any firm interpretive conclusions as to the observed isotope effect; e.g., it is difficult to attempt to assess the different effects of hydrogen bonding in H_2O and D_2O; however, it does not seem unreasonable that a change in isotopic composition of the medium may have very little effect on preequilibrium (4), and that the observed isotope effect may be predominantly a kinetic effect attributable to (5).

This effect is too small to provide a compelling argument for significant loss of a substrate atom–proton stretching vibration as the transition state is approached, and, indeed, no such vibrational loss is expected for (5). Also, exchange of boron-bonded hydrogen with solvent is negligible relative to the rate of hydrolysis under conditions where the isotope effect is observed; hence, it is not reasonable to consider a secondary effect arising from isotopic substitution at boron. It is reasonable, however, to consider the boron–fluorine–hydrogen angle in the conjugate acid of the substrate to be bent (an argument for a nonlinear BFH configuration can be constructed from a simple valence-shell electron pair repulsion model).[21] If the activated complex is, as suggested, one involving cleavage of the boron–fluorine bond with impending liberation of HF, a BFH bending vibration would be lost in the transition state. Such a loss seems consistent with the (small) magnitude of the isotope effect.

One should also consider the possibility of an alternate mechanism, involving a one-step bimolecular electrophilic displacement of a $(CH_3)_3NBH_2^+$ fragment via attack of solvated proton at fluorine. Melander and Myhre have shown that such A-SE2 reactions are consistent with correlations of rate with the Hammett acidity function,[22] and although the A-SE2 pathway should be subject to general-acid catalysis, such would be difficult to demonstrate because of the dominant influence of lyonium ion in the regions of acidity where the acid-dependent pathway predominates. Unless a highly unsymmetrical transition state were to be involved, however, such a displacement would be expected to give rise to a more pronounced normal-isotope effect. Although the preference for mechanism is based on considerable speculation, it would appear that the stoichiometric model denoted by (4) and (5) with dissociative activation of substrate conjugate acid is at least as consistent as the A-SE2 scheme in consideration of data available at this time. Irrespective of mechanistic detail it is clear that, relative to other haloborane–amines, this greater tendency of the fluoro derivative to exhibit acid-catalyzed hydrolysis points up another interesting example of parallel behavior in the reactivities of substituted amine–boranes and a variety of metal coordination compounds. It is quite possible, moreover, that in both types of substrate it is the presence of a highly electronegative coordinated ligand that provides, through a protonation mechanism, a low-energy (acid-catalyzed) pathway for reaction that is less accessible with compounds having analogous, though less electronegative, boron and metal-bonded substituents.

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