nonapical borons. In $B_{10}H_{10}{}^{2-}$ the two borons appear at 23 and 53 ppm, respectively,[10,11] whereas in $B_{10}Cl_{10}{}^{2-}$ they appear at 23.4 and 28.7 ppm.[5] It is thus surprising that in 1,-6,8-$B_{10}H_7Cl_3{}^{2-}$ the halogenated apex is shifted that far downfield while the other apex moves up. An examination of the [11]B nmr spectra of several ions containing four, five, six, seven, and eight chlorines[9] showed that subsequent halogenation of the nonapical borons shifts the apical boron upfield until it ends up where it is seen in the perchloro ion. Halogenation shifts all nonapical borons downfield; consequently in both $B_{10}H_7Cl_3{}^{2-}$ and $B_{10}H_4Cl_6{}^{2-}$ (28.4 ppm) they appear at positions intermediate between $B_{10}H_{10}{}^{2-}$ and B_{10}-$Cl_{10}{}^{2-}$. The shift is greater for the chlorinated boron. While we may attribute the downfield shifts to the "inductive electron withdrawal" by the chlorines, we have no ready explanation for the reverse trend exhibited by some of the apical borons.

General Observations. If the compounds discussed in this paper are regarded as undesirable side products, the conditions which suppress them are clearly indicated. However, we were also interested in conditions which would make these reactions into useful synthetic methods. Though our

best yield of the nitroso derivative was below the best value reported by Wiesboeck,[2] the reaction with $Fe(NO_3)_3$ is so sensitive to conditions that we have no doubt the yield can be raised considerably by further modifying the reaction conditions within the optimum reaction times. In addition to the general advantages of not having to work with gaseous reactants, our reaction shows no evidence of producing any of the explosive red intermediate reported in the reaction where NO_2 was used.[2] However, increasing the yield of the chlorinated species may prove to be more difficult, since the coupling rate is much greater than the rate of halogenation.

Contribution from the Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

Synthesis and Mechanism of Hydrolysis of Amine–Cyanoboranes[1]

CHARLES WEIDIG, SURJIT S. UPPAL, and HENRY C. KELLY*

Hydrolysis of cyanoborane adducts of morpholine and dimethylamine are described by the expression rate = $k[R_2NH\cdot BH_2$-CN][OH⁻] over the range pH 6–12.5. At constant pH (12.4), k is insensitive to an 18-fold change in total buffer concentration suggesting specific lyate ion catalysis. For a given concentration of lyate ion, rates are 60–70% slower in water than in deuterium oxide and exchange of the nitrogen-bonded proton with solvent is rapid compared to the rate of hydrolysis. The addition of H_2O_2 to the alkaline hydrolysate significantly retards the rate. Cyanoborane adducts of trimethylamine and N-methylmorpholine react very slowly and at rates independent of alkali up to 0.9 M OH⁻. The proposed mechanism for hydrolysis of the secondary amine adducts involves the removal by OH⁻ of the nitrogen-bonded proton in a rapid preequilibrium followed by the rate-determining decomposition, probably *via* a dissociative pathway, of substrate conjugate base analogous to the accepted mechanism for base hydrolysis of amminecobalt(III) complexes. The presence of a nitrogen-bonded proton also seems to be important in influencing the mechanism of halogenation of such cyanoboranes. Synthesis of secondary amine–cyanoboranes *via* the reaction of $BH_3CN⁻$ with the corresponding amine salt is accompanied by scrambling of the hydrogen between nitrogen and boron.

Introduction

The cyanotrihydroborate anion $BH_3CN⁻$, first prepared by Wittig[2] in 1951 as the lithium salt, has drawn attention in recent years as a useful reducing agent[3–5] and has been the subject of investigations of hydrogen exchange and hydrolysis,[6] of rearrangement to the isocyanotrihydroborate isomer,[7] and of the spectra, structure, and bonding in substituted borane

adducts[5] and metal cyanotrihydroborate complexes.[8–10] Such studies have been aided by the greater accessibility of this ion through its preparation as the sodium salt,[7] a factor which has also facilitated development of its derivative chemistry. Thus, recent work of Spielvogel and coworkers has been concerned with the structure of species obtained on acidification of solutions of $BH_3CN⁻$ in tetrahydrofuran,[11] and the utilization of such solutions for the synthesis of new nitrogen base donor–cyanoborane addition compounds has been noted.[11,12]

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The availability of such amine–cyanoboranes presents an opportunity for further exploration of the nature of substituent effects on the kinetics and mechanistic pathways of reactions of boron–nitrogen addition compounds. The sensitivity of the mechanism of hydrolysis of such compounds to substitution at nitrogen and boron is apparent from previously reported studies on pyridine–arylboranes,[13-15] amine–boranes,[16-19] and amine–haloboranes,[20,21] and we wish to report here some specific effects arising from the introduction of cyanide ion as a boron-bonded ligand on the mechanism of hydrolysis of such adducts.

Experimental Section

All manipulations of sodium cyanotrihydroborate were carried out in a well-ventilated hood.

Materials. Sodium cyanotrihydroborate was obtained from Alfa Inorganic Chemicals as a gray-brown solid and subjected to Soxhlet extraction with tetrahydrofuran to give a cream-colored solid from which solvent was removed by evaporation *in vacuo.* Tetrahydrofuran, benzene, morpholine, 4-picoline, N,N,N',N'-tetramethylethylenediamine (TMED), N,N-dimethylformamide, and various reagent grade inorganic chemicals were obtained from Matheson Coleman and Bell. Tetrahydrofuran was distilled after boiling under reflux with lithium tetrahydroaluminate (Ventron). *Caution must be exercised in such distillations.*[22] Benzene was distilled from sodium. Anhydrous hydrogen chloride, dimethylamine, and trimethylamine were obtained from Matheson Gas Products. Deuterium oxide of 99.8% purity was obtained from Mallinckrodt or Columbia Organic Chemicals.

Apparatus. Specific preparations of amine–cyanoboranes (described below) were carried out utilizing standard taper glassware. Infrared spectra were obtained on samples contained in KBr wafers using a Perkin-Elmer Model 237 infrared spectrometer. Proton nmr were obtained with a Varian A-60A spectrometer at 60 MHz using tetramethylsilane as reference. The ^{11}B nmr spectra were recorded with a Varian HA-100 spectrometer at 32.1 MHz using trimethyl borate as external standard. Analyses of C, H, N, and B were performed by M-H-W Laboratories, Garden City, Mich., or Galbraith Laboratories, Knoxville, Tenn. Molecular weights were determined at 50° with a Mechrolab, Inc., vapor pressure osmometer, Model 301A, calibrated with benzil and using N,N-dimethylformamide as solvent. The concentrations of solutions were in the range 0.05–0.40 M. Results compared favorably with mass spectra recorded on a Finnigan 1015 mass spectrometer operating at an ionizing voltage of 70 eV. Solid samples were vaporized in a heated inlet system before being subjected to the ionizing voltage. A Sargent thermonitor controlled water bath was utilized in kinetic studies and for investigations of proton exchange. Temperatures were maintained to ±0.05°. A Beckman Expandomatic pH meter was used for pH and pD determinations.

Deuterium Compounds. Gaseous deuterium chloride was prepared from benzoyl chloride and D_2O according to the procedure of Brown and Groot.[23] Solutions of DCl in D_2O were prepared and their concentrations determined by titration with standard NaOH. The DCl salt of N-deuteriomorpholine was prepared by stirring 50 g (0.57 mol) of morpholine with 290 ml of a solution containing 1.65 mol of DCl in D_2O for 12 hr, evaporating the solvent *in vacuo*, and treating the residue five times successively with 35 ml of D_2O for 30

min each at 35–40°. After each washing, the solvent was removed by evaporation *in vacuo.* The product showed an absorption at 2200 cm^{-1} (ν_{N-D}) and the absence of absorption in the N–H stretching region at 3100 cm^{-1}. Sodium deuterioxide was prepared from sodium peroxide and D_2O under nitrogen atmosphere in a glove bag.[24]

The preparation of $NaDCO_3$ was accomplished by passing CO_2 (dried over $CaSO_4$) into a solution containing 22.5 g of sodium carbonate in 150 ml of D_2O. The product was collected by filtration, washed with D_2O, and dried *in vacuo.* A sample of sodium cyanotrideuterioborate, $NaBD_3CN$, was prepared according to a previously described procedure using $NaBH_3CN$, deuterioacetic acid, DCl, and D_2O.[4] The product was recovered from tetrahydrofuran in 66% yield and revealed strong absorption at 1800 cm^{-1} (ν_{B-D}) and no significant absorption in the B–H stretching region.

Buffer solutions employed for the determination of pD were prepared according to previously described procedures[25,26] and employing certificates of analysis for NBS standard reference materials $NaHCO_3$, Na_2CO_3, Na_2HPO_4, and KH_2PO_4. The pD values for various buffer systems were determined from direct readings on the pH meter using the NBS buffer solutions for calibration.

N-**Methylmorpholine Hydrochloride.** Gaseous hydrogen chloride was bubbled through a cooled (5°) solution containing 50 g of N-methylmorpholine in 100 ml of ethanol for a period of 30 min. The resulting white precipitate was collected by filtration, washed with cold ethanol, and dried overnight *in vacuo*; yield 61.3 g (92% theory).

Trimethylamine–Cyanoborane. Sodium cyanotrihydroborate (8.6 g, 0.14 mol) was added with stirring under streaming dry N_2 to 150 ml of ice-cold tetrahydrofuran contained in a four-neck, 1-l. flask equipped with two pressure-equalizing addition funnels, a reflux condenser, and mechanical stirrer. A solution of hydrogen chloride in tetrahydrofuran (1 M) was added dropwise with stirring until the evolution of hydrogen ceased (*ca.* 1 hr.). Excess acid was neutralized by adding a solution of trimethylamine in tetrahydrofuran (2.1 M) until a test with Hydrion paper showed pH $\sim$7. Additional amine (8.9 g, 0.15 mol) was then added and the reaction mixture was stirred overnight at 25°. A solid residue was separated from the bright yellow solution by filtration through a coarse sintered-glass funnel under nitrogen and washed with 100 ml of tetrahydrofuran. The product was recovered from the filtrate by evaporation of the solvent *in vacuo.* It was then dissolved in 200 ml of a mixture of ethanol and diethyl ether (1:10 by volume) at 25°, reprecipitated by the addition of pentane, and dried *in vacuo* over P_2O_5. Vacuum sublimation at 70° gave 4.33 g (32% theory) of a white crystalline solid, mp 63°. *Anal.* Calcd for $(CH_3)_3N \cdot BH_2CN$: C, 49.04; H, 11.32; N, 28.60; B, 11.04; mol wt 98. Found: C, 48.93; H, 11.35; N, 28.84; B, 10.90; mol wt 98. The infrared spectrum showed strong absorption in the B–H stretching region at 2410 cm^{-1} and less intense absorption in the C≡N stretching region at 2185–2280 cm^{-1}. The ^{1}H nmr spectrum (benzene solution) exhibits a singlet, attributed to methyl protons, at −2.25 ppm relative to $(CH_3)_4Si$ (external standard) and the ^{11}B nmr spectrum (benzene solution) consists of a well-resolved 1:2:1 triplet at +33.2 ppm relative to $(CH_3O)_3B$ (external standard) with J_{B-H} at 108 Hz. The high-field shift in the ^{11}B spectrum observed on substitution of cyanide for hydride (δ +33.2 ppm for $(CH_3)_3N \cdot BH_2CN$ compared to +24.9 ppm for $(CH_3)_3N \cdot BH_3$)[27] is consistent with effects of –CN substitution on chemical shifts reported in species such as $1,10$-$B_{10}Cl_8(CN)_2{}^{2-}$ and $1,10$-$B_{10}H_8(CN)_2{}^{2-}$.[28-30]

Morpholine–Cyanoborane. By a similar procedure, the reaction of sodium cyanotrihydroborate (7.7 g, 0.12 mol) with hydrogen chloride and morpholine (11.13 g, 0.128 mol in excess of the quantity required to neutralize excess acid) in tetrahydrofuran gave, after vacuum sublimation at 115°, 4.43 g (29%) of a white crystalline product, mp 104–106°. *Anal.* Calcd for $C_4H_8ONH \cdot BH_2CN$: C, 47.67; H, 8.80; N, 22.24; B, 8.59; mol wt 126. Found: C, 47.49; H, 8.72; N, 22.10; B, 8.42; mol wt 125. The equivalent weight (31.2) was determined iodometrically using Br_2 as oxidant.[31] This indicates 4 equiv/

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mol and is consistent for a molecule containing two hydridic (boron-bonded) hydrogen atoms where the iodometric equivalence of hydride is given by $H^- + I_2 \longrightarrow H^+ + 2I^-$.[32] The infrared spectrum revealed a strong absorption band in the B–H stretching region at 2387 cm^{-1} and a distinct, sharp singlet (absent in the spectrum of morpholine-borane) in the $-C\equiv N$ stretching region at 2166 cm^{-1}. The ^{1}H spectrum in DMSO-d_6 was similar to that of a sample of morpholine-borane. The signal due to the four protons on carbon atoms adjacent to the amino nitrogen in morpholine-cyanoborane was shifted slightly (*ca.* 7 cps) downfield from the corresponding resonance in morpholine-borane. A similar downfield shift of lesser magnitude (*ca.* 3 cps) was observed for the protons on carbon atoms adjacent to oxygen. The ^{11}B spectrum of morpholine-cyanoborane in ethanol produced a poorly resolved triplet at +38.8 ppm from external (CH$_3$-O)$_3$B with $J_{B-H} = 98.5$ Hz.

Tetramethylethylenediamine-Bis(cyanoborane). A similar procedure was employed using sodium cyanotrihydroborate (5.7 g, 0.091 mol), hydrogen chloride, tetrahydrofuran, and TMED (5.8 g, 0.050 mol after neutralization of acid). The solid product was washed with cold water and dried *in vacuo* over P$_2$O$_5$. A total of 3.02 g (34%) of white powder was obtained; mp 166–170°. *Anal.* Calcd for [(CH$_3$)$_2$NCH$_2$]$_2$·2BH$_2$CN: C, 49.55; H, 10.40; N, 28.89; B, 11.16; mol wt 194. Found: C, 49.58; H, 10.58; N, 28.82; B, 11.00; mol wt 189. In the infrared spectrum, strong absorptions were observed at 2415, 2250, and 2188 cm^{-1}. The ^{1}H nmr spectrum (DMSO-d_6) exhibited two sharp singlets with relative areas 3:1 at −2.7 and −3.2 ppm from (CH$_3$)$_4$Si (internal standard). These are attributed, respectively, to the methyl and methylene protons of the diamine portion of the molecule; resonance due to the boron-bonded hydrogens was not observed.

4-Picoline–Cyanoborane. Sodium cyanotrihydroborate (4.7 g, 0.075 mol), tetrahydrofuran, hydrogen chloride, and 4-picoline (7.3 g, 0.078 mol in excess of the acid equivalence) produced, after sublimation *in vacuo* at 110°, 2.94 g (30%) of white crystalline solid, mp 60–61°. *Anal.* Calcd for C$_6$H$_7$N·BH$_2$CN: C, 63.70; H, 6.87; N, 21.23; B, 8.20; mol wt 132. Found: C, 63.88; H, 7.02; N, 21.43; B, 7.95; mol wt 132. Characteristic infrared absorptions were found at 2410, 2230, and 2187 cm^{-1}. The ^{1}H nmr in CDCl$_3$ consisted of three resonances centered at −8.3, −7.4, and −2.5 ppm relative to an internal reference of (CH$_3$)$_4$Si. The areas under the three peaks were in the ratio of 2:2:3. Each of the first two resonances was split into doublets ($J_{ab} = 6.5$ cps) of equal intensity and the third was a sharp singlet. The doublets are assigned to the ring protons and the singlet is assigned to the 4-methyl substituent.

N-Methylmorpholine–Cyanoborane. A total of 15 g (0.24 mol) of NaBH$_3$CN was dissolved in 150 ml of tetrahydrofuran and the solution added dropwise with stirring to a suspension of 32.9 g (0.24 mol) of *N*-methylmorpholine hydrochloride in 250 ml of tetrahydrofuran. The solution was warmed to room temperature and then brought to reflux until cessation of gas evolution (1 hr). The NaCl was separated by filtration and the solvent removed from the filtrate by evaporation *in vacuo*. A white crystalline solid was obtained upon vacuum sublimation of the residue. This was recrystallized from water. *Anal.* Calcd for O(CH$_2$)$_4$N(CH$_3$)·BH$_2$CN (mol wt 139.99): C, 51.48; H, 9.36; N, 20.01. Found: C, 51.29; H, 9.45; N, 20.21. The infrared spectrum (Nujol) revealed absorption in the B–H stretching region at 2410 cm^{-1} and the absence of absorption in the N–H stretching region. The ^{11}B spectrum in benzene yielded a triplet (ratio 1:2:1) at +33.6 ppm from external (CH$_3$O)$_3$B with $J_{B-H} = 104.9$ Hz.

Dimethylamine–Cyanoborane. A similar procedure was employed using 15 g (0.24 mol) of NaBH$_3$CN, anhydrous hydrogen chloride, and dimethylamine (0.24 mol in excess of that quantity required to neutralize excess acid) in tetrahydrofuran. The product was subjected to sublimation twice *in vacuo* at 90°. A white hygroscopic product was obtained (2.2 g, 11% theory); mp 46–48°. *Anal.* Calcd for (CH$_3$)$_2$NH·BH$_2$CN (mol wt 83.93): C, 42.92; H, 10.83; N, 33.38. Found: C, 42.72; H, 10.65; N, 33.23. The infrared spectrum revealed a strong absorption band at 2395 cm^{-1} (ν_{B-H}), a singlet at 2185 cm^{-1} ($\nu_{C\equiv N}$), and a broad band centered at 3120 cm^{-1} attributed to N–H stretching.

N-Deuteriomorpholine–Cyanoborane. A solution of 7.54 g (0.12 mol) of NaBH$_3$CN in 150 ml of tetrahydrofuran was added with stirring to a suspension of 14.7 g (0.13 mol) of *N*,*N*-dideuteriomorpholinium chloride in 300 ml of tetrahydrofuran. The mixture was heated to reflux until cessation of gas evolution (1.5 hr). Solids were collected by filtration under nitrogen and solvent was removed from the

filtrate by evaporation *in vacuo* to give a white solid residue. Vacuum sublimation at 100° for 3 days gave 5.4 g (0.043 mol), 35% yield, of white crystals (needles), mp 108–110°. The product was subjected to two additional sublimations. *Anal.* Calcd for O(CH$_2$)$_4$-ND·BH$_2$CN (mol wt 126.97): C, 47.30; H, 7.94; N, 22.06. Found: C, 46.99; H, 8.23; N, 21.90. The infrared spectrum revealed strong absorptions at 3110 cm^{-1} (ν_{N-H}) and 2400 cm^{-1} (ν_{B-H}), a weak band at 2290 cm^{-1} (ν_{N-D}), and a weak doublet at 1775–1835 cm^{-1} (ν_{B-D}). The ^{11}B nmr spectrum obtained in ethanol solution yielded a poorly resolved multiplet as opposed to the triplet obtained for morpholine–cyanoborane.

Mass Spectra. For the four compounds investigated, m/e peaks corresponding to parent ions (p$^+$) were small at the ionizing voltage of 70 eV, but significant peaks for p$^+$ − 1 fragments were obtained: (CH$_3$)$_3$N·BH$_2$CN, 97; O(CH$_2$)$_4$NH·BH$_2$CN, 125; C$_6$H$_7$N·BH$_2$CN, 131; [(CH$_3$)$_2$NCH$_2$]$_2$·2BH$_2$CN, 193.

Oxidation with I$_2$. The addition of 20 ml of 0.068 N morpholine-cyanoborane to 30 ml of 0.1 N KIO$_3$ solution containing 4 N H$_2$SO$_4$ and excess KI resulted in oxidation of less than 2% of the cyanoborane in 10 min at 20°. This contrasts to the rapid reaction of morpholine-borane toward I$_2$. Slow hydride oxidation by iodine also was observed with trimethylamine–cyanoborane in 50% aqueous dioxane. A similar decrease in reactivity has been observed on substitution of chloride for hydride in the borane adduct of trimethylamine.[21]

Kinetic Studies. For a typical run, a weighed quantity of amine-cyanoborane and 100 ml of a given buffer solution were contained in separate flasks and equilibrated at a given temperature. The initial time, t_0, was taken as the time of addition of solvent to substrate. The rate was determined by following the disappearance of soluble hydride with time. Due to the slow reaction of I$_2$ with substrate the direct iodometric method previously used for the determination of hydride in amine–borane solutions was not applicable.[18,32] For the secondary amine-cyanoboranes, hydride oxidation by bromine was found to be rapid, however, and a modified procedure involving this reagent was employed. Bromine was generated from standard KBrO$_3$ and excess KBr in acid (H$_2$SO$_4$) solution. This was followed by an iodometric determination of the Br$_2$ present in excess of that required to consume soluble hydride present in periodically withdrawn samples of hydrolysate. Initial concentrations of morpholine–cyanoborane and dimethylamine–cyanoborane were usually (8.0–11.0) × 10^{-3} M. Concentrations of buffer components ranged from 0.05 to 0.9 M total buffer.

The bromine oxidation of hydride also was employed to determine rates of hydrolysis of tertiary amine–cyanoboranes. Although, by this procedure, only about half the theoretical quantity of hydride contained in these substrates is rapidly oxidized by Br$_2$ (see Discussion), the substrates proved quite unreactive toward hydrolytic decomposition and the analytical method was adequate for the purpose of monitoring small losses of hydride with time.

Concentrations of hydroxide ion were determined at different temperatures from measurements of pH and values of pK_w obtained by interpolation from data of Covington, Robinson, and Bates.[33] The OD$^-$ concentrations were similarly obtained from pD determinations and the interpolated values of pK_w for deuterium oxide.

Exchange Studies. A sample of substrate (0.05–0.10 g) and a quantity of D$_2$O (50 ml) contained in separate vessels were brought to a given constant temperature and combined. After a given period of time, usually about 1–5 min, the hydrolysis reaction was quenched by chilling the solution in an ice-water bath. Solvent was removed *in vacuo* and an infrared spectrum taken of the dried residue.

Results and Discussion

Data for the hydrolysis of several amine–cyanoboranes which, in alkaline solution, proceeds *via* eq 1 are given in

$$R_2NH \cdot BH_2CN + 2H_2O + 2OH^- \longrightarrow R_2NH + B(OH)_4^- +$$
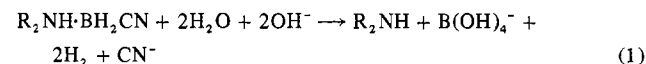$$2H_2 + CN^- \tag{1}$$

Table I. Substrates fall into one of two categories with respect to their hydrolytic behavior. At constant hydrogen ion concentration a first-order dependence of rate on substrate is observed for the cyanoborane adducts of morpholine and dimethylamine and the pH dependence of the resulting first-order rate constant, determined over 5–6 pH units,

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Table I. Hydrolysis of Amine–Cyanoboranes in Water

Temp, °C	pOH	$10^5 k_1,^a$ sec^{-1}	$k_2,^b M^{-1}$ sec^{-1}	Buffer
		Morpholine–Cyanoborane Substrate		
60.5	2.84	872	6.03	j
60.5	5.04	7.34	8.05	k
60.5	5.64	2.43	10.58	k
60.5	6.21	0.448	7.27	k
60.5	7.01	0.0898	9.19	k
52.0	3.01	249	2.57	j
44.6	3.07	116	1.35	j
36.4	3.21	32.7	0.524	j
25.0	3.50	3.82	0.121	j
9.2	2.12	11.0	0.0144	m
52.0	3.76^c	57.8^d	3.33	l
36.4	4.12^c	4.93^d	0.650	l
25.0	4.37^c	0.842^d	0.197	l
9.2	3.18^c	1.89^d	0.0288	n
36.4	4.12^c	5.95^e	0.784	l
36.4	3.25	32.2^f	0.566	j
		Dimethylamine–Cyanoborane Substrate		
36.4	1.86	31.7	0.0229	m
36.4	2.70^c	7.26^d	0.0364	n

[OH$^-$], M	$10^6 k_1,^a$ sec^{-1}
N-Methylmorpholine–Cyanoborane Substrate at 60.5°	
0.89	3.43
0.69	3.82
0.55	3.56
0.28	2.72
	2.71,^{g} 2.86,^{h} 2.59^i
Trimethylamine–Cyanoborane Substrate at 60.5°	
0.28	Very small

$^a k_1$ = d ln [amine–cyanoborane]/dt. $^b k_2 = k_1/$[OH$^-$]. ^{c} pOD. ^{d} R$_2$NH·BH$_2$CN in D$_2$O, OD$^-$. ^{e} R$_2$ND·BH$_2$CN in D$_2$O, OD$^-$. ^{f} R$_2$-ND·BH$_2$CN in H$_2$O, OH$^-$. ^{g} H$_2$O (no added OH$^-$). ^{h} D$_2$O (no added OD$^-$). ^{i} 0.9 M KCl in H$_2$O. ^{j} HCO$_3^-$, CO$_3^{2-}$. ^{k} H$_2$PO$_4^-$, HPO$_4^{2-}$, ^{l} DCO$_3^-$, CO$_3^{2-}$. ^{m} HPO$_4^{2-}$, PO$_4^{3-}$. ^{n} DPO$_4^{2-}$, PO$_4^{3-}$.
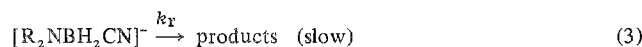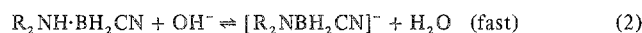
shows the reaction also to be first order in hydroxide ion. Studies at various concentrations of phosphate buffer reveal for a given pH no significant effect of a change in total buffer concentration (Table II), and although general base catalysis cannot be altogether precluded from such observations, due to the possible dominant effect of OH$^-$ in such systems, the results are suggestive of specific lyate ion catalysis.

An interesting departure in this behavior is found for the adducts of the tertiary amines. Thus, *N*-methylmorpholine-cyanoborane undergoes only slight hydrolysis at 60.5° and at a rate which is relatively insensitive to base up to nearly 0.9 M hydroxide ion, and no hydrolysis of trimethylamine-cyanoborane could be detected in 0.28 M NaOH at 60.5° over a period of 1-2 weeks. This suggests that a nitrogen-bonded proton is an important structural feature for the base-catalyzed reaction and it is proposed that removal of this proton by hydroxide ion occurs to facilitate the hydrolytic decomposition of the substrate. The proposed stoichiometric mechanism is similar to that originally proposed by Garrick[34] and later supported by Basolo and coworkers[35,36] for the base-catalyzed hydrolysis of various amminecobalt-(III) complexes, commonly described as SN1cb. It is presumed to involve removal by hydroxide ion of the nitrogen-bonded proton of the amine–cyanoborane in a rapid preequilibrium followed by the rate-determining decomposition of the conjugate base of the substrate (eq 2 and 3). A first-or-

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Table II. Effect of Total Phosphate Buffer Concentration on Rate of Morpholine–Cyanoborane Hydrolysis

Temp, °C	pH	[Buffer], M	$10^5 k_1,^a$ sec^{-1}
60.5	7.35	0.05^b	2.55
60.5	7.35	0.10^b	2.57
60.5	7.35	0.15^b	2.43
9.2	12.45	0.05^c	11.0
9.2	12.45	0.93^c	11.0

$^a k_1$ = d ln [amine–cyanoborane]/dt. ^{b} H$_2$PO$_4^-$, HPO$_4^{2-}$. ^{c} HPO$_4^{2-}$, PO$_4^{3-}$.

$$R_2NH \cdot BH_2CN + OH^- \rightleftharpoons [R_2NBH_2CN]^- + H_2O \quad \text{(fast)} \quad (2)$$

$$[R_2NBH_2CN]^- \xrightarrow{k_r} \text{products} \quad \text{(slow)} \quad (3)$$

der dependence of rate on both substrate and hydroxide ion is predicted with a second-order rate constant equal to the product $K_{eq}k_r$ where K_{eq} represents the equilibrium constant for the conversion of substrate to its conjugate base. No details of intimate mechanism of the rate-determining step are apparent. Water may be an energetically important participant. If such is the case and if proton transfer to [R$_2$-NBH$_2$CN]$^-$ is involved, the reaction should be subject to general base catalysis. In the absence of such evidence and in view of the observed solvent isotope effect (see below) the rate-limiting step, (3), is suggested to involve predominantly dissociative activation. Speculation on the mode of such decomposition might include departure of CN$^-$ and rapid hydrolysis of the resulting R$_2$NBH$_2$ species. Alternatively, a solvent-assisted dissociation without strong energetic requirement for proton transfer could be envisoned, but such suggestions regarding details of step 3 are only conjectural at this time.

The proposed mechanism demands that exchange of the nitrogen-bonded proton with solvent be rapid compared to the rate of hydrolysis. This has been demonstrated through a separate study of proton exchange in morpholine–cyanoborane. Exposure of the substrate to D$_2$O introduces deuterium at the amino nitrogen, as evidenced by the disappearance of absorption in the 3100-cm^{-1} region, attributed to ν_{N-H}, and the appearance of an absorption band around 2200–2220 cm^{-1} (ν_{N-D}) in samples of unhydrolyzed aminecyanoborane recovered from solution. This deuterium is rapidly replaced by ^{1}H when the *N*-deuterio substrate is treated with H$_2$O. Thus, the composition of the substrate is determined by the solvent and, within experimental error, the same rate of hydride decomposition is observed in aqueous solvent of given isotopic composition whether morpholine-cyanoborane or the *N*-deuterio compound is originally employed.

Although the rates of hydrolysis of morpholine–cyanoborane and dimethylamine–cyanoborane are not highly sensitive to a change in solvent from water to deuterium oxide, they are slightly enhanced in D$_2$O. Figure 1 shows the temperature dependence of the solvent isotope effect for the hydrolysis of morpholine–cyanoborane over the range 9.2–60.5°. Activation parameters, determined by linear regression analysis, are $\Delta H^{\ddagger} = 21.5$ kcal/mol ($r = 0.9994$) and $\Delta S^{\ddagger} = 9.4$ eu for the reaction in water and $\Delta H^{\ddagger} = 19.6$ kcal/mol ($r = 0.9999$) and $\Delta S^{\ddagger} = 3.8$ eu in deuterium oxide. For dimethylamine–cyanoborane, $k_{H_2O}/k_{D_2O} = 0.63$ at 36.4°. Since a change from ordinary to heavy water causes an alteration not only in the nature of the solvent but also in substrate and lyate ion, the overall isotope effect will be a composite of individual effects of these species and insufficient data are available at present to permit the assessment of spe-
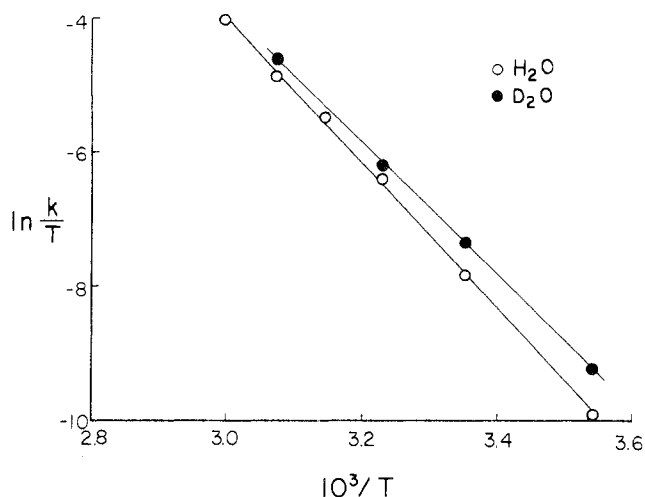
Figure 1. Temperature dependence of the solvent isotope effect for the hydrolysis of morpholine-cyanoborane (9.2-60.5°).

cific contributions. Numerous cases of specific hydroxide ion catalyzed reactions proceeding comparably faster in D_2O than in H_2O have been documented.[37] The existence of a small inverse effect here may be further suggestive that proton transfer from solvent is not occurring in the rate-limiting step (reaction 3), again consistent with the concept of specific base catalysis, since such proton transfer would be expected to impose a significant contribution toward a normal isotope effect. The substrates, however, must be regarded as weak Bronsted acids and, since exchange of the amino proton with solvent hydrogen is rapid, a significant isotope effect for acid dissociation is predicted with the dissociation constant being greater in H_2O than in D_2O.[38,39]

If the questionable assumption is made that the change from ordinary to heavy water produces relatively little effect on the rate of disappearance of substrate conjugate base (*i.e.*, that k_r is subject to a negligible isotope effect), that solvation effects are about the same, and that k_{H_2O}/k_{D_2O} therefore reflects the ratio of K_{eq} values for (2) in water and deuterium oxide, respectively, then the direction of the experimental isotope effect should be determined by the relative magnitudes of the corresponding acid dissociation constants for normal and deuterated substrates in the respective solvents as opposed to the relative values of the ion products for H_2O and D_2O. Employing $k_{H_2O}/k_{D_2O} = 0.61$ for morpholine-cyanoborane at 25°, $pK_w(H_2O) = 14.00$, and $pK_w(D_2O) = 14.87$,[33] the ratio $K_a/K_a' = 4.5$.[40]

Adamson and Basolo discussed the corresponding question in their study of the base-catalyzed hydrolysis of the chloropentaamminecobalt(III) ion wherein rapid exchange of ammine hydrogen with solvent hydrogen occurs and where the rate in heavy water was found to be about 56% of that in ordinary water at 18° with the isotope effect decreasing with decreasing temperature.[35] Arguing that differences in solvation should be small, they attributed the major contribution to the observed isotope effect to the preequilibrium (4) in which the chloroamidotetraamminecobalt(III) ion is pro-

posed to be formed and suggested such preequilibrium to be supported by the rather large positive activation entropy (+37 eu) for which the major contribution is thought to be the entropy of (4). Based upon data at 18 and 25°, $\Delta H^{\ddagger} = 28.7$ kcal/mol for hydrolysis of $Co(NH_3)_5Cl^{2+}$.

$$Co(NH_3)_5Cl^{2+} + OH^- \rightleftharpoons Co(NH_3)_4NH_2Cl^+ + H_2O \qquad (4)$$
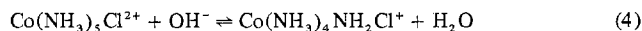
A more positive $\Delta S^{\ddagger}$ term is rather expected for the metal ion reaction than for cyanoborane hydrolysis since, unlike the preequilibrium proposed in (2), reduction of charge is pronounced in (4). Also, there is a statistical factor favoring a positive entropy term for the metal ion reaction wherein any of 15 equivalent ammine protons may be removed in forming the conjugate base. Preequilibrium (2) may contribute something to the positive entropy of activation for cyanoborane hydrolysis, however, since hydroxide ion probably causes greater orientation of solvent water than does the conjugate base of the substrate in which the charge is more dispersed.

Another analogy to the base-catalyzed hydrolysis of metal complexes is found when alkaline solutions of morpholine-cyanoborane are treated with hydrogen peroxide. Thus, the addition at 36.4° of 75 ml of $0.2 M H_2O_2$ to 25 ml of a solution of substrate at pH 10.5 was found to retard the rate (negligible hydrolysis for 4 days). Since extensive conversion of H_2O_2 by OH^- to the strongly nucleophilic but more weakly basic HO_2^- ion occurs, such retardation is consistent with the postulate that OH^- indeed serves not as a nucleophile but as a base as suggested in (2).[41]

The presence of a nitrogen-bonded proton also appears to be important in influencing the reactivity of amine-cyanoboranes toward other oxidants. Thus, whereas in aqueous solution at 25° rapid and complete oxidation of hydride by bromine occurs in adducts of morpholine and dimethylamine, thereby enabling facile determination of hydride in such species, the generation of bromine in the presence of tertiary amine-cyanoboranes results in rapid oxidation of only half the contained hydride, with the remainder reacting only very slowly. Thus, within experimental error, the same thiosulfate titer is required for solutions of trimethylamine-cyanoborane which have been exposed to bromine for 10-15 sec as for those which have been allowed to stand in the presence of Br_2 for 1 hr. Bromination leading to bromide ion replacement of both hydride ions in the boron coordination sphere of $(CH_3)_3N \cdot BH_2CN$ can be carried out under conditions more vigorous than those normally used in analytical hydride determinations, however, and these and related halogenation and other oxidation reactions of amine-cyanoboranes are currently being investigated.

Another mechanistic curiosity is raised by the results of our attempt to prepare *N*-deuteriomorpholine-cyanoborane by a modification of the Schaeffer and Anderson synthesis[42] of amine-boranes employing *N,N*-dideuteriomorpholinium chloride and $NaBH_3CN$. An unexpected doublet at 1773-1835 cm^{-1} in the infrared spectrum of the product has been attributed to boron-deuterium stretching vibrations, and the assignment of the 3110-cm^{-1} band to ν_{N-H} implies that proton scrambling between boron and nitrogen occurs during this synthesis. The indication that deuterium has been partially incorporated into the boron coordination sphere is further supported by the ^{11}B spectrum which, in contrast to

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(39) W. F. K. Wynne-Jones, *Chem. Rev.*, **17**, 115 (1935).
(40) $K_{eq}/K_{eq}' = K_aK_w'/K_a'K_w$ where K_{eq} denotes the equilibrium constant for reaction 2, K_a is the acid dissociation constant of the substrate, K_w is the ion product for water, and primed symbols denote the corresponding constants for processes involving the deuterated species $R_2ND \cdot BH_2CN$, D_2O, and OD^-.

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(42) G. W. Schaeffer and E. R. Anderson, *J. Amer. Chem. Soc.*, **71**, 2143 (1949).

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the triplet observed for $O(CH_2)_4NH \cdot BH_2CN$, shows multiple resonance which is not readily resolved. Future proposals of models for the mechanism of cyanoborane–amine formation by the reaction of cyanotrihydroborate with amine salts must accomodate this hydrogen exchange.

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

Use of a Substituent Effect in Borazine Chemistry for the Synthesis of 2,4-Dichloroborazine

O. T. BEACHLEY, Jr.,* and T. R. DURKIN

A two-step reaction sequence has been developed for the specific synthesis of 2,4-dichloroborazine, $HCl_2B_3N_3H_3$, using readily available starting materials. The procedure involves the initial preparation of a new unsymmetrically substituted borazine, $Cl_2[N(CH_3)_2]B_3N_3H_3$, from $Cl_3B_3N_3H_3$ and $N(CH_3)_2H$. This reaction to form $Cl_2[N(CH_3)_2]B_3N_3H_3$ is essentially quantitative and demonstrates the existence of a strong substituent effect in borazine chemistry. The compound $Cl_2[N(CH_3)_2]B_3N_3H_3$ is then allowed to react with B_2H_6 in diethyl ether to form $HCl_2B_3N_3H_3$. The factors influencing the B_2H_6 reaction have been studied in order to optimize the yield of $HCl_2B_3N_3H_3$. The compound $Cl[N(CH_3)_2]_2B_3N_3H_3$ has also been prepared but its instability at room temperature limits its usefulness as a synthetic intermediate. The ^1H nmr data and the thermal stability of the compounds in the series $Cl_{3-x}[N(CH_3)_2]_xB_3N_3H_3$ are compared.

Introduction

The syntheses of unsymmetrically substituted borazines present unusual problems in inorganic chemistry. A series of B-disubstituted borazines[1] $(H)(X)(Y)B_3N_3H_3$ in which X and Y are CN, OCN, or Cl has recently been reported. These compounds, which have unique combinations of electron-withdrawing and electron-donating substituents, are readily prepared from an appropriate B-chloroborazine and silver(I) salt. However, the initial starting material for their synthesis, 2,4-dichloroborazine, $HCl_2B_3N_3H_3$, is not readily available. There is no known procedure for the specific preparation of $HCl_2B_3N_3H_3$. The compound has only been obtained previously in small yields from reactions designed to prepare $H_2ClB_3N_3H_3$.[2,3]

In this paper, we report the results of a research project designed to develop a series of reactions for the specific synthesis of $HCl_2B_3N_3H_3$ in high yield from readily available starting materials. Our approach to the problem was to make use of a reaction,[4] the exchange of a dimethylamino group for hydrogen on a boron of a borazine ring using B_2H_6, which we discovered while studying the Lewis basicity of $H_2[N(CH_3)_2]B_3N_3H_3$. Therefore, we synthesized the previously unkown compound $Cl_2[N(CH_3)_2]B_3N_3H_3$ and studied its reactions with diborane. During the course of this research, we also prepared $Cl[N(CH_3)_2]_2B_3N_3H_3$ in order to evaluate it as a potential precursor to B-monosubstituted borazines. The series of compounds $Cl_x[N(CH_3)_2]_{3-x}B_3N_3H_3$ has been investigated with respect to their spectral and physical properties in order to study systematically the substituent effects of the Cl and $N(CH_3)_2$ groups.

Experimental Section

Materials. All compounds described in this investigation were manipulated in a vacuum line or a purified nitrogen atmosphere. All solvents were dried by conventional procedures. The compound[5] $Cl_3B_3N_3H_3$ was prepared by allowing BCl_3 to react with NH_4Cl in a tube at 200° and purified by recrystallization from *n*-pentane. Diborane[6] was prepared from $NaBH_4$ and H_3PO_4. The compound[7] $[N(CH_3)_2]_3B_3N_3H_3$ was synthesized from $Cl_3B_3N_3H_3$ and excess $N(CH_3)_2H$ in *n*-pentane.

Preparation of $Cl_2[N(CH_3)_2]B_3N_3H_3$. The new compound $Cl_2[N(CH_3)_2]B_3N_3H_3$ was prepared by allowing $Cl_3B_3N_3H_3$ (1 mol) to react with a stoichiometric quantity (2 mol) of $N(CH_3)_2H$. In a typical experiment, 1.689 g (9.18 mmol) of freshly recrystallized $Cl_3B_3N_3H_3$ was dissolved in 25 ml of dry diethyl ether. To this solution, 18.26 mmol of $N(CH_3)_2H$ was added by condensation at −196°. Upon allowing the mixture to warm slowly to room temperature with stirring, a white precipitate ($N(CH_3)_2H_2Cl$) formed. After 30 min, the reaction mixture was filtered to remove $N(CH_3)_2H_2Cl$ and then the ether was removed from the filtrate by vacuum distillation. The compound $Cl_2[N(CH_3)_2]B_3N_3H_3$ (1.635 g, 92.3% yield based on $Cl_3B_3N_3H_3$) remained in the flask as a white crystalline solid. It had a melting point of 92–92.5° and was identified by its analytical data and spectral properties. The compound can be recovered unchanged after standing at room temperature for several days. It can be purified by sublimation at room temperature to a 0° cold finger. *Anal.* Calcd for $Cl_2[N(CH_3)_2]B_3N_3H_3$: N, 29.11; Cl, 36.83. Found: N, 29.08; Cl, 36.28.

Preparation of $HCl_2B_3N_3H_3$. Reaction of $Cl_2[N(CH_3)_2]B_3N_3H_3$ with B_2H_6. The compound $HCl_2B_3N_3H_3$ was prepared by allowing $Cl_2[N(CH_3)_2]B_3N_3H_3$ to react with B_2H_6 in an appropriate solvent. The experimental conditions for the reaction were varied in order to optimize the yield of $HCl_2B_3N_3H_3$. The effects of changing the mole ratio of $Cl_2[N(CH_3)_2]B_3N_3H_3$ to B_2H_6 from 0.69 to 1.25, the reaction time from 1.5 to 24 hr, and the nature of the solvent (diethyl ether, *n*-pentane, or neat) were studied. The following experimental procedure maximized the yield of HCl_2B_3-

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