

Exact mass for $C_4F_9NO_2S$: calcd, 296.9506; found, 296.9465 \pm 0.0075.

Preparation of $SF_5N=C(Cl)CF_3$. The compound $SF_5NHC(O)CF_3$ (1.89 g, 7.9 mmol) was sublimed onto PCl_5 (2.08 g, 10.0 mmol) in a 100-mL glass reaction cylinder. Several milliliters of CCl_4 was added, and the reaction vessel was frozen and degassed. After warming slowly to room temperature, the mixture was heated at 60–70 °C for 48 h. Infrared analysis of the reaction volatiles revealed that CCl_4 , HCl , $POCl_3$, and a compound believed to be the expected reaction product¹² were present. There was no evidence for unreacted $SF_5NHC(O)CF_3$. Repeated trap-to-trap distillations and placement on $AlCl_3$ to remove any remaining $POCl_3$ ⁴⁵ yielded $SF_5N=C(Cl)CF_3$ (3.8 mmol, 47.8% yield): IR (gas) 1745 (w), 1690 (m), 1285 (m), 1245 (s), 1200 (vs), 973 (s), 910 (vs), 885 (s), 850 (w), 675 (w), 630 (w), 605 (m) cm^{-1} ; mass spectrum (70 eV) m/e (relative intensity) 240, 238 [$M - F$]⁺ (1.0, 4.8), 222 [$M - Cl$]⁺ (2.5), 190, 188 [$M - CF_3$]⁺ (2.5, 6.3), 137, 135 (5.0, 15.6), 127 [SF_5]⁺ (100.0), 102 (12.5), 101 (13.8), 89 (32.5), 69 (41.3).

Preparation of $SF_5N=C(Cl)CH_3$. The amide $SF_5NHC(O)CH_3$ (0.20 g, 1.1 mmol) and PCl_5 (0.42 g, 2.0 mmol) were placed into a 75-mL glass reaction cylinder in an inert-atmosphere box. Carbon tetrachloride ($\sim 1/2$ mL) was added to the reaction cylinder which was then chilled to -196 °C and degassed. The reaction mixture was then warmed to room temperature and heated at 60–70 °C for 48 h. The product was purified by repeated trap-to-trap distillations and by placement on $AlCl_3$ to remove any excess $POCl_3$.⁴⁵ $SF_5N=C(Cl)CH_3$ (0.2 mmol, 18.2% yield): a colorless liquid with 50 torr vapor pressure at room temperature; IR (gas) 1677 (s), 1421 (m), 1330 (m), 1225 (vs), 1133 (m), 998 (s), 904 (vs), 870 (vs), 689 (m), 679 (m), 631 (m), 622 (m), 598 (s) cm^{-1} ; mass spectrum (70 eV) m/e (relative intensity) 203 M^+ (0.2), 202 (0.7), 190, 188 [$M - CH_3$]⁺ (0.6, 1.5), 184 [$M - F$]⁺ (0.5), 168 [$M - Cl$]⁺ (38.4), 127 [SF_5]⁺ (100.0), 89 (22.7), 76 (4.7); ¹H NMR δ 2.60 (s, CH_3).

Preparation of $SF_5N=C(Cl)C(Cl)=NSF_5$. The compound $SF_5NHC(O)C(O)NHSF_5$ (1.70 g, 5 mmol) and PCl_5 (2.08 g, 10.0 mmol) were put into a 75-mL glass reaction cylinder in an inert-atmosphere box. The cylinder was degassed and frozen to -196 °C, and 1–2 mL of CCl_4 were added. After warming to room temperature the mixture was allowed to stand for 24 h before being heated at 90–100 °C for

24 h. At this time the volatile gasses were removed to the vacuum line for separation by trap-to-trap distillation. The product $SF_5N=C(Cl)C(Cl)=NSF_5$ (<25% yield) was collected primarily in a -8 °C trap. IR (gas): 1670 (s), 1140 (m), 99 (m), 915 (vs), 875 (vs), 825 (m), 735 (m), 600 (s) cm^{-1} . Mass spectrum (70 eV) m/e (relative intensity): 343, 341 [$M - Cl$]⁺ (0.3, 0.7), 272, 270, 268 [$M - SF_4$]⁺ (0.9, 2.3, 1.4), 233 (1.4), 197, 195 (0.7, 1.72), 190, 188 [$SF_5N=C(Cl)$]⁺ (5.7, 15.0), 131 (14.5), 127 [SF_5]⁺ (100.0), 108 (1.5), 89 (25.0).

Preparation of $SF_5N=C=NSF_5$. The urea $SF_5NHC(O)NHSF_5$ (3.12 g, 10.0 mmol) and PCl_5 (3.12 g, 15 mmol) were put into a 100-mL glass reaction vessel in an inert-atmosphere box. The cylinder was degassed and frozen to -196 °C and 2 mL of CCl_4 was added. The reaction vessel was warmed slowly to room temperature and heated at 60 °C for ~ 16 h. At this time the volatile reaction products were removed to the vacuum line for trap-to-trap distillation. Even after repeated distillations the product could not be totally separated from the solvent CCl_4 . The resulting solution was light orange in color. IR (gas): 2154 (s), 1839 (m), 1417 (m), 1355 (m), 1300 (w), 1167 (w), 1029 (m), 993 (m), 918 (vs), 883 (s), 805 (vs), 662 (m), 585 (s) cm^{-1} . Mass spectrum (70 eV) m/e (relative intensity): 294 M^+ (2.9), 275 [$M - F$]⁺ (5.8), 230 (1.4), 172 (4.3), 155 (2.2), 153 (2.2), 127 [SF_5]⁺ (100.0), 108 (2.2), 89 (21.7), 64 (8.7), 51 (1.5), 44 (2.9).

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Registry No. $SF_5NHC(O)F$, 80409-40-1; $SF_5NHC(O)CF_3$, 80409-41-2; $SF_5NHC(O)CH_3$, 80409-42-3; $SF_5NHC(O)CH=CH_2$, 80409-43-4; $SF_5NHC(O)CH_2CH_2Cl$, 80409-44-5; $SF_5NHC(O)C(O)NHSF_5$, 80409-45-6; [$SF_5NHC(O)$]₂ CH_2 , 80409-46-7; $SF_5NHC(O)CH_2C(O)OH$, 80409-47-8; [$SF_5NHC(O)CF_2$]₂, 80409-48-9;

$SF_5NC(O)CF_2CF_2C(O)$, 80409-49-0; $SF_5N=C(Cl)CF_3$, 2375-40-8; $SF_5N=C(Cl)CH_3$, 80409-50-3; [$SF_5N=C(Cl)$]₂, 2375-46-4; $SF_5N=C=NSF_5$, 58776-14-0; NSF_3 , 15930-75-3; COF_2 , 353-50-4; HF , 7664-39-3; $CF_3C(O)F$, 354-34-7; $CH_3C(O)Cl$, 75-36-5; SF_5NCO , 2375-30-6; CH_3COOH , 64-19-7; $CH_2=CHCOOH$, 79-10-7; $C-H_2=CHC(O)Cl$, 814-68-6; $ClC(O)C(O)Cl$, 79-37-8; $CH_2(COOH)_2$, 141-82-2; $ClC(O)CF_2CF_2C(O)Cl$, 356-15-0; PCl_5 , 10026-13-8.

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Hypochlorite Oxidation of Morpholine-Borane

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Morpholine-borane reacts with sodium hypochlorite in a 1:4 mole ratio wherein three OCl^- species are utilized for hydride oxidation and a fourth is consumed in the chlorination of morpholine. The determination of kinetic parameters, based upon the stopped-flow spectrophotometric measurement of the rate of disappearance of OCl^- at 290 nm (pH 9–11), is complicated by these consecutive competitive reactions of hypochlorite. At a given pH, the second-order rate constant for the reaction of OCl^- with morpholine is about 10^3 times greater than that for attack of hypochlorite on amine-borane; thus, a reliable determination of the latter constant was based upon "initial rate" studies under pseudo-first-order conditions involving a large stoichiometric excess of morpholine-borane. The rate of reaction of hypochlorite with amine-borane is also first order in hydrogen ion and is subject to a normal substrate isotope effect with $O(CH_2)_4NH \cdot BH_3$ reacting about 1.6 times more rapidly than $O(CH_2)_4NH \cdot BD_3$. At a given lyonium ion concentration, the reaction is enhanced by a factor of about 3.5 in D_2O . It is proposed that the rate-limiting step involves oxidative attack of hypochlorous acid at a boron-hydrogen bond in the amine-borane and that subsequent oxidation of the two remaining hydridic hydrogen atoms is rapid relative to the chlorination of morpholine. The inverse solvent isotope effect is attributed to a higher concentration of $DOCl$ in D_2O relative to that of $HOCl$ in normal water at a given pD (pH), but is likely that this influence is partially offset by a normal secondary isotope effect associated with attack of $HOCl$ ($DOCl$) at the B-H bond. A four-center activated complex involving the elements O, Cl, B, and H that is formally similar to other transition-state configurations proposed for selected reactions of amine-boranes is considered.

The relatively high solubility of morpholine-borane in water¹ and the high level of kinetic stability displayed by its solutions²

have made this reagent an attractive source of hydridic hydrogen for reactions in aqueous media. Studies of the

mechanism of morpholine-borane reduction of selected functional groups in water and mixed aqueous solvents have been reported,³⁻⁵ and the industrial application of morpholine-borane as a reducing agent in aqueous solutions has been demonstrated.^{1,6}

Recently, as part of a study of hemes and related metal porphyrin complexes as models of peroxidase enzymes, we have explored oxyhalide ions such as chlorite, ClO_2^- , as substrates for the oxidation of heme iron(III) to hyperoxidized reaction intermediates, which play an important role in the catalytic activity of the (model) heme systems.⁷ So that the mechanism of oxidation might be elucidated and, specifically, that hypochlorite might be probed as a possible reaction intermediate in the heme/chlorite system, a preliminary study of the reactivity of morpholine-borane with chlorite and hypochlorite was undertaken to determine whether this hydride displays a kinetic selectivity that would enable it to serve as a scavenger for hypochlorite ion. Indeed, under the specific conditions employed, morpholine-borane was found to react only slowly with sodium chlorite but to be oxidized by aqueous hypochlorite solutions at rates appropriate for measurement on a stopped-flow time scale. Such findings coupled with our long-standing interest in amine-borane oxidations prompted us to explore in some detail the kinetics and mechanism of the morpholine-borane/hypochlorite reaction in aqueous solution.

Experimental Section

Materials. Morpholine-borane was obtained from Aldrich in 90% purity or prepared as previously described.^{2,8} After its recrystallization from water, iodometric analysis⁹ showed the product to be of $\geq 99.9\%$ purity. Sodium hypochlorite (Mallinckrodt) was acquired as an alkaline stabilized 5% aqueous solution. Other reagents and buffer materials were of reagent grade quality. Solutions were prepared with water that had been deionized and passed through a Barnstead mixed-bed ion-exchange column. The effluent showed a conductance < 0.01 ppm as NaCl. Morpholine, obtained from Fisher or Matheson Coleman and Bell as a pale yellow liquid, was distilled in vacuo to obtain a colorless distillate for use in kinetic experiments.

Deuterium oxide was obtained from Aldrich Chemical Co. as Gold Label D_2O (isotopic purity $> 99\%$). Carbonate buffer solutions were prepared by dissolving appropriate amounts of Na_2CO_3 and NaHCO_3 in D_2O , and the ionic strengths were adjusted with NaCl. pD values were obtained by adding 0.41 to the pH meter readings observed with each solution.^{10,11} A blue-tip glass electrode was employed to compensate for effects of sodium ion at high pH. A stock solution of 0.075 M morpholine-borane in D_2O was prepared and subsequently used for the preparation of D_2O solutions 6–36 mM in morpholine-borane. Solutions of 0.8 mM NaOCl at pD 9.87, 10.45, and 11.15 were obtained by adding 0.2 mL of stock 0.1 M NaOCl (in NaOH) to 10 mL of the appropriate deuterated buffer and diluting to 25 mL with D_2O . For such solutions, $\geq 99\%$ of contained hydrogen was in the deuterated form. Sodium tetrahydridoborate- d_4 (NaBD_4) was obtained from Thiokol/Ventron (isotopic purity $> 99\%$). Boron trifluoride-diethyl ether complex (Matheson Coleman and Bell) was distilled in vacuo.

Morpholine-borane- d_3 ($\text{O}(\text{CH}_2)_4\text{NH}\cdot\text{BD}_3$) was prepared from NaBD_4 and $\text{BF}_3\cdot\text{Et}_2\text{O}$ via a previously reported method for the syn-

thesis of amine-boranes.⁸ Recrystallization from water gave a white crystalline product of purity $> 99.9\%$ determined through iodometry. Recrystallization from D_2O gave *N*-deuteriomorpholine-borane- d_3 ($\text{O}(\text{CH}_2)_4\text{ND}\cdot\text{BD}_3$) evidenced by the absence of absorption in the N-H stretching region of the infrared spectrum (KBr wafer) and the prevalence of a band at 2350 cm^{-1} attributed to $\nu_{\text{N-D}}$. The assignment of this band to an N-D stretching mode (rather than $\nu_{\text{B-H}}$) was confirmed through its disappearance and the appearance of a band at $3180\text{--}3195\text{ cm}^{-1}$ ($\nu_{\text{N-H}}$) upon recrystallization from H_2O . Strong absorption in the B-D stretching region ($\sim 1775\text{ cm}^{-1}$) was prevalent in both adducts. The ^{11}B NMR spectrum of *N*-deuteriomorpholine-borane- d_3 in D_2O showed a clean singlet, characteristic of amine- BD_3 adducts, 16–17 ppm on the high-field side of $\text{BF}_3\cdot\text{Et}_2\text{O}$ (external standard).

Methods. Conventional visible and UV spectra were obtained with either a Gilford Model 250 or a Beckman UV 5230 spectrophotometer. Beckman IR 4250 and IR 33 spectrophotometers were used for infrared studies. pH determinations were obtained with use of a Corning Model 130 digital pH meter. Stoichiometric and kinetic studies were carried out with a Durrum D-110 stopped-flow spectrophotometer (Kel-F syringes) in conjunction with a Tektronix oscilloscope. In a typical stopped-flow experiment, the absorbance decrease at 290 nm, corresponding to the disappearance of hypochlorite ion, was measured following the stopped-flow mixing of solutions of morpholine-borane, or morpholine, with buffered solutions of NaOCl. Reaction mixtures contained a total carbonate concentration ($[\text{HCO}_3^-] + [\text{CO}_3^{2-}]$) of 35 mM and ionic strength $\mu = 0.1\text{ M}$ (adjusted with NaCl). In all cases pH > 9 was maintained to prevent the spontaneous decomposition of NaOCl within the time of the stopped-flow measurement. Sodium hypochlorite solutions containing about 10 mM NaOCl were obtained by dilution of a stock 0.13 M solution of NaOCl in NaOH. These were further diluted with carbonate buffer to give solutions of appropriate NaOCl content for stopped-flow experiments. Typical concentration ranges were 0.16–20 mM NaOCl and 1.5–50 mM morpholine-borane.

The determination of reaction stoichiometry involved a stopped-flow spectrophotometric "titration" of NaOCl with morpholine-borane. The spectrophotometer was calibrated by establishing an initial (reference) absorbance at 290 nm with a solution obtained via the stopped-flow mixing of a solution of 1.2 mM NaOCl in carbonate buffer with an equal volume of water. Samples of the NaOCl solution were then mixed with equal volumes of solutions containing different amounts of morpholine-borane, and the difference between initial and final absorbance levels ($\Delta A = A_0 - A_\infty$) was determined as a function of the morpholine-borane concentration. The same experimental mixing technique was employed in kinetic studies to obtain the time dependence of ΔA .

The morpholine-borane/hypochlorite system was also subjected to iodometric analysis to determine the redox equivalency of reactants. In one series of experiments, measured quantities of amine-borane were mixed with a stoichiometric excess of NaOCl. After completion of the reaction (several seconds), each solution was treated with KI and acidified with H_2SO_4 to liberate a quantity of I_2 equivalent to the amount of excess oxidant. This was then titrated with standard (0.01 N) $\text{Na}_2\text{S}_2\text{O}_3$. In a second series, reactions were carried out in the presence of excess morpholine-borane. The concentration of unreacted borane remaining in each solution was determined iodometrically by using a known excess of standard KIO_3 and titrating with $\text{Na}_2\text{S}_2\text{O}_3$ in the presence of acidified KI to an amylose starch end point.⁹

All studies of substrate isotope effects were carried out by consecutively measuring rates of reaction of hypochlorite with morpholine-borane and morpholine-borane- d_3 . Consecutive measurements were also carried out in H_2O and D_2O to establish the solvent isotope effect. For studies with D_2O , small amounts of solvent were used to rinse the drive syringes between kinetic runs.

$\text{p}K_a$ values for HOCl and DOCl were determined spectrophotometrically. Seven buffered solutions each containing a stoichiometric concentration of all hypochlorite species $[\text{HOCl}]_0 = [\text{HOCl}] + [\text{OCl}^-] = 0.8\text{ mM}$ were prepared, one (using acetic acid-acetate buffer) at pH 3, another at pH 10.6, and five in the region pH 7.0–8.1. In all cases, the total buffer concentration was 33 mM and the ionic strength (μ) 0.1 M. Immediately after the preparation of each solution, its ultraviolet spectrum was recorded and shown by repetitive scans to be reproducible, indicating no significant decomposition of hypochlorite during the absorbance measurement. Values of the extinction

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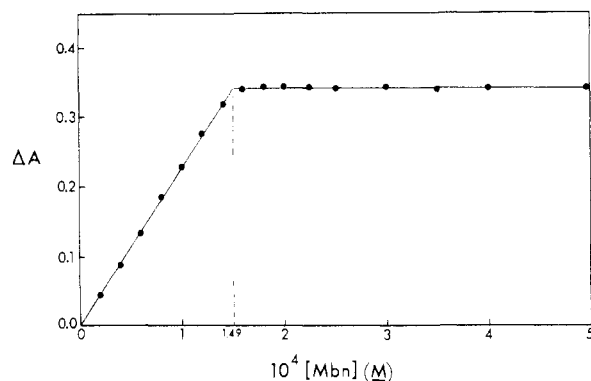


Figure 1. Stopped-flow spectrophotometric titration of NaOCl with morpholine-borane (Mbn) at pH 9.27, $\lambda = 290$ nm, $t = 25$ °C, $[\text{NaOCl}]_0 = 0.6$ mM: $[\text{NaOCl}]/[\text{Mbn}] = 4.02$. Comparable ratios are obtained at pH 10.0 (3.87) and pH 10.98 (4.03).

Table I. Iodometric Analysis of Morpholine-Borane/NaOCl Reaction Mixtures at $[\text{NaOCl}]_0^a = 4.1 \times 10^{-3}$ M and $t = 25$ °C

$10^3 \times [\text{Mbn}]_0, ^a$ M	$10^3 \times [\text{I}_2], \text{M}$	10^3 [excess reagent], M	$[\text{NaOCl}]/[\text{Mbn}]^b$
1.50	0.300 ^c	0.100 ^d	2.93
2.00	1.80 ^c	0.600 ^d	2.93
2.75	4.20 ^c	1.40 ^d	3.04
0.250	3.36 ^e	3.36 ^f	2.96
0.500	2.63 ^e	2.63 ^f	2.95
0.750	1.91 ^e	1.91 ^f	2.92
1.00	1.26 ^e	1.26 ^f	2.85

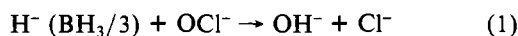
^a Initial concentrations. ^b Redox mole ratio. ^c I_2 consumed according to $\text{O}(\text{CH}_2)_4\text{NH}\cdot\text{BH}_3 + 3\text{I}_2 + 3\text{H}_2\text{O} \rightarrow \text{O}(\text{CH}_2)_4\text{NH} + \text{B}(\text{OH})_3 + 6\text{H}^+ + 6\text{I}^-$. ^d Mbn in excess. ^e I_2 produced according to $2\text{I}^- + \text{OCl}^- + \text{H}_2\text{O} \rightarrow \text{I}_2 + \text{Cl}^- + 2\text{OH}^-$. ^f OCl^- in excess.

coefficients ϵ_{HOCl} and ϵ_{OCl^-} at 290 nm were calculated from measured absorbances at pH 3 and 10.6, respectively. Absorbance readings in the region pH 7.0–8.1 established the observed extinction coefficient, ϵ_0 , where, for a 1-cm cell path, $A = \epsilon_0[\text{HOCl}]_0$.¹²

For the determination of the extent of exchange of boron-bonded hydrogen in morpholine-borane with solvent under the reaction conditions employed in kinetic studies, a 0.2-g sample of morpholine-borane was dissolved in 25 mL of D_2O and the solution allowed to stand at 25 °C for 4 h. Solvent was removed by rotary evaporation and the residue allowed to stand over Drierite for several days. A second sample was dissolved in and subsequently recovered from 25 mL of deuterated carbonate buffer at pH 9.5. Infrared spectra were obtained with each sample (KBr wafers).

Results

Reaction Stoichiometry. A stopped-flow spectrophotometric "titration" curve for the reaction of sodium hypochlorite with morpholine-borane (Mbn) at pH 9.27 is shown in Figure 1. The 4:1 molar equivalency ratio, $[\text{NaOCl}]:[\text{Mbn}]$, is independent of pH over nearly a 100-fold change in $[\text{H}^+]$. Iodometric analysis of the redox stoichiometry, on the other hand, yields a $[\text{NaOCl}]:[\text{Mbn}]$ ratio of 3:1 (Table I) as expected for reaction of the six-electron equivalent borane with a two-electron oxidant in accordance with (1). This difference



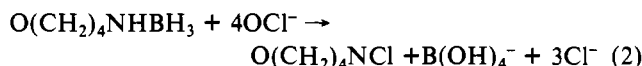
between molecular stoichiometry and iodometric equivalence results from the fact that whereas three hypochlorite ions are required per molecule of morpholine-borane for oxidation of hydridic hydrogen, a fourth is consumed in chlorination of (byproduct) morpholine to *N*-chloromorpholine, which serves as a two-electron oxidant of I^- to I_2 .¹³ The clarity of the

Table II. Morpholine-Borane Concentration Dependence of "Initial Rate" at pH 10.08, $t = 25$ °C, and $\mu = 0.1$ M

$10^3 \times [\text{NaOCl}], \text{M}$	$10^3 \times [\text{Mbn}], \text{M}$	$-\text{d}A/\text{d}t, ^a$ s ⁻¹	$-10^4 \text{d}[\text{NaOCl}]/\text{d}t, \text{M s}^{-1}$	$k, ^b$ M ⁻¹ s ⁻¹	
0.160	1.5	0.062	1.08	450 ^c	
	3.0	0.116	2.02	421 ^c	
	6.0	0.171	2.98	310 ^c	
	10	0.250	4.36	273	
	20	0.502	8.75	273	
	30	0.823	14.3	298	
	40	0.924	16.1	252	
	50	1.28	22.3	279	
	0.535	6	0.721	12.6	393 ^c
		10	1.01	17.6	329 ^c
20		1.69	29.4	275	
30		2.17	37.8	236	
40		2.99	52.1	243	
1.97	50	3.98	69.3	259	
	10	4.49	78.2	397 ^c	
	20	7.40	129	327 ^c	
	30	9.74	170	288	
	40	13.2	230	292	
	50	15.5	270	274	

^a $-\lim_{\Delta t \rightarrow 0} \Delta A/\Delta t$. ^b $k \equiv -\text{d}[\text{NaOCl}]/(\text{d}t[\text{NaOCl}][\text{Mbn}])$.
^c Values discarded.

spectrophotometric titration indicates quantitative hypochlorite oxidation of hydride without significant loss via hydrolysis consistent with the overall stoichiometry depicted in (2).



Reaction Kinetics. Stopped-flow studies show the reaction of morpholine-borane with NaOCl to be complex. With morpholine-borane in 10–500-fold excess, the early stages of reaction are, as expected, accompanied by a decrease in optical density at 290 nm corresponding to disappearance of OCl^- ; however, after a few milliseconds, a pronounced increase in the rate of absorbance change is observed, and the nonlinearity of a plot of $\log [\text{OCl}^-]$ vs. time shows an overall first-order treatment of the system to be unjustified. A more satisfactory treatment is found in an examination of "initial rates" of reaction, i.e., the rates of change in optical density in the early stages of reaction corresponding to <5% consumption of NaOCl.

Since the reaction is quantitative in the presence of excess morpholine-borane, the hypochlorite extinction may be calculated from the total absorbance changes that occur upon reaction of different amounts of NaOCl, enabling a given rate of change in absorbance to be translated directly into a rate of change of hypochlorite concentration. In Table II, such "initial-rate" data at pH 10.05 are presented for reactions at three different initial NaOCl concentrations in the presence of different amounts of a stoichiometric excess of morpholine-borane. The Mbn concentration dependence is more apparent in Figure 2, where lines have been drawn to include the origin for each set of data. It is important to note and is most easily seen in data at the higher initial NaOCl concentrations that points obtained at the lower morpholine-borane concentrations invariably lie above the respective lines. Alternatively, it would appear that each set of data provides a reasonably linear relationship with a nonzero intercept; however, this implies a residual rate at zero morpholine-borane concentration, which is conceptually unreasonable. Samples of NaOCl mixed in the stopped-flow apparatus with water containing no morpholine-borane are sufficiently kinetically stable to exclude the possibility of significant spontaneous

(12) Since $\epsilon_0[\text{HOCl}]_0 = \epsilon_{\text{HOCl}}[\text{HOCl}] + \epsilon_{\text{OCl}^-}[\text{OCl}^-]$ and $[\text{HOCl}]_0 = [\text{HOCl}] + [\text{OCl}^-]$, it follows that $(\epsilon_0 - \epsilon_{\text{HOCl}})/(\epsilon_{\text{OCl}^-} - \epsilon_0) = [\text{OCl}^-]/[\text{HOCl}] = K_a/[\text{H}^+]$. Thus, a plot of $(\epsilon_0 - \epsilon_{\text{HOCl}})/(\epsilon_{\text{OCl}^-} - \epsilon_0)$ vs. $1/[\text{H}^+]$ is linear with zero intercept and slope = K_a .

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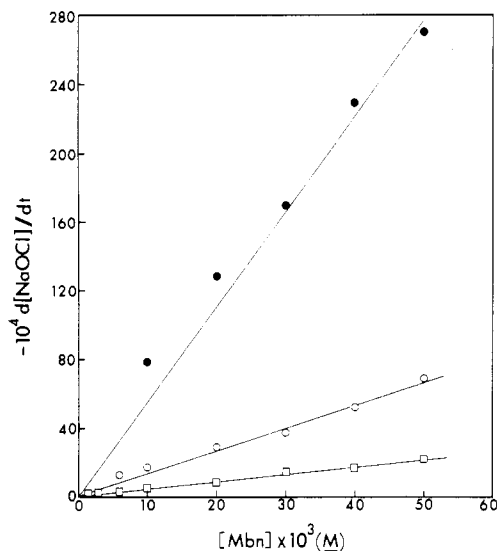


Figure 2. Variation of the "initial rate" of disappearance of NaOCl with initial morpholine-borane concentration at pH 10.05 and $t = 25^\circ\text{C}$. $[\text{NaOCl}]_0$: (\square) 0.16 mM; (\circ) 0.535 mM; (\bullet) 1.97 mM.

Table III. pH Dependence of the Second-Order Rate Constant ($\text{Mbn} + \text{NaOCl}$) at $t = 25^\circ\text{C}$

pH	k_2^a $\text{M}^{-1} \text{s}^{-1}$	pH	k_2^a $\text{M}^{-1} \text{s}^{-1}$
8.92	5030	10.32	145
9.27	1560	10.57	94
9.68	395	10.98	32
10.05	272		

$$^a k \equiv -d[\text{NaOCl}]/(dt[\text{NaOCl}][\text{Mbn}]).$$

decomposition of NaOCl. In addition, absorbance traces obtained in "initial-rate" studies show reasonable agreement between observed and calculated initial NaOCl concentrations. This observation, together with an integral (4:1) stoichiometric relationship, precludes the possibility of hypochlorite being rapidly scavenged by an oxidizable impurity in the amine-borane.

As will be seen in the discussion to follow, points at lower morpholine-borane concentrations reflect limitations in the usefulness of "initial-rate" measurements and are to be discarded. It is evident from data obtained at higher morpholine-borane concentrations that the initial rate of disappearance of NaOCl is first-order in hypochlorite and first-order in morpholine-borane. Second-order rate constants calculated under these conditions are given in Table II, and their pH dependence is shown in Table III. The reaction is first-order in hydrogen ion concentration ($\log k$ vs. pH is linear with slope = -1.01 ; correlation coefficient = 0.99).

Morpholine/NaOCl. The stopped-flow "titration" of NaOCl with morpholine, carried out as described for the morpholine-borane/NaOCl system, yields a molar equivalency $[\text{NaOCl}]/[\text{O}(\text{CH}_2)_4\text{NH}] = 1.01$ (1.02 at pH 9.27; 0.97 at pH 10.05; 1.00 at pH 10.98). In the presence of excess morpholine and at initial NaOCl concentrations sufficiently high to give conveniently measurable changes in absorbance ($\epsilon_{\text{NaOCl}} = 290$; $\lambda_{\text{max}} = 290 \text{ nm}$), the reaction was too fast for a conventional pseudo-first-order kinetic treatment. It also proved to be too rapid for a study of "initial rates" inasmuch as the initial absorbance changes were lost in the mixing process. For this reason, a second-order analysis was employed, a typical study being depicted in Figure 3. Results obtained for different buffered solutions each containing a given initial NaOCl concentration but with varying amounts of morpholine are shown in Table IV. At a given pH, the observed second-order rate constant is over three orders of magnitude greater than

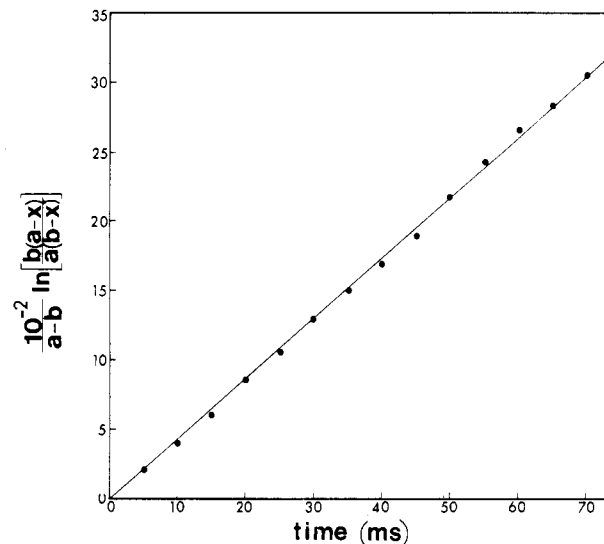


Figure 3. Second-order treatment of the morpholine/sodium hypochlorite reaction: $a = [\text{morpholine}]_0 = 0.1 \text{ mM}$; $b = [\text{NaOCl}]_0 = 0.6 \text{ mM}$; $x =$ concentration of reactant consumed; pH 10.98; $t = 25^\circ\text{C}$; $\mu = 0.1 \text{ M}$.

Table IV. pH Dependence of the Rate of Reaction of Morpholine with NaOCl at $[\text{NaOCl}]_0 = 6 \times 10^{-4} \text{ M}$ and $t = 25^\circ\text{C}$

$10^3 [\text{morpholine}]_0, \text{ M}$	$10^{-4} k_2, \text{ M}^{-1} \text{s}^{-1}$		
	pH 10.30	pH 10.98	pH 11.20
0.1	14.0	4.43	3.28
0.2	15.1	4.11	3.45
0.3	14.6	4.04	3.41
0.4	12.6	4.00	3.20
0.5	12.6	3.85	3.14
0.6	13.2	3.94	3.63
0.8	13.7	4.09	3.47
av	13.7 ± 1	4.07 ± 0.2	3.37 ± 0.2

Table V. Substrate Isotope Effect for Reaction of Morpholine-Borane with NaOCl at $t = 25^\circ\text{C}$ and $\mu = 0.1 \text{ M}$

pH	k_{H} $\text{M}^{-1} \text{s}^{-1} \text{ } ^a$	k_{D} $\text{M}^{-1} \text{s}^{-1} \text{ } ^b$	$k_{\text{H}}/k_{\text{D}}$
10.86	40	25.3	1.58
10.29	143	91	1.57
9.82	396	257	1.54
9.25	1600	1080	1.48

$$^a -d[\text{NaOCl}]/(dt[\text{O}(\text{CH}_2)_4\text{NH}\cdot\text{BH}_3]), \quad ^b -d[\text{NaOCl}]/(dt[\text{O}(\text{CH}_2)_4\text{NH}\cdot\text{BD}_3]).$$

the corresponding second-order constant obtained in the morpholine-borane/NaOCl system. Even at the lower morpholine concentrations employed for second-order analysis, the reaction was too fast for accurate measurement by the stopped-flow method below pH 10.

Isotope Effects. The effect of deuterium substitution at boron in retarding the rate of hypochlorite oxidation of morpholine-borane is shown in Table V. Identical rates of reaction were observed with $\text{O}(\text{CH}_2)_4\text{NH}\cdot\text{BD}_3$ and $\text{O}(\text{C}-\text{H}_2)_4\text{ND}\cdot\text{BD}_3$, but this is expected in view of the rapid exchange of nitrogen-bonded hydrogen with solvent. By contrast, boron-bonded hydrogen exchange is negligible in water or carbonate buffer at pH 9.5 over periods that are long in comparison to the time required for solution preparation and kinetic analysis. Thus, morpholine-borane, recovered from each solution after 4 h of exposure, displayed its original strong absorbance in the B-H stretching region ($2300\text{--}2400 \text{ cm}^{-1}$) and negligible absorption in the B-D region ($\sim 1600\text{--}1800 \text{ cm}^{-1}$). A pronounced *inverse* solvent isotope effect is shown in Table VI and Figure 4, where, for a given lyonium ion

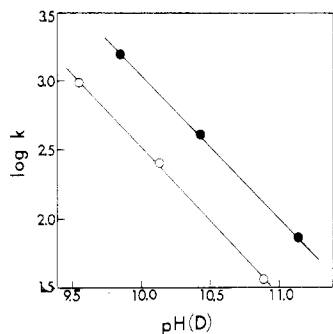


Figure 4. pH dependence of the solvent isotope effect in the reaction of morpholine–borane with NaOCl at $t = 25^\circ\text{C}$ and $\mu = 0.1\text{ M}$: (O) pH (H_2O); (●) pD (D_2O). $k \equiv -d[\text{NaOCl}]/(dt[\text{Mbn}][\text{NaOCl}])$.

Table VI. Solvent Isotope Effect for Reaction of Morpholine–Borane with NaOCl at $t = 25^\circ\text{C}$ and $\mu = 0.1\text{ M}$

pH	$k_{\text{H}_2\text{O}},^a \text{ s}^{-1}$	pD	$k_{\text{D}_2\text{O}},^a \text{ s}^{-1}$
9.56	990	9.87	1600
10.13	255	10.45	416
10.88	40.8	11.15	73.6

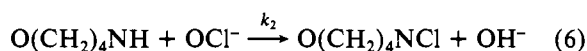
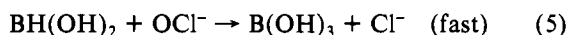
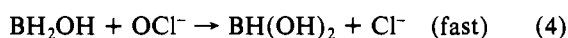
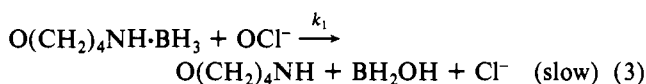
$$^a k \equiv -d[\text{NaOCl}]/(dt[\text{O}(\text{CH}_2)_4\text{NH}\cdot\text{BH}_3]).$$

concentration, or given pH(D), the observed second-order rate constant is seen to be enhanced by a factor of ~ 3.4 in D_2O . Spectrophotometric studies of acid dissociation constants for normal and deuterated hypochlorous acid gave $\text{p}K_a(\text{HOCl}) = 7.47$ (lit.¹⁴ 7.53) and $\text{p}K_a(\text{DOCl}) = 8.21$.

Discussion

Kinetic complexities in the system arise from competitive reactions involving hypochlorite oxidation of morpholine–borane and the subsequent chlorination of morpholine. The system is further complicated by the fact that 3 mol of hypochlorite is consumed in the oxidation of hydride in the amine–borane. For the moment we shall adopt the model given in Scheme I for the stoichiometric mechanism, temporarily postponing consideration of the hydrogen ion dependence.

Scheme I



Since loss of hypochlorite is slowest in the initial stages of reaction, it seems clear that attack of oxidant on amine–borane is rate limiting. The presumption that (3) is accompanied by oxidation of the first of three available hydridic hydrogens is supported by the substrate isotope effect (discussed below). That it is accompanied by B–N bond cleavage is conjectural as is the representation here, and in (4) and (5), of specific hydroxyborane species. Although hydrated and hydroxylated boranes have been proposed to be formed in the low-temperature solvolysis of diborane¹⁵ and as short-lived intermediates in the hydrolytic decomposition of amine–boranes at room temperature,² whether or not such species occur here free from the influence of the amine nitrogen is unknown and, in

fact, somewhat irrelevant. What is important is the supposition of rapid oxidation of the two remaining hydridic hydrogen atoms after rate-limiting oxidation of the first. This would appear to be a valid assumption. It is expected that hydride-containing reaction intermediates would be susceptible to rapid hydrolysis (those produced via amine–borane hydrolysis are known to be highly unstable kinetically²). The fact that all hydride is oxidized by hypochlorite to the exclusion of hydrolysis suggests that, whatever their formulation, residual hydride species formed by, and subsequent to, the rate-limiting attack on amine–borane will undergo rapid reaction with hypochlorite.

The determination of k_2 is based upon independent measurement. Although this step is fast relative to (3), for working purposes we consider it to be slow relative to (4) and (5); i.e., one morpholine–borane molecule consumes three formula units of hypochlorite prior to the chlorination of morpholine. Since $-d[\text{Mbn}]/dt = 1/3(-d[\text{NaOCl}]/dt)$, second-order rate constants given in Table I must be divided by 3 to obtain corresponding values of k_1 . Thus, at a given pH, k_2/k_1 will be on the order of 3×10^3 . Clearly, competition between morpholine and its precursor borane adduct for hypochlorite must be considered in any effort to evaluate k_1 through measurement of the rate of loss of hypochlorite. Indeed, “initial-rate” measurements described here are meaningful in the determination of k_1 only in studies where concentrations of morpholine–borane are very large relative to that of OCl^- . For example, in accord with Scheme I, for an original morpholine–borane:hypochlorite concentration ratio of 10:1, the molar quantity of morpholine produced on reaction of 1% of the available hypochlorite would be about 3×10^{-4} times that of the existing morpholine–borane. Since k_1/k_2 is in approximately the same ratio, this quantity of morpholine, if allowed to accumulate, would be sufficient to permit the free base to compete about equally with morpholine–borane for remaining hypochlorite. Similarly, for an initial $[\text{Mbn}]/[\text{NaOCl}]$ ratio of 100:1, morpholine would be 10% as effective as morpholine–borane in competition for hypochlorite. It is clear, therefore, that k_1 values derived from “apparent” second-order rate constants obtained from initial rate studies at the lower morpholine–borane concentrations will be too high due to a measurable contribution of (6) and that reliable measurements of k_1 derive from data at the higher morpholine–borane concentrations as shown in Table II and in Figure 2 from slopes of lines drawn to include the origin.

Although eq 3–6 are useful in a preliminary consideration of stoichiometric mechanism, Scheme I does not accommodate the observed pH dependence of k . The fact that the initial rate is first-order in $[\text{H}^+]$ suggests the possibility of hypochlorous acid serving as the kinetically significant form of the oxidant. The normal substrate isotope effect implies stretching of a boron–hydrogen bond in the activated complex, whereas the inverse solvent isotope effect may best be considered in the light of the relative acidities of HOCl and DOCl in H_2O and D_2O , respectively.¹⁶ Relative $\text{p}K_a$ values show that at a given pH(D), the DOCl concentration in D_2O will be greater than that of HOCl in normal water by a factor of about 5.5. Although an inverse solvent isotope effect is observed with respect to morpholine–borane oxidation, the rate in D_2O is greater by a factor of only 3.5. Thus, for attack on amine–borane by conjugate acid, HOCl should react faster than DOCl by a factor of about 1.6; the corresponding second-order rate constants being $k \approx 1.15 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for HOCl and

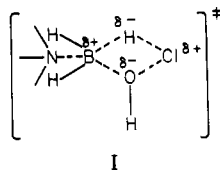
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(16) A preequilibrium protonation of substrate by solvated hydrogen ion or its deuterium analogue also would be consistent with an inverse solvent isotope effect; however, since this would require formation of a species containing five-coordinate boron or nitrogen, we consider it to be a less attractive alternative.

$k \approx 7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for DOCl.

An intimate mechanism based upon these effects with HOCl substituted for OCl⁻ in Scheme I involves bimolecular attack of hypochlorous acid at the boron-hydrogen bond of the amine-borane. A four-center activated complex is suggested in I, wherein dashed lines depict energetically, and therefore

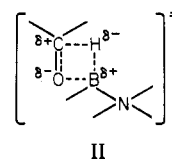


kinetically, significant processes of bond formation and cleavage and where original and incipient bond dipoles are denoted. Collapse of I in aqueous media would lead to the formation of morpholine, BH₂OH (solvated), and chloride ion and the regeneration of H₃O⁺ with rapid establishment of appropriate acid-base equilibria.

The normal substrate isotope effect is interpreted then as a primary effect associated with stretching of the B-H bond in the activated complex. It is in line with the relatively small boron-hydrogen isotope effects reported for other borane reactions thought to proceed via rate-limiting B-H cleavage processes, e.g., the solvolysis of substituted aryl pyridine-boranes.¹⁷⁻¹⁹ As noted above, the inverse solvent isotope effect is considered to be a result simply of a lower concentration of HOCl, relative to DOCl, at comparable concentrations of lyonium ion. For reaction with molecular hypochlorous acid, therefore, the effect is normal and considered to be a secondary effect arising through perturbation of the bonding to oxygen, i.e., cleavage of the O-Cl linkage and formation of an O-B bond. Thus, in amine-borane oxidation, as in the chlorination

of morpholine and other amines by hypochlorite,²⁰ chlorine serves as an electrophilic center reacting formally as Cl⁺ (as suggested by a consideration of assigned oxidation states in HOCl).

It may be worth noting that, with respect to the distribution of bond dipoles, I is formally similar to certain four-center activated complexes that have been proposed for other boron hydride reactions, one of which involves addition of the elements of B and H across the carbonyl group in the amine-borane reduction of selected aldehydes and ketones (II).⁵



Although the rate of the hypochlorite chlorination of morpholine is enhanced with increasing hydrogen ion concentration, mechanistic details of this reaction have not been explored here. It is anticipated that further insight into hypochlorite and other oxyhalide oxidations of amine-boranes may be obtained through studies on borane adducts of tertiary amines wherein complications of amine chlorination are minimized or avoided. An extension to various substituted amine-borane adducts in an effort to elucidate specific substituent effects should also prove worthwhile.

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Registry No. O(CH₂)₄NH·BH₃, 4856-95-5; O(CH₂)₄NH·BD₃, 80584-36-7; O(CH₂)₄ND·BD₃, 80584-37-8; O(CH₂)₄NH, 110-91-8; NaOCl, 7681-52-9.

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Synthesis, Characterization, and Some Reactions of Bis(tri-*tert*-butylarsine)hydridoplatinum(II) Complexes

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The complex *trans*-PtH₂(As(*t*-Bu)₃)₂ (**1**), which is the first dihydridoplatinum(II) complex not containing any phosphorus donor ligands, has been prepared from a facile reaction of As(*t*-Bu)₃ with K₂PtCl₄. Treatment of **1** with protic acids HX (X = Cl, Br, or CF₃CO₂) affords the monohydrido complexes PtHX(As(*t*-Bu)₃)₂ (**2**, X = Cl; **3**, X = Br; **5**, X = CF₃CO₂). A similar reaction with HI gives the dinuclear complex *trans*-Pt₂I₂(μ-I)₂(As(*t*-Bu)₃)₂ (**6**) instead of the expected PtHI(As(*t*-Bu)₃)₂ (**4**). Complex **4** is prepared from the reaction of **1** with I₂. Complex **1** also reacts readily with CO to give a tetranuclear cluster, Pt₄(CO)₅(As(*t*-Bu)₃)₄ (**7**). Carbon monoxide reacts with **2** and displaces the chloride, but the reaction is reversible; isolable cationic complexes *trans*-[PtH(CO)(As(*t*-Bu)₃)₂]X (**8**) (X = BF₄ or PF₆) are formed when the reaction is carried out in the presence of LiBF₄ or LiPF₆. Treatment of **2** with 1 molar equiv of AgPF₆ in methanol affords the cationic complex *trans*-[PtH(MeOH)(As(*t*-Bu)₃)₂]PF₆ (**9**); presence of moisture in the reaction mixture results in the formation of the aqua complex *trans*-[PtH(H₂O)(As(*t*-Bu)₃)₂]PF₆ (**10**). Complexes **9** and **10** react readily with CO to give **8** and with CH₃CN to give *trans*-[PtH(CH₃CN)(As(*t*-Bu)₃)₂]X (**11**). Addition of 1 molar equiv of P(*t*-Bu)₃ to **2** gives a mixture of *trans*-PtHCl(As(*t*-Bu)₃)(P(*t*-Bu)₃) (**12**), *trans*-PtHCl(P(*t*-Bu)₃)₂, and unreacted **2**. The infrared and ¹H NMR spectral parameters for the dihydride as well as the monohydrides are discussed.

Introduction

Following the discovery of the first stable hydridoplatinum(II) complex,² *trans*-PtHCl(PEt₃)₂, there has been

rapid development in the chemistry of transition-metal hydrides.³⁻¹⁰ Undoubtedly, much of the interest in these com-

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