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Hypochlorite Chlorination of Tertiary Amine–Boranes

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Numerous tertiary alkylamine–boranes undergo successive B-chlorination on treatment with sodium hypochlorite. Stopped-flow spectrophotometric studies of the disappearance of NaOCl in the presence of amine–borane show the rate of the initial (monochlorination) reaction to be described by the expression $-\mathrm{d}[\mathrm{NaOCl}]/\mathrm{d}t = k[\mathrm{R_3N{\cdot}BH_3}][\mathrm{NaOCl}]$. Subsequent chlorination processes occur more slowly as evidenced by the trend in second-order rate constants in the trimethylamine–borane system at pH 8.5: $k_{\mathrm{Me_3N{\cdot}BH_3}} > k_{\mathrm{Me_3N{\cdot}BH_2Cl}} > k_{\mathrm{Me_3N{\cdot}BHCl_2}}$. Monochlorination also displays a first-order dependence on hydrogen ion in the region pH 8–10.2, but a maximum rate is observed in the vicinity of the pK_a of hypochlorous acid (7.5), suggesting HOCl to be the active species in the initial attack on amine–borane. Subsequent reaction of the amine–monochloroborane, however, appears to be insensitive to pH in the region 6.9–8.7. Small amounts of H_2 are evolved during chlorination, probably due to some hydrolytic decomposition of amine–chloroboranes. This activity of tertiary amine–boranes toward hypochlorite contrasts with that of selected secondary amine–boranes which have been proposed to undergo quantitative hydride *oxidation* followed by chlorination of free amine.

Introduction

In a previous study,[1] the reaction of morpholine–borane with hypochlorite was proposed to proceed via a rate-determining oxidative attack of HOCl at a boron–hydrogen linkage followed by rapid oxidation of residual hydridic hydrogen and N-chlorination of the resulting amine. This proposal was based upon measured rates of initial reactions of NaOCl with amine–borane and amine, respectively, on substrate and solvent isotope effects, and upon iodometric and stopped-flow titrimetric studies, which show all hydridic hydrogen to be consumed without hydrolytic decomposition. In an effort to extend studies of the amine–borane reaction without complexities introduced by consecutive competitive chlorination of free amine, we chose to explore the reactivity of hypochlorite with selected tertiary amine–boranes. Results show striking stoichiometric and kinetic dissimilarities to the hypochlorite–secondary amine–borane systems.

Experimental Section

Materials and Methods. Trimethylamine–borane, triethylamine–borane, and $NaBH_4$ were obtained from Alfa Products. *N*-Methylmorpholine, quinuclidine, and *p*-dioxane were obtained from Mallinckrodt, and hydrogen chloride was purchased from Matheson. Boron trifluoride–diethyl ether complex, $BF_3{\cdot}Et_2O$, was obtained from Aldrich and was purified by distillation in vacuo. $Me_3N{\cdot}BH_3$ was purified by sublimation in vacuo; mp 91–93 °C (lit.[2] mp 93.5 °C). Dimethylamine–borane was prepared from $Me_2NH{\cdot}HCl$ and $NaBH_4$ according to the procedure of Schaeffer and Anderson[3] and then sublimed in vacuo; mp 33–35 °C (lit.[2] mp 37 °C). Dioxane was boiled under reflux with aqueous HCl under a stream of N_2, following which solid KOH was added to the cooled solution. The dioxane was separated from the aqueous layer, dried over KOH, and collected by fractional distillation from sodium (bp 101 °C). Tetrahydrofuran and diethyl ether (Mallinckrodt) were boiled under reflux with $LiAlH_4$ and distilled from their respective solutions. (*Caution*: *$LiAlH_4$ solutions of THF must be handled with care.*[4]) Sodium hypochlorite was obtained as an alkaline stabilized 5% aqueous solution from Mallinckrodt. Samples of this solution were diluted with H_2O to prepare new stock solutions, which were analyzed iodometrically.[5] Samples of the stock were then diluted with appropriated buffer solution immediately before use.

Elemental analyses of C and H were performed by Galbraith Laboratories Inc., Knoxville, TN. Hydridic hydrogen was determined either by iodometry[6] or by measurement of the H_2 evolved on hydrolysis of the compound in aqueous acid. Boron and nitrogen analyses were obtained with use of a previously described titrimetric procedure,[7] and chloride was determined by the Volhard method.[8] Determinations of N and Cl in quinuclidine–chloroborane also were performed by Galbraith. Conventional visible and ultraviolet spectra were obtained with a Gilford Model 250 spectrophotometer. Infrared spectra were obtained on KBr wafers of crystalline materials with Beckman Model 4250 and Model 33 spectrophotometers. ^1H NMR spectra were obtained with a Varian Model EM-390 spectrometer using $CDCl_3$ as a solvent and Me_4Si as an external standard. All melting points were determined with an Electrothermal capillary melting point apparatus. pH values were obtained on a Corning Model 130 digital pH meter.

The products obtained from mixtures of NaOCl and amine–boranes under various reacion conditions were isolated by extraction with Et_2O and subsequent removal of solvent by rotary evaporation in vacuo. They were identified from their melting points and IR and NMR spectra.

Stoichiometry and Kinetic Studies. Stopped-flow spectrophotometric experiments were carried out with a Durrum-Gibson D-110 spectrophotometer in conjunction with a Tektronix oscilloscope. All solutions were prepared with deionized water that was either redistilled or passed through a Barnstead mixed-bed ion-exchange column to obtain an effluent having a conductivity <0.01 ppm (measured as NaCl). Reaction mixtures containing carbonate or phosphate buffer were adjusted to a total buffer concentration of 35 mM and, through addition of NaCl, to an ionic strength $\mu = 0.1$ M.

Determination of reaction stoichiometry involved a stopped-flow spectrophotometric "titration" of NaOCl with amine–borane wherein the decrease in optical density was followed at 292 nm. The initial reference absorbance was obtained from a stopped-flow mixture of a carbonate- or phosphate-buffered solution, 1.2 mM in NaOCl, with an equal volume of water. Equal volumes of solutions each containing a different amount of amine–borane were then mixed with separate samples of buffered NaOCl solution. The difference between the initial and final absorbance corresponding to consumption of a stoichiometrically equivalent amount of hypochlorite ($\Delta A = A_0 - A_\infty$) was determined as a function of the amine–borane concentration.

Kinetic studies were carried out with use of a similar mixing technique to determine the time dependence of ΔA. In some cases, "initial rates" were obtained by determining the nearly linear change in absorbance with time that occurs immediately following the stopped-flow mixing of reagents.

Amine–Boranes and Amine–Chloroboranes. *N*-Methylmorpholine–borane was prepared by a previously reported procedure involving the addition of freshly distilled *N*-methylmorpholine to a tetrahydrofuran solution of THF–borane.[9] Quinuclidine–borane was prepared from quinuclidine hydrochloride (Aldrich) and $NaBH_4$ by a previously described adaptation[10] of the method of Schaeffer and

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Table I. Stopped-Flow Spectrophotometric "Titration" of NaOCl with Selected Tertiary Amine-Boranes in H_2O ($\lambda = 292$ nm, $t = 25$ °C, $\mu = 0.1$ M)

amine-borane	pH	mol ratio [NaOCl]: [amine-borane]
$Me_3N\cdot BH_3$	7.60	1.03
	8.32	1.07
	8.89	1.13
	9.18	1.03
$Et_3N\cdot BH_3$	7.56	1.27
	8.01	1.27
$Qn\cdot BH_3$[a,b]	8.2[c]	1.14
NMMbn[d]	7.18	1.10
	8.07	1.14

[a] $Qn\cdot BH_3 = C_7H_{13}N\cdot BH_3$. [b] The solvent is 12.5% *p*-dioxane–87.5% H_2O by volume. [c] pH denotes pH meter reading in 12.5% *p*-dioxane–87.5% H_2O. [d] NMMbn = $O(CH_2)_4N(CH_3)\cdot BH_3$.

Anderson.[3] The product was purified by sublimation in vacuo; mp 160–162 °C.

Amine–monochloroboranes were prepared by the method of Nöth and Beyer[2] by passing hydrogen chloride (dried over P_2O_5) through a benzene solution of the amine–borane. Yields reported are of crude product. Purification was carried out by recrystallization from benzene–petroleum ether mixtures. Melting points, infrared spectra, and ^1H NMR spectra were obtained on samples of recrystallized material.

A yield of 5.5 g (75% of theory) of $Me_3N\cdot BH_2Cl$ was obtained from 5.0 g (68.5 mmol) of $Me_3N\cdot BH_3$ in 150 mL of C_6H_6; mp 83–84 °C (lit.[2] mp 85 °C). Strong absorption was observed at 2400 cm^{-1} (ν_{B-H}). The ^1H NMR showed a singlet (CH_3) at $\delta = 2.8$. Anal. Calcd for $C_3H_{11}NBCl$ ($M_r = 107.39$): H(hydridic), 1.88; B, 10.07; N, 13.04; Cl, 32.02. Found: H(hydridic), 2.02; B, 10.21; N, 13.10; Cl, 32.8.

Triethylamine–chloroborane was obtained in a yield of 4.3 g (83% of theory) from 4.0 g (34.8 mmol) of $Et_3N\cdot BH_3$ in 75 mL of C_6H_6: mp 40–41 °C (lit.[10] mp 43°C); ν_{BH} (strong) centered at 2420 cm^{-1}; ^1H NMR at $\delta = 2.9$ (quartet) and 1.2 (triplet). Anal. Calcd for $C_6H_{17}NBCl$ ($M_r = 149.47$): H(hydridic), 1.35; B, 7.24; N, 9.37, Cl, 23.72. Found: H(hydridic), 1.42; B, 7.20; N, 9.21; Cl, 23.09.

A 1.3-g yield (73% of theory) of quinuclidine–chloroborane was obtained from 1.4 g (11.2 mmol) of quinuclidine–borane in 75 mL of C_6H_6; mp 131–133 °C. A strong doublet was found in the 2400-cm^{-1} region (ν_{B-H}), and the ^1H NMR revealed signals at δ = 1.8 (multiplet), 2.1 (septet), and 3.1 ppm (triplet). Anal. Calcd for $C_7H_{15}NBCl$ ($M_r = 159.47$): C, 52.72; H, 9.48; H(hydridic), 1.26; B, 6.78; N, 8.78; Cl, 22.23. Found: C, 52.53; H, 9.52; H(hydridic), 1.23; B, 6.70; N, 8.72; Cl, 22.12, 22.24 (Galbraith).

N-Methylmorpholine–chloroborane was produced in a yield of 1.2 g (84% of theory) from 1.1 g (9.6 mmol) of *N*-methymorpholine–borane and HCl in benzene. Recrystallization from benzene–petroleum ether produced white crystals, mp 55–57 °C, which displayed strong absorption at 2040 cm^{-1} (ν_{B-H}). Anal. Calcd for $C_5H_{13}BNOCl$ ($M_r = 149.42$): C, 40.19; H, 8.77; H(hydridic), 1.35; B, 7.24; N, 9.37; Cl, 23.73. Found: C, 40.05; H, 8.90; H(hydridic), 1.15; B, 7.52; N, 9.26; Cl, 22.12.

In a typical experiment designed to isolate and identify product(s) of the reaction of tertiary amine–boranes with NaOCl, a 0.71-g (9.7-mmol) sample of $Me_3N\cdot BH_3$ was dissolved in 40 mL of phosphate buffer (pH 7.4). This solution was diluted to 100 mL with H_2O and then treated with 100 mL of an aqueous solution containing 15 mmol of NaOCl and stirred at 25 °C for 1–2 h. The solution was extracted three times each with 40 mL of Et_2O, and the combined ether extracts were dried over anhydrous $MgSO_4$. Et_2O was removed by rotary evaporation, and the white residue was purified by sublimation in vacuo; mp 86–89°C (lit.[2] mp for $Me_3N\cdot BH_2Cl$ 85 °C). Infrared and ^1H NMR spectra were identical with those of an authentic sample of $Me_3N\cdot BH_2Cl$.

Trimethylamine–dichloroborane was obtained by adding 3.0 g (41 mmol) of $Me_3N\cdot BH_3$ to 50 mL of 2 M NaOCl and stirring for 6–8 h at 25 °C. The product was extracted with Et_2O and purified by sublimation in vacuo; mp 149–150 °C (lit.[11] mp 151 °C). The infrared spectrum showed a strong sharp singlet at 2460 cm^{-1} (ν_{B-H}).

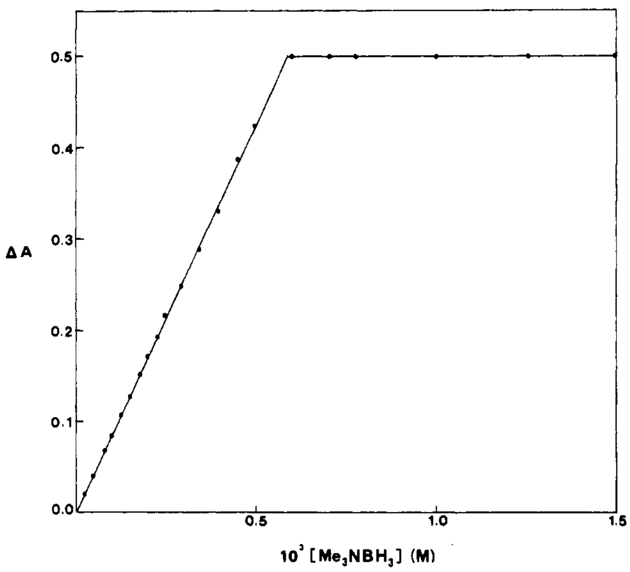

Figure 1. Stopped-flow spectrophotometric titration of NaOCl with $Me_3N\cdot BH_3$ (pH 7.60, $\lambda = 292$ nm, $t = 25$ °C, $\mu = 0.1$ M, $[NaOCl]_0 = 0.6 \times 10^{-3}$ M, $[NaOCl]/[Me_3N\cdot BH_3] = 1.03$). Comparable ratios are obtained at pH 8.32 (1.07), 8.89 (1.13), and 9.18 (1.03).

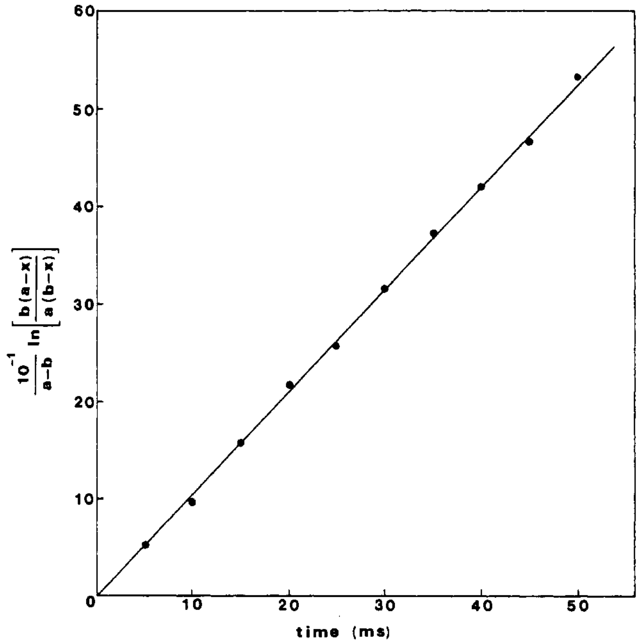

Figure 2. Second-order treatment of the reaction of $Me_3N\cdot BH_3$ with NaOCl ($a = [Me_3N\cdot BH_3]_0 = 1.0 \times 10^{-3}$ M, $b = [NaOCl]_0 = 0.6 \times 10^{-3}$ M, x = concentration of reactant consumed, pH 7.60, $t = 25$ °C, $\mu = 0.1$ M).

Results and Discussion

Stopped-flow spectrophotometric studies of the reaction of NaOCl with several tertiary amine–boranes in the region pH 7–8.5 reveal a molecular stoichiometry, $[OCl^-]\cdot$[amine–borane] = 1:1. A typical "titration" curve for the NaOCl–$Me_3N\cdot BH_3$ system is shown in Figure 1, and stoichiometric results for reaction of hypochlorite with a series of tertiary amine–boranes are summarized in Table I. At higher pH (>9), the determination of reaction stoichiometry for $Me_3N\cdot BH_3$ and *N*-methylmorpholine–borane (NMMbn) is obscured because the initial decrease in absorbance resulting from reaction of amine–borane with NaOCl is followed by a slower measurable decline in optical density corresponding to one or more ad-

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Table II. pH Dependence of Initial Rate of Reaction of NaOCl with Tertiary Amine-Boranes in H_2O ($t = 25$ °C, $\mu = 0.1$ M)

pH	$10^{-2}k_2$, M^{-1} s^{-1} [a]	pH	$10^{-2}k_2$, M^{-1} s^{-1} [a]
	$Me_3N \cdot BH_3$		
6.64	260	8.89	39
7.16	155	9.19	17
7.60	145	10.2	1.5
8.33	82		
	$Et_3N \cdot BH_3$		
6.66	610	8.82	95
7.15	575	9.12	38
7.56	340	10.2	3.1
8.06	280		
	$O(CH_2)_4N(CH_3) \cdot BH_3$		
6.67	100	8.76	135
7.18	270	8.97	58
7.51	450	9.51	16
8.07	345	10.2	1.7
	$C_7H_{13}N \cdot BH_3$ [b]		
8.2	180	9.4	74
9.2	115		

[a] $k_2 = -d[NaOCl]/(dt[NaOCl][R_3NBH_3])$. [b] The pH readings are in 12.5% *p*-dioxane–87.5% H_2O.

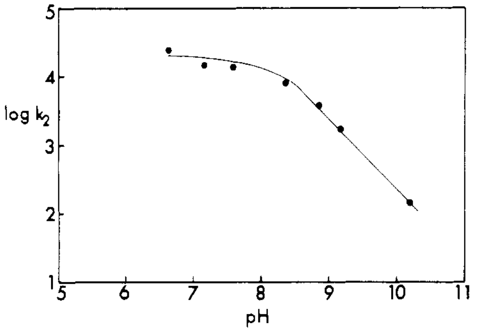

Figure 3. pH dependence of the second-order rate constant obtained from "initial rate" studies of the reaction of $Me_3N \cdot BH_3$ with NaOCl ($t = 25$ °C, $\mu = 0.1$ M).

ditional hypochlorite-consuming processes. In the lower region of pH, the initial reaction is sufficiently fast to be kinetically "decoupled" from subsequent processes on the stopped-flow time scale and rate studies show it to be first order in both hypchlorite and amine–borane. A representative second-order treatment is shown in Figure 2. Values of second-order rate constants are in reasonable agreement with those obtained from "initial rate" studies where the change in optical density with time is followed during the first 4–5% of reaction under conditions of 3–4-fold excess amine–borane (Table II). Such initial rate measurements have been extended to regions of higher pH where, for $Me_3N \cdot BH_3$ and NMMbn, complexities introduced by consecutive reactions make the second-order treatment inapplicable.

Preparative-scale investigations show the reaction to be accompanied by evolution of small amounts of H_2 and to yield amine–monochloroboranes as principal products. With extended reaction times, dichloroborane adducts are obtained. Clearly, the initial reaction, which displays a stoichiometric molar equivalence of hypochlorite to amine–borane, involves monochlorination at boron. Additional B-chlorination processes then occur at successively lower rates.

Monochlorination also displays a pH dependence. The logarithmic profile for $Me_3N \cdot BH_3$ (Figure 3) shows the second-order rate constant to be proportional to hydrogen ion concentration above pH 8, but tending to plateau at higher acidities as pH approaches pK_a for hypochlorous acid (7.53[12]). This suggests HOCl to be the kinetically significant species in the initial attack on amine–borane. A similar pH profile is observed for $Et_3N \cdot BH_3$.

Table III. Rates of Initial Reaction of NaOCl with Amine–Boranes and Amine–Chloroboranes in 12.5% Dioxane–87.5% H_2O (by Volume) at 25 °C[a]

substrate	$10^{-2}k_2$, M^{-1} s^{-1} [b]	"pH"[c]	substrate	$10^{-2}k_2$, M^{-1} s^{-1} [b]	"pH"[c]
$Me_3N \cdot BH_3$	27	8.5	$Me_3N \cdot BH_2Cl$	4.2	8.7
$Me_3N \cdot BH_2Cl$	2.3	6.9	$Me_3N \cdot BHCl_2$	1.3	8.5
	7.0	7.3	$Et_3N \cdot BH_3$	130	8.5
	9.3	7.8	$Et_3N \cdot BH_2Cl$	4.3	8.5
	5.5	8.2	$Qn \cdot BH_3$[d]	110	8.5
	8.7	8.5	$Qn \cdot BH_2Cl$[d]	1.5	8.5

[a] Initial rate measurements. [b] $k_2 = -d[NaOCl]/(dt[NaOCl] \cdot [substrate])$. [c] "pH" denotes reading on pH meter of solution containing 12.5% *p*-dioxane–87.5% H_2O by volume. [d] Qn = $C_7H_{13}N$.

Table IV. pH Dependence of the Reaction of NaOCl with $Me_2NH \cdot BH_3$

Stopped-Flow Spectrophotometric Titration of NaOCl with $Me_2NH \cdot BH_3$ ($\lambda = 292$ nm, $t = 25$ °C, $\mu = 0.1$ M, $[NaOCl]_0 = 1.2 \times 10^{-3}$ M)

pH	mol ratio $[NaOCl]$: $[Me_2NH \cdot BH_3]$	pH	mol ratio $[NaOCl]$: $[Me_2NH \cdot BH_3]$
8.18	3.6	9.13	3.7
8.79	3.7	10.2	3.8

Variation of "Initial Rate" of Monochlorination of $Me_2NH \cdot BH_3$ with pH

pH	$10^{-4}k_2$, M^{-1} s^{-1} [a,b]	pH	$10^{-4}k_2$, M^{-1} s^{-1} [a,b]
8.79	2.5	10.22	0.12
9.13	0.88		

[a] $k_2 = -d[NaOCl]/(dt[NaOCl][Me_2NHBH_3])$. [b] $\log k_2 = -0.9$pH.

Table III presents values of the second-order rate constants, obtained from "initial rate" measurements, for the monochlorination of a series of tertiary amine–boranes as well as for reactions of amine–chloroboranes with NaOCl in solutions containing 12.5% (by volume) *p*-dioxane. The relative independence of the rate of chlorination of $Me_3N \cdot BH_2Cl$ on hydrogen ion concentration is evident. Thus, the biphasic nature of the kinetics of the NaOCl–$Me_3N \cdot BH_3$ reaction at high pH is explained in terms of consecutive chlorination reactions (Scheme I) wherein, as a result of the decrease in rate of (1) with decreasing acidity, $Me_3N \cdot BH_2Cl$ becomes measurably competitive with $Me_3N \cdot BH_3$ for hypochlorite above pH 8.5. Hydrogen evolution is attributed to hydrolytic decomposition of chloroborane–amine adducts, which are known to be less kinetically stable than the parent amine–boranes.[13]

Scheme I

$$Me_3N \cdot BH_3 + HOCl \rightarrow Me_3N \cdot BH_2Cl + H_2O \quad (1)$$

$$Me_3N \cdot BH_2Cl + HOCl\ (OCl^-) \rightarrow Me_3N \cdot BHCl_2 + H_2O\ (OH^-) \quad (2)$$

This pattern of reactivity contrasts with that found in the hypochlorite–morpholine–borane system wherein the observed molar stoichiometry ($[OCl^-]$:[Mbn] = 4:1) has been attributed to a rate-determining oxidative attack of HOCl at a B–H bond of the borane followed by consumption of an additional 2 mol of hypochlorous acid in the oxidation of remaining hydride and a fourth for the chlorination of byproduct morpholine.[1]

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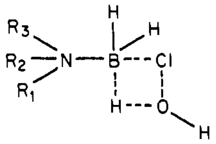
Titration data, the apparent absence of H_2 evolution, and the demonstration of a 3:1 *redox* stoichiometry (*N*-chloromorpholine serves as a two-electron oxidant of I^-) have been interpreted as evidence for essentially quantitative oxidation of all hydridic hydrogen by hypochlorite. Stoichiometric and kinetic studies of the reaction of NaOCl with $Me_iNH\cdot BH_3$ (Table IV) suggest such a pattern of reactivity to be generally characteristic of secondary amine–boranes. The question is raised, then, as to whether tertiary amine–boranes react by a distinctly different pathway from secondary amine–boranes or whether chloroboranes are formed via a single mechanism in both systems, in which case observed stoichiometric and kinetic differences reflect differences in (subsequent) reactivity of tertiary and secondary amine–chloroboranes.

Implication of HOCl as the reagent involved in rate-limiting attack seems to be a common feature in the reactions of both tertiary and secondary amine–boranes. If different mechanisms are involved, then, necessarily, the mode of attack by HOCl on the borane adducts must be different. A speculative model of a (four-center) activated complex leading to the formation of chloroborane–amine is depicted in I and involves an orientation of OH and Cl with respect to a B–H bond *opposite* to what has been suggested for HOCl attack on Mbn.[1] Defense of such a model requires one to accept the notion that when R_1, R_2, or R_3 = H, the favored pathway involves attack by oxygen of the HOCl molecule (rather than chlorine) at boron. This might be considered a reflection of differences in the capacity of N-bonded substituents (alkyl vs. hydrogen) to transmit electron density inductively to the boron center. Alternatively, the presence of an N–H group might permit a hydrogen-bonded interaction with HOCl that would stabilize an activated complex favoring O-atom attack on boron. Subsequent attack on amine–monochloroboranes and amine–dichloroboranes would be expected to occur at progressively slower rates due to the electron-withdrawing influence of boron-bonded chlorine.



I

R_1, R_2, R_3 = alkyl

The alternate view, that chloroboranes are formed in either case, requires acceptance of the premise that, unlike the case with tertiary amine–boranes, successive chlorination of secondary amine–boranes proceeds progressively *faster* as more chlorine is introduced into the coordination sphere of boron. It also requires stepwise chlorination from $R_2NH\cdot BH_3$ through $R_2NH\cdot BCl_3$ to occur quantiatively without hydrolytic loss of hydridic hydrogen, followed by rapid hydrolysis of the amine–trichloroborane to produce free secondary amine, which will be subject to rapid chlorination. Though not disproven, this scheme seems unlikely in view of the reported instability of secondary amine–haloboranes in aqueous media.[14]

Of the two alternatives, we tend to favor that involving separate transition-state configurations. Admittedly, there are disadvantagous features to a scheme that suggests an apparently subtle change from N–H to N-alkyl to cause an alteration in reaction pathway as opposed to a change in the rate of a comparable transformation proceeding by a common pathway. On the other hand, the B–H bond is not inherently highly polarized and it may not be unreasonable to imagine N-alkyl substitution to alter the directional polarization of a transition-state configuration, particularly in view of the well-known changes effected by B-substitution on reaction mechanism in the hydrolysis of amine–boranes[9,10,13,15–18] as well as the effect of N-substitution in establishing the relative importance of acid-independent and acid-dependent pathways for hydrolysis of alkylamine–, arylamine–, and selected heterocyclic amine–boranes.[9,10,18]

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Equilibria and Kinetics of Complexation of Bidentate Ligands with the Macrocyclic Complex $Ni([14]aneN_4)^{2+}$

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The kinetics of reaction of several bidentate ligands X (ethylenediamine, glycinate, oxalate) with planar $Ni([14]aneN_4)^{2+}$ to produce cis octahedral $Ni([14]aneN_4)(X)$ has been examined. Both forward and reverse rate constants have been determined. The forward reaction is first order in nickel complex, independent of [X] over the range 2–40 mM, and first order in $[OH^-]$; the rate law is $k_f = 13[OH^-]$ s^{-1}. The reverse reaction is first order in nickel complex, first order in $[OH^-]$, and inverse first order in [X]; the rate law is $2.6 \times 10^{-2}[OH^-]/[X]$ s^{-1}. A mechanism is proposed for the reaction. In the forward direction, the folding of the macrocycle (base-catalyzed trans → cis isomerization) is rate determining, followed by rapid coordination of the bidentate ligand. In the reverse direction, rapid preequilibrium dissociation of the bidentate ligand is followed by rate-determining cis → trans isomerization. This mechanism is in sharp contrast to a recent study of the reaction of bidentate ligand with the related complex $Ni(trien)^{2+}$. Stability constants for the reaction of X with $Ni([14]aneN_4)^{2+}$ are reported.

Introduction

The kinetic stability of nickel(II) macrocycle complexes is strongly influenced by the macrocycle ring size, with the saturated tetraaza macrocycle $[14]aneN_4$ (1,4,8,11-tetraazacyclotetradecane) providing a complex of remarkable kinetic inertness toward dissociation.[1] Tetradentate macrocyclic ligands exhibit an overriding tendency to coordinate to metal ions in a planar geometry. This is especially true in the case

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(1) Busch, D. H. *Acc. Chem. Res.* **1978**, *11*, 392.

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