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Acid-Catalyzed Hydrolysis of Trimethylamine–Azidoborane

KENNETH R. SKILLERN and HENRY C. KELLY*

The rate of $Me_3N\cdot BH_2N_3$ hydrolysis at 25 °C is relatively insensitive to $[H^+]$ at pH >1 but increases markedly with increasing acidity above 0.1 M H^+ reaching a maximum in 8.1 M H_2SO_4. A decrease in rate, observed with a further increase in acidity to 10 M H_2SO_4, is attributed to a commensurate lowering of the activity of water. In HCl, $HClO_4$, and H_2SO_4 solution, the kinetics are described by $-d[Me_3N\cdot BH_2N_3]/dt = k_2[Me_3N\cdot BH_2N_3]a_w$ where a_w denotes water activity with k_2 showing a dependence on the Hammett acidity function, h_0, as depicted by the expression $k_2 = k_r K h_0/(1 + K h_0)$. Thus, the logarithm of k_2 is linear with $-H_0$ with near unit slope in the range $H_0 = +1$ to -3 but approaches a limiting value, k_r, in 8.1 M H_2SO_4 and becomes invariant with further changes in acidity from $H_0 = -4$ to -5. In the acid-dependent region, rates in water and D_2O at a given H_0 (D_0) are nearly equal; however, $k_{H_2O}/k_{D_2O} \simeq 2.2$ in 8.1 M H_2SO_4 (D_2SO_4) at 25 °C. An A-2 mechanism involving rapid preequilibrium protonation of substrate followed by rate-limiting attack by H_2O on substrate conjugate acid is strongly suggested. The limiting rate, therefore, is viewed as that of the bimolecular reaction of water with $Me_3NBH_2N_3H^+$, which is formed stoichiometrically at high acidity. A value $K \sim 3 \times 10^{-4}$ M^{-1} is calculated for the equilibrium constant for protonation of $Me_3N\cdot BH_2N_3$ at 25 °C. From studies of temperature dependence, the values $\Delta H° = 6.6$ kcal/mol and $\Delta S° = 6.1$ eu are estimated for protonation of the azidoborane, and $\Delta H^\ddagger = 16.9$ kcal/mol and $\Delta S^\ddagger = -21.8$ eu for the subsequent hydrolytic decomposition of $Me_3N\cdot BH_2N_3H^+$. It is suggested that protonation occurs at the azide ligand enabling its departure as the relatively labile HN_3 species. A comparable pathway may exist for the acid-catalyzed hydrolysis of $Me_3N\cdot BH_2F$.

Introduction

The influence of boron-bonded ligands on the kinetics and mechanistic pathways of hydrolysis of amine–boranes, $R_nNH_{3-n}\cdot BH_yX_{3-y}$, has been reported for X = aryl[1-3], as well as hydride,[4-7] cyanide,[8] and various halide ions.[9,10] Similarities in the reactions of such species and selected organic and transition-metal complex substrates also have been noted, including the anomalous effect of the F^- ligand both in the hydrolysis of trimethylamine–haloboranes and in the aquation of haloammine complexes of cobalt(III).[11-13] In each of these systems, an acid-catalyzed pathway is favored presumably involving protonation of the strongly electronegative fluoride ion and its subsequent departure in the form of the conjugate acid, HF. In order to further explore such ligand effects, and in view of the reported similarity of N_3^- and F^- in promoting the acid-catalyzed aquation of substituted amminecobalt(III) complexes,[14,15] we were prompted to explore the hydrolytic properties of trimethylamine–azidoborane.

Experimental Section

Materials. Trimethylamine–borane was obtained from Aldrich Chemical Co. and sublimed in vacuo before use. Trimethylamine was obtained from Matheson Gas Products, hydrogen iodide (57% aqueous solution) from Matheson Coleman and Bell, and sodium azide from Alfa Inorganics. Deuterium oxide (99.8 atom % D) and deuteriosulfuric acid (>98% D_2SO_4 in D_2O) were obtained from Diaprep Inc. Solutions of DCl in D_2O were prepared by the method of Brown and Groot[16] from D_2O and benzoyl chloride. Trimethylammonium iodide was prepared by treatment of aqueous HI with gaseous Me_3N. After evaporation of water, the solid was recrystallized from hot MeOH and dried in vacuo. Stock solutions of H_2SO_4, $HClO_4$, and HCl were prepared from the concentrated

reagents and standardized with NaOH.

Analyses and Spectra. Carbon, total hydrogen, and nitrogen analyses were performed by MHW Laboratories, Garden City, Mich. Hydridic hydrogen was determined by measurement of the H_2 evolved during hydrolysis of the substrate. The corresponding hydrolysate was employed for the determination of boron by a titrimetric procedure.[17] Mass spectra were recorded on a Finnigan 1015 S/L mass spectrometer operating at an ionizing voltage of 70 eV. Visible and UV spectra were obtained on a Cary Model 15 recording spectrophotometer, and infrared spectra of samples of amine–azidoboranes (neat liquids) on a Beckman IR-10. The ${}^1H$ NMR spectra were recorded on a Varian A-60A spectrometer at 60 MHz using Me_4Si as internal standard and ${}^{11}B$ NMR spectra on a Varian HA-100 spectrometer at 32.1 MHz using $(MeO)_3B$ (sealed capillary) as external standard. Sidebands generated by an external Hewlett-Packard (HP) 200 CD oscillator were used to calibrate the spectra by measuring frequencies with a HP 5211 B frequency counter.

Bis(trimethylamine)dihydroboron(1+) Iodide. A modification of the method of Miller and Muetterties[18] was employed as follows. A 12-in. length of 1.5-in. diameter iron pipe was fitted with cast iron caps, one having been tapped and threaded to hold a stainless steel stopcock through which the apparatus could be attached to a high-vacuum apparatus. A Pyrex sleeve sealed at one end was constructed to fit within the metal tube to hold reactant materials. In a typical run, the desired weighed amounts of Me_3NHI and $Me_3N\cdot BH_3$ were placed in the glass sleeve and a loose wad of glass wool placed in the top of the sleeve to reduce loss of powder on subsequent evacuation. After the apparatus was fully assembled, air was slowly removed, following which the tube and contents were heated in a drying oven for 12 h at 100 °C and 8 h at 175 °C. While warm, the pipe again was attached to the vacuum apparatus and volatile material, including unreacted $Me_3N\cdot BH_3$, was removed by sublimation. The remaining product was cooled under dry nitrogen and extracted and recrystallized from hot ethanol. Typically, 20–25-g quantities

of $(Me_3N)_2BH_2I$ were obtained in 88–90% yield.

Trimethylamine–Azidoboranes. Bis(trimethylamine)dihydroboron(1+) azide, $(Me_3N)_2BH_2N_3$, was prepared from $(Me_3N)_2BH_2I$ by direct ion exchange on Amberlite IRA-400 resin in the azide form. Solutions of the boronium iodide salt (0.05–0.10 M) were passed over the column which was then washed with water until no further N_3^- was eluted as determined by addition of aqueous Fe(III).[19] Effluents and washings were combined and reduced in volume on a rotary evaporator until a viscous oil remained. The oil was transferred to a small round-bottom flask which was attached through a short path distillation assembly to a high-vacuum aparatus. The oil was heated to 85 °C in vacuo to remove additional amounts of water and to promote crystallization of $[(Me_3N)_2BH_2]N_3$. This salt was pyrolyzed in situ by heating in vacuo to 130–140 °C. Pyrolysis was evidenced by evolution of trimethylamine and liquification of the solid residue. A clear liquid was collected by distillation which also resulted in accumulation, in the condenser, of a sublimate later identified as $Me_3N \cdot BH_3$ by its melting point (93 °C) and infrared spectrum. In a typical preparation, 11.3 g of distillate was obtained from an initial 49.0 g (0.19 mol) quantity of the iodide salt, crude yield $\simeq$ 58% theory (based on $(Me_3N)_2BH_2I$). About 33% of the original boron appeared as $Me_3N \cdot BH_3$.

Three fractions were collected via vacuum distillation of the liquid product. The lowest boiling fraction was identified as trimethylamine–azidoborane: bp 60–65 °C (0.05 mm); 3.4 g, 30% recovery; 17% yield based on $(Me_3N)_2BH_2I$. A typical analysis is as follows. Anal. Calcd for $Me_3N \cdot BH_2N_3$ (113.96): C, 31.62; H, 9.73; N, 49.16; B, 9.49; H(hydridic), 1.77. Found: C, 31.74; H, 9.43; N, 48.95; B, 8.84; H(hydridic), 1.50. The ^1H NMR spectrum (benzene solution) consisted of a singlet at 1.87 ppm downfield from Me_4Si. The ^{11}B spectrum (in benzene) was composed of a 1:2:1 triplet (J_{B-H} = 157 Hz) with a chemical shift of 22.5 ppm. Strong absorption in the B–H stretching region was evidenced by a broad infrared band centered at 2400 cm^{-1}. A small parent ion (P$^+$) peak appeared in the mass spectrum at m/e 114 with a much larger (P – 1) peak at 113. The predominance of the P – 1 fragment over the parent ion was not unexpected, since similar fragmentation had been reported for cyanoborane adducts of numerous nitrogen bases including trimethylamine–cyanoborane.[8]

The highest boiling fraction, bp 98–100 °C (0.01 mm), crystallized slowly upon cooling to 25 °C and was identified as trimethylamine–triazidoborane. Yield $\sim$4 g = 10% theory based on $(Me_3N)_2BH_2I$. Anal. Calcd. for $Me_3N \cdot B(N_3)_3$ (195.98): C, 18.4; H, 4.6; N, 71.5. Found: C, 18.6; H, 5.0; N, 66.1. The ^1H NMR spectrum (benzene solution) consisted of a singlet at 1.68 ppm (1.72 in CCl$_4$). A singlet also was observed in the ^{11}B spectrum (benzene) at 19.2 ppm. The infrared spectrum of the neat (supercooled) liquid showed strong, broad absorption bands centered at 2140 and 1350 cm^{-1} with prominent shoulders at 2070 and at 1415 and 1380 cm^{-1}; an intense doublet at 990 and 950 cm^{-1}; strong, sharp bands at 1450, 1470, 1490, 1250, and 1120 cm^{-1}; medium, broad absorption at 3460 cm^{-1}, in the region 2640–2720 cm^{-1}, and at 2280 cm^{-1}; and medium, sharp absorption at 3040, 2970, 1160, 725, and 655 cm^{-1}. No absorption was observed in the B–H stretching region around 2400 cm^{-1}. *Caution—this compound exploded during analysis.*[20] *It is advised that it be stored and handled in an inert atmosphere (dry) box. The detonation of $Me_3N \cdot BH_2N_3$ near 200 °C also has been reported by Miller and co-workers.*[21]

A fraction of intermediate volatility remained unidentified. Its infrared spectrum showed absorption in regions also found in $Me_3N \cdot BH_2N_3$ and $Me_3N \cdot B(N_3)_3$, plus a prominent peak absent in the spectra of the mono- and triazido complexes at 1075 cm^{-1}. A strong band at 2390 cm^{-1} (ν_{BH}) and intense absorption in the 2100-cm^{-1} region (ν_{N_3}) also were observed, the relative intensity (ν_{BH}/ν_{N_3}) being less than that found in the spectrum of $Me_3N \cdot BH_2N_3$.

Kinetics Studies. Rates of hydrolysis were measured by following the disappearance of soluble hydride with time by a modified iodometric procedure employing KBrO$_3$ and by titrating I$_2$ with Na$_2$S$_2$O$_3$ to a (Vitex) starch endpoint in aqueous acid solution.[8] Samples of substrate and the desired acid solution were brought to temperature equilibrium ($\pm$0.05 °C) in a Sargent Thermonitor constant-temperature bath and then mixed to start the hydrolysis reaction (t_0 taken as the time of mixing). Periodically, aliquot samples were removed for hydride analysis.

Values of H_0 were obtained by interpolation of the data of Rochester[22] or by spectrophotometric measurements using 4-

Table I. Hammett Acidity Function Values in Hydrochloric Acid at 25 °C

| [acid],[a] M	D_0[b]	H_0[b]	H_0[c]
1.0		−0.16	−0.20
1.5		−0.45	−0.47
2.0	−0.62	−0.66	−0.69
2.5		−0.87	−0.87
3.0	−1.01	−1.05	−1.05
3.5		−1.22	−1.23
4.0	−1.36	−1.38	−1.40

[a] HCl in H$_2$O; DCl in D$_2$O. [b] This study. [c] Reference 24.

chloro-2-nitroaniline as an indicator. The D_0 values of DCl and D$_2$SO$_4$ solutions also were obtained through measurement of the optical densities of acid solutions of this indicator at 421 nm. The pK_a values for 4-chloro-2-nitroanilinium ion were taken equal to −1.02 and −0.46 in H$_2$O and D$_2$O, respectively.[23]

Extraction from D$_3$O$^+$. A 0.147-g (1.29 mmol) sample of $Me_3N \cdot BH_2N_3$ was dissolved in 50 mL of 0.72 M DCl solution at 45.1 °C. Over a period of 44 h, corresponding to 1.3 half-lives for hydrolysis of the substrate, four 10-mL samples were periodically removed, and the azidoborane was extracted from the aqueous medium with diethyl ether. Each extract was reduced in volume in a stream of dry N$_2$ and dried with anhydrous MgSO$_4$. A sample of the ether solution was then applied to NaCl plates and the solvent evaporated to produce a film. Infrared spectra were obtained on each sample so prepared. In no case was the spectrum significantly different from that of the original sample of $Me_3N \cdot BH_2N_3$; i.e., there was no evidence of significant exchange of deuterium for hydrogen in the substrate.

Results and Discussion

Acidity Functions. Previous work by Högfeldt and Bigeleisen[23] has shown D_0 for DCl–D$_2$O solutions to be equivalent to H_0 for HCl–H$_2$O solutions in the region 10^{-4} to 1 M and a comparable equivalence has been demonstrated for H$_2$SO$_4$ (D$_2$SO$_4$) solutions in the range 0.1–12 M. Since, for the purposes of this study, it was desirable to extend this comparison, D_0 and H_0 values were experimentally determined in normal and deuterated hydrochloric acid from 1 to 4 M. Results are shown in Table I in which H_0 values of Paul and Long[24] also are compared over the same range of HCl concentration.

Hydrolysis of Me$_3$N·BH$_2$N$_3$. The stoichiometry of trimethylamine–azidoborane hydrolysis in acidic solution is shown in eq 1, with kinetic data presented in Table II.

$$Me_3N \cdot BH_2N_3 + H^+ + 3H_2O \rightarrow Me_3NH^+ + B(OH)_3 + 2H_2 + HN_3 \quad (1)$$
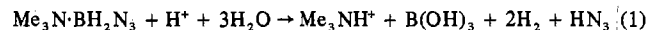
Disappearance of azidoborane is first order in substrate as described by the relation $-d[S]_0/dt = k_1[S]_0$, where $[S]_0$ denotes the total stoichiometric concentration of $Me_3N \cdot BH_2N_3$ existing at time t. Figure 1 shows the acid dependence of k_1 in terms of its logarithmic variation with the Hammett function, H_0, from studies in concentrated hydrochloric, perchloric, and sulfuric acids, and with pH for studies in aqueous buffer solutions of lower hydrogen ion concentration.[25] At 25 °C, the linear dependence with unit slope which is observed from $H_0 \simeq$ +1 to −3 is disrupted at higher acid concentrations with a maximum appearing at 8.1 M H$_2$SO$_4$ and a decrease in rate occurring with additional increases in acidity. No satisfactory linear relationship with acid concentration is apparent; i.e., a plot of k_1 vs. stoichiometric concentration of each of the three acids employed shows pronounced curvature over the range 1–10 M.

An alternative treatment of data, depicted in Figure 2, reflects the acid dependence of a second kinetic parameter k_2 $\equiv k_1/a_w$ where a_w denotes activity of water.[26] A near unit slope is obtained over the lower range of acidity with a plateau region approached at higher concentrations and extending to $H_0 \simeq$ −5. Consequent to this treatment, this plateau region represents a limiting rate at high acidity. Thus, the decrease in k_1 with decreasing H_0 at high acidity is interpreted as a result

Table II. Rates of Hydrolysis of Trimethylamine-Azidoborane

H_2SO_4

[Acid], M	t, °C	$-H_0{}^a$	$10^5 k_1$, s^{-1} ^{b}	$a_W{}^c$	$10^5 k_2$, M^{-1} s^{-1} ^{d}
5.00	10	2.31	2.19		
7.00		3.36	8.30		
8.10		3.89	10.8	0.226	0.861
9.00		4.44	8.33		
10.0		4.98	6.55		
8.10	15		21.4	0.234	1.65
8.10	19.9		34.4	0.242	2.34
3.00	25	1.36	1.38, 1.51	0.824	0.0302, 0.0330
3.00^e		1.36^f	1.25		
3.94		1.80	4.21	0.725	0.105
6.00		2.74	30.9	0.480	1.16
7.00		3.28	53.5	0.362	2.66
8.10		3.90	64.0	0.250	4.44
8.10^e		3.90^f	29.9, 28.7		
8.50		4.11	59.9	0.212	5.09
9.00		4.38	54.9	0.170	5.82
9.50		4.67	38.6	0.136	5.11
10.0		4.95	29.2	0.107	4.92
3.00	35	1.38	5.80	0.83	0.126
3.00^e		1.38^f	5.10		
8.10			168	0.267	11.34
3.00	45.1	1.38	21.1	0.83	0.458
3.00^e		1.38^f	17.5		
3.00	60	1.38	105	0.83	2.28
3.00^e		1.38^f	92.5		

HCl

[Acid], M	t, °C	$-H_0{}^g$	$10^5 k_1$, s^{-1} ^{b}	$a_W{}^c$	$10^5 k_2$, M^{-1} s^{-1} ^{d}
0.1	25	−0.98	0.0089	0.99	0.00016
0.8		0.08	0.0581	0.964	0.00109
2.0		0.69	0.326	0.899	0.00653
3.0		1.05	1.10	0.835	0.0237
4.0		1.40	2.86	0.760	0.0678
5.0		1.76	9.07	0.680	0.240
6.0		2.12	22.7	0.590	0.693
0.5	45.1	−0.26	0.430		
0.8		0.1	1.04, 0.849	0.964	0.0194, 0.0159
0.8^h		0.1^f	0.958		
1.0		0.135	1.30		
2.0		0.605	4.85, 4.47		
2.0^h		0.605^f	4.41		
2.5		0.77	6.53		
3.0		0.95	13.3		
4.0		1.25	38.2		
4.0^h		1.25^f	37.4		
0.10	60.3		1.38	0.99	
0.20			2.26		
0.40			3.25		
0.78		0.06	5.40	0.964	
0.10	72.5	1.09	7.63	0.99	

$HClO_4$

[Acid], M	t, °C	$-H_0{}^a$	$10^5 k_1$, s^{-1} ^{b}	$a_W{}^c$	$10^5 k_2$, M^{-1} s^{-1} ^{d}
2.99	25	1.29	1.66	0.828	0.0361
4.00		1.80	5.86	0.723	0.146
5.00		2.31	19.4	0.602	0.581
6.00		2.90	49.7	0.463	1.93

$NaHSO_4$

[HSO$_4{}^-$], M	t, °C	$-H_0{}^{a,i}$	$10^7 k_1$, s^{-1}	[HSO$_4{}^-$], M	t, °C	$-H_0{}^{a,i}$	$10^7 k_1$, s^{-1}
1.0	25	−0.36	3.48	0.75^k	25	−0.50	5.52
0.5^j		−0.68	3.00	1.0^l		−0.36	6.83

Other

[Buffer], M	t, °C	pH	$10^7 k_1$, s^{-1}	[Buffer], M	t, °C	pH	$10^7 k_1$, s^{-1}
0.1^m	45.1	4.75	30	⋯			4°
0.5^m			26	0.50^p		1.9	38
0.2^m	60.3		900	⋯	60.3		53^n
⋯	45.1		6^n	0.10^p	60.3	6.3	70

^{a} $H_0 \equiv -\log h_0$; values are from ref 22 for $t = 25$ °C, by interpolation for $t \neq 25$ °C. ^{b} $k_1 = -\mathrm{d}\ln[\mathrm{S}]_0/\mathrm{d}t$. ^{c} $a_W = p/p_0$, ref 40 for $t = 25$ °C, by interpolation from ref 40–42 for $t \neq 25$ °C. ^{d} $k_2 = k_1/a_W \times 1/55.5$ to give k_2 in units M^{-1} s^{-1}. ^{e} D_2SO_4 in D_2O. ^{f} D_0. ^{g} Values from ref 24 for $t = 25$ °C, by interpolation from ref 22 for $t \neq 25$ °C. ^{h} DCl in D_2O. ^{i} No correction for added Na$_2$SO$_4$. ^{j} 0.5 M Na$_2$SO$_4$. ^{k} 0.75 M Na$_2$SO$_4$. ^{l} 1.0 M Na$_2$SO$_4$. ^{m} [HOAc] + [OAc$^-$]. ^{n} 1.0 M KCl in H$_2$O. ^{o} 0.1 M NaOH. ^{p} [H$_2$PO$_4{}^-$] + [HPO$_4{}^{2-}$].
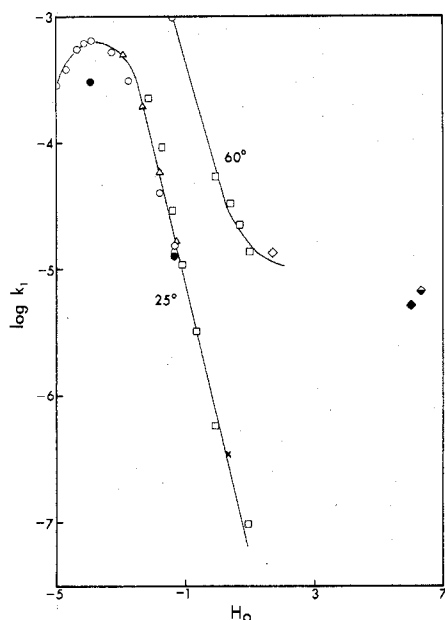
Figure 1. Variation of $Me_3N \cdot BH_2N_3$ hydrolysis rate with acidity at 25 and 60 °C. $k_1 = -d \ln [Me_3N \cdot BH_2N_3]/dt$: O, H_2SO_4; ●, D_2SO_4; △, $HClO_4$; □, HCl; ×, HSO_4^-; ◇, 0.5 M H_3PO_4, $H_2PO_4^-$ buffer, pH 1.7; ◆, 0.1 M $H_2PO_4^{2-}$ buffer, pH 6.3; ◆, H_2O.
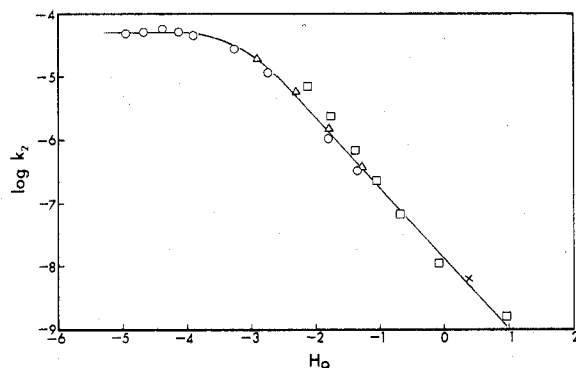
Figure 2. Variation of rate of $Me_3N \cdot BH_2N_3$ hydrolysis with Hammett H_0 function at 25 °C. $k_2 \equiv (1/a_w)(-d \ln [Me_3N \cdot BH_2N_3]/dt)$: O, H_2SO_4; △, $HClO_4$; □, HCl; ×, HSO_4^-. For $H_0 = +1$ to -3, slope $= -1.1$; correlation coefficient $= 0.989$.

of a commensurate decrease in activity of water. This leads to the empirical rate equation

$$-d[S]_0/dt = k_2[S]_0 a_w \tag{2}$$

with k_2 displaying a first-order dependence on h_0 between H_0 values of +1 and about -3 and approaching h_0 independence at higher concentrations.

Attempts to elucidate the nature and kinetic behavior of species in strong acid media have led to a variety of models for mechanisms of acid-catalyzed reactions along with suppositions that a correlation of empirical rate data with a specific acidity function could be employed to diagnose a particular mechanistic scheme.[22,24,27,28] The Zucker–Hammett hypothesis,[29] wherein a linear correlation of rate with h_0 or [H+] was taken to be indicative of, respectively, an A-1 or A-2 mechanism, represented one of the early and better known of such postulates, and this treatment as well as subsequent attempts to treat cases that do not lend themselves to clear categorization in terms of the Zucker–Hammett theory, in which various parameters are employed in an effort to classify acid-catalyzed reactions, have been reviewed in detail. With respect to the hydrolysis of trimethylamine–azidoborane, it is clear that exclusive categorization in terms of mechanism

is not possible using standard criteria of the Zucker–Hammett theory; i.e., no linearity exists in [H+] and the linear log k_1, H_0 relation observed at lower acid concentrations becomes inverted at high acidity. Nor is a less unequivocal assignment of mechanism justified from an examination of other relationships.[30] In spite of this, it appears that a not totally unsatisfactory argument may be presented for a scheme which has features of the conventional A-2 mechanism.[31]

Considering the A-2 scheme, the sequence of steps depicted in eq 3 and 4 are considered wherein S denotes substrate, i.e.,

$$S + H^+ \rightleftharpoons SH^+ \quad \text{(fast)} \tag{3}$$

$$SH^+ + H_2O \xrightarrow{k_r} \text{products} \quad \text{(slow)} \tag{4}$$
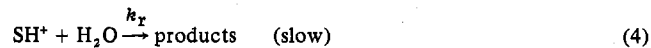
$Me_3N \cdot BH_2N_3$, and SH+ the corresponding conjugate acid. According to transition-state theory, the rate may be depicted by eq 5 where ‡ denotes the activated complex, and $k°$, the

$$\text{rate} = k°[HS^+] a_w \gamma_{HS^+}/\gamma_{\ddagger} \tag{5}$$

bimolecular rate constant when activity coefficients are equal to unity.[32-36] Assuming eq 3 to be reversible and rapid relative to eq 4 and recognizing the definition of h_0, it follows that

$$[HS^+] = K_{eq}[S] \gamma_S a_{H^+}/\gamma_{HS^+} = K_{eq}[S] h_0 \tag{6}$$

where K_{eq} represents the equilibrium constant for eq 3. Since, at any time, the stoichiometric amount of azidoborane, $[S]_0$, will equal that present in both basic and acidic forms, i.e., $[S]_0 = [S] + [HS^+]$, it follows that $[S] = [S]_0/(1 + K_{eq}h_0)$, wherein

$$\text{rate} = \frac{k° K_{eq}(\gamma_{HS^+}/\gamma_{\ddagger})[S]_0 a_w h_0}{1 + K_{eq}h_0} \tag{7}$$

The *form* of eq 7 is recognizable as one applying to pathways which correspond to the general *model* of eq 3 and 4 and describes the pattern of kinetics of numerous catalytic processes including enzyme reactions proceeding via a Henri or Michaelis–Menten mechanism.[37,38] Specifically, eq 7 predicts an h_0 dependence of rate at low values of h_0 with a conversion to zero-order dependence in solutions of acidity sufficient for the condition $K_{eq}h_0 \gg 1$. A first-order dependence on h_0 at the relatively low acidity is contingent on invariance with the medium of the ratio $\gamma_{HS^+}/\gamma_{\ast}$. Such invariance seems reasonable if one considers that HS+ and ‡ will be of identical charge type and, presumably, will be compositionally distinguished only by a molecule of water. Although an identity ($\gamma_{HS^+} = \gamma_{\ast}$) seems possible, it is only necessary for the ratio $\gamma_{HS^+}/\gamma_{\ast}$ to remain constant to produce a first-order dependence of rate on h_0.

Experimentally, the hydrolysis of $Me_3N \cdot BH_2N_3$ is found to be compatible with the form of eq 7 where

$$k_2 = \frac{k° K_{eq} h_0 \gamma_{HS^+}/\gamma_{\ddagger}}{1 + K_{eq}h_0} \tag{8}$$

with limiting cases of first- and zero-order dependence on h_0 shown in the logarithmic plot of Figure 2. In accordance with eq 8, one obtains from the plateau region of Figure 2, $k° \cdot \gamma_{HS^+}/\gamma_{\ast} = 5 \times 10^{-5}$ M^{-1} s^{-1} and, in the region of low acidity by extrapolation to log $h_0 = 0$, $k° K_{eq} \gamma_{HS^+}/\gamma_{\ast} = 1.5 \times 10^{-8}$ M^{-2} s^{-1}, from which the value $K_{eq} = 3 \times 10^{-4}$ M^{-1} is obtained. In principle, these parameters can be obtained through a reciprocal plot of $1/k_2$ vs. $1/h_0$ which is linear (correlation coefficient $= 0.995$) with slope $(k° K_{eq} \gamma_{HS^+}/\gamma_{\ast}) = 1.9 \times 10^{-8}$ M^{-2} s^{-1}, in reasonable agreement with the value obtained from the logarithmic relationship of Figure 2; however, there is considerable error introduced in the intercept of such a plot and K_{eq} is best obtained through use of the limiting rate data of Figure 2 or Table II. The K_{eq} value so obtained does not seem unreasonable, and leads to $K_a \equiv a_{H^+}a_S/a_{HS^+} \simeq 3.3 \times 10^4$ for the protonated azidoborane. A lower limit of 500 for the

K_a of the conjugate acid of trimethylamine–fluoroborane has been estimated from previous kinetic studies of the acid-catalyzed hydrolysis of this substrate.[13] In terms of eq 3, 4, and 7, the plateau region in Figure 2 is physically interpreted as the upper limit of the rate of hydrolysis resulting from the rapid stoichiometric conversion of substrate to conjugate acid (HS⁺) at high acidity. Thus, $k°\gamma_{HS^+}/\gamma_\ddagger$ is equated to k_r in eq 4.

The limited solvent isotope data also seem not inconsistent with the assignment of A-2 character to this mechanism. In the h_0-dependent region (3 M H_2SO_4 at 25 °C and 0.8, 2.0, and 4.0 M HCl at 45 °C) $k_{H_2O}/k_{D_2O} \simeq 1.3$[9] Since this presumably represents a composite effect of eq 3 and 4, it alone is of limited value; however, a discernible solvent isotope effect is obtained in 8.1 M H_2SO_4 where the rate is attributed to eq 4 alone. Further, the magnitude of this effect, $k_{H_2O}/k_{D_2O} \simeq 2.2$, does not seem inconsistent with its assignment as a secondary effect arising through rate-limiting attack of water on substrate conjugate acid. This implies an *inverse* isotope effect for eq 3, consistent with what is frequently expected and encountered for isotope effects involving acid–base equilibria. For example, such inverse isotope effects have been reported for various reactions thought to proceed by A-1 pathways which involve preequilibrium protonation as in eq 3 followed by rate-limiting processes in which no isotope effect is associated.[24,27,28]

Also shown in Table II are data depicting the temperature dependence of rate in two regions of acidity. Since values of a_w at the desired temperatures are required to calculate appropriate k_2 values, it was necessary to interpolate data obtained by extrapolation of the molal concentration dependence of a_w in H_2SO_4 solutions at 0, 25, 40, and 60 °C to a molal concentration (12.5 m) corresponding to 8.1 M H_2SO_4.[40–42] In some cases this extrapolation involved fitting a fourth-power polynominal equation to the data of Harned and Owen,[41] tabulated up to 7 m H_2SO_4, to estimate values of a_w at the higher molality. The H_0 values employed at temperatures other than 25 °C were obtained from data compiled by Rochester.[22]

A concentration of 3.0 M H_2SO_4 was chosen for elucidation of the temperature dependence in a region where the rate is linear in h_0. Relatively little change in a_w (~0.83) or H_0 (−1.36 to −1.38) is found in this region from 25 to 60 °C (Table II). Since, according to eq 8, k_2 contains a term in h_0 at this concentration, a plot was constructed of ln $(k_2/T) + 2.303H_0$ vs. $1/T$ from data points at 25, 35, 45.1, and 60 °C. A linear relationship was obtained (correlation coefficient = 0.999) yielding activation parameters $\Delta H^\ddagger = 23.5$ kcal/mol and $\Delta S^\ddagger = -15.7$ eu. An additional study in 0.8 M HCl at 25, 45.1, and 60 °C ($a_w \sim 0.96$; $H_0 \sim -0.08$) gave comparable values; i.e., correlation coefficient = 0.998, $\Delta H^\ddagger = 23.3$ kcal/mol, and $\Delta S^\ddagger = -16.8$ eu. In terms of the mechanism depicted in eq 3 and 4, these activation parameters represent the composite sums of the enthalpy (entropy) of protonation plus the corresponding activation enthalpy (entropy) of eq 4, i.e., $\Delta H_3° + \Delta H_4^\ddagger$ and $\Delta S_3° + \Delta S_4^\ddagger$, respectively. In an effort to separate terms, the variation of rate in 8.1 M H_2SO_4 was examined at five temperatures from 10 to 35 °C ($a_w \sim 0.23-0.25$). If it is assumed that the plateau region is maintained at this concentration over the full range of temperature, i.e., that at 8.1 M H_2SO_4, h_0 independence is preserved from 10–35 °C, then the temperature dependence of this limiting rate should enable resolution of $\Delta H^\ddagger$ and $\Delta S^\ddagger$. This assumption seems reasonable in view of the data obtained in 5–10 M H_2SO_4 at 10 °C plus the degree of linearity obtained in the plot of ln (k_2/T) vs. $1/T$. Linear regression analysis of these data gave a correlation coefficient = 0.999 with $\Delta H_4^\ddagger = 16.9$ kcal/mol and $\Delta S_4^\ddagger = -21.8$ eu, from which

are calculated $\Delta H_3° = +6.6$ kcal/mol and $\Delta S_3° = +6.1$ eu. It should be noted that the composite $\Delta S^\ddagger$ value (~−16 eu) is of comparable sign and magnitude to other composite activation entropies determined for acid-catalyzed processes thought to proceed via the A-2 mechanism, wherein the major contribution to the entropy term is presumed to be a bimolecular rate-limiting step comparable to eq 4.[28]

In aqueous solutions of low acidity where $h_0 = a_{H^+}$, the rate of hydrolysis is found to be relatively insensitive to changes in hydrogen ion concentration. The observed rate ($k_1 = 6 \times 10^{-7}$ s⁻¹) in 1 M KCl, attributed to an effect on the substrate of water alone, is relatively unchanged in 0.1 M NaOH ($\mu = 1$) at 45.1 °C. Although a slight increase is observed at this temperature in acetate buffer (pH 4.75), no significant additional effect is encountered on going to H_3PO_4–$H_2PO_4^-$ buffer at pH 1.9. It is tempting to attribute this residual rate to a dissociative mechanism involving rate-determining loss of N_3^- from boron, analogous to the uncatalyzed aquation of amine–haloboranes.[10] The role of acid in catalyzing the decomposition of the azidoborane adduct, therefore, is viewed as analogous to that proposed for acid catalysis of trimethylamine–fluoroborane decomposition.[13] In both cases, the highly electronegative ligand may serve as the site for preequilibrium protonation enabling, in a subsequent rate-limiting step, its departure as a more labile leaving group, i.e., as its respective conjugate acid, HN_3 or HF. Comparable mechanistic schemes for the acid-catalyzed hydrolysis of transition-metal complexes containing N_3^- and F^- ligands have been cited.[11–15]

In our previous study of trimethylamine–fluoroborane hydrolysis, an A-1 mechanism was proposed based primarily upon the linearity of log k with H_0 over the entire range of acidity explored.[13] It was acknowledged that, since an examination of rates in solutions more concentrated than 6 M H_2SO_4 was precluded due to the rapid decomposition of substrate, the absence of a plateau region might be due solely to an upper limit on the range of acidity which could be employed, in which case, within the limits of the study described an H_0 independence at high acidity would not have been detected. The small normal isotope effect observed for hydrolysis of the fluoroborane adduct in two regions of acidity ($k_{H_2O}/k_{D_2O} = 1.2-1.5$), however, may be considered somewhat more compatible with an A-2 scheme rather than A-1, and in view of the h_0-dependent and -independent behavior of the rate of $Me_3N·BH_2N_3$ hydrolysis, as well as other data which seem consistent with the assignment of an A-2 mechanism for this substrate, it seems reasonable to suggest that $Me_3N·BH_2F$ may indeed react via an analogous (A-2) route. That such is the case is perhaps at least as attractive a presumption as one requiring the azido- and fluoroborane substrates to solvolyze via distinctly different mechanistic pathways.

An additional observation suggesting that protonation of the azide ligand occurs to provide a more favorable path for its departure from the boron coordination sphere is found in hydrolysis of the azidoborane fraction of intermediate volatility. In aqueous acetate and phosphate buffers, this sample undergoes an initial rapid loss of hydride. The plot of log (H⁻) vs. time shows curvature with decreasing negative slope but becomes linear with increasing time to yield a pseudo-first-order rate constant approximately equal to the value of k_1 obtained with $Me_3N·BH_2N_3$ under comparable conditions. As indicated above, this fraction has not been chemically resolved; however, it appears to consist of more than one hydride-containing species, one of which is the monoazidoborane. Since another is kinetically more reactive than $Me_3N·BH_2N_3$, it cannot be trimethylamine–borane. If one assumes the presence of only two species, an extrapolation of rate data to zero time allows estimation of the relative hydride content of both

components. Such estimates are consistent with assignment of the fraction as a mixture of Me₃N·BH₂N₃ and Me₃N·BH(N₃)₂ in a mole ratio of approximately 1:2. If the second component is indeed the diazidoborane, a suggestion compatible with the infrared spectrum of the fraction, it seems reasonable that this component be the kinetically more active one. First, there is a statistical factor favoring its reactivity due to the availability of two azide ligands for protonation. Further, if the activated complex for hydrolysis of substrate conjugate acid involves impending loss of HN_3 via cleavage of the boron–azido nitrogen linkage, a process presumably facilitated energetically by water, then the transition state may be stabilized through delocalization of positive charge of the incipient boronium ion into the remaining boron-bonded N_3 ligand. A comparable effect due to H^- would not be possible in the cationic complex originating from loss of HN_3 from the *mono*azidoborane. This interpretation remains highly speculative in view of the uncertainty in the composition of the fraction. It is somewhat reminiscent of, but different from, the inductive substituent effects proposed to explain the *decrease* in kinetic activity observed on replacement of hydride by a second halide ion in the hydrolysis of the trimethylamine–haloboranes, $Me_3N·BH_2I$ and $Me_3N·BHI_2$.[10]

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Contribution from the Laboratoire de Chimie de Coordination du CNRS, B. P. 4142, 31030 Toulouse, Cedex, France, and Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

Microwave Spectrum and Structure of Trimethylamine–Boron Trifluoride. Me₃N·BX₃ Adduct Stability and the Reorganization Energies of BF₃ and BH₃

PATRICK CASSOUX,[1a] ROBERT L. KUCZKOWSKI,*[1b] and ALAIN SERAFINI[1a]

The microwave spectrum of deuterium and carbon-13 enriched samples of trimethylamine–boron trifluoride have been assigned. The structure of the complex has been determined as $d(BN) = 1.636 \pm 0.004$ Å, $d(BF) = 1.387 \pm 0.005$ Å, $d(CN) = 1.476 \pm 0.005$ Å, $d(CH) = 1.10 \pm 0.03$ Å, $\angle CNC = 108.6 \pm 0.2°$, $\angle FBF = 112.4 \pm 0.2°$, and $\angle HCH = 111 \pm 2°$. The reorganization energies of BF₃ and BH₃ upon complexation with trimethylamine have been calculated using an ab initio method (IBMOL6) as 27.9 and 15.1 kcal/mol, respectively. This work shows that the differences in the reorganization energies of the two acids parallel their Me₃N adduct stabilities and quantitatively account for a major contribution to their difference in stability.

Introduction

An accurate structure for the heavy atoms in Me₃N·BH₃ was recently completed.[2,3] The B–N internuclear distance was 1.638 ± 0.010 Å which is virtually identical with the value 1.636 ± 0.004 Å in Me₃N·BF₃.[4] It was therefore suggested[2] that the lesser stability of Me₃N·BF₃ vs. Me₃N·BH₃ might be rationalized by the assumption that the reorganization energy of BF₃ is greater than for BH₃. In order to test such a

suggestion by estimating the reorganization energies of the two species, it would be extremely valuable to have precise values for the BF₃ geometry in the adduct.[5] Also, a comparison of the Me₃N geometry in both adducts is desirable as well as comparisons with other compounds such as Me₃N·BX₃ (X = Cl, Br, I,[6] and CH₃CN·BF₃[7]). For these reasons we have reinvestigated the microwave spectrum of Me₃N·BF₃ with sufficient isotopic species to determine the heavy-atom