Inorg. Chem. **1996,** *35,* 7225−7228 **7225**

Acid-Catalyzed Amine−Borane Reduction of Nitrite

Kevin E. Bell[†] **and Henry C. Kelly***

Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

Received February 9, 1996[⊗]

The rate of reduction of nitrite by trimethylamine−borane was followed by observing the decrease in nitrite absorbance under pseudo-first-order conditions. The reaction is acid-catalyzed and exhibits a first-order dependence on both amine−borane and total nitrite concentration. The molar equivalence of $NaNO_2$ to $(CH_3)_3NBH_3 = 2:1$. Equimolar amounts of hydrogen and nitrous oxide are formed, and the molar ratio of nitrite reacted to N_2O produced is 2:1. In concentrated HCl or H_2SO_4, a correlation of rate with the Hammett acidity function, h_o, is observed. The reaction is subject to a pronounced *inverse* solvent isotope effect ($k_{D_2O}/k_{H_2O} \simeq 2.7$) and a modest *normal* substrate effect ($k_{(CH_3)_3N\cdot BH_3}/k_{(CH_3)_3N\cdot BD_3} \simeq 1.4$). The reaction is first-order in H_3O^+ in the region pH 0.7−2.7, but a second-order dependence is observed above pH 4 with the transition occurring at pH $\simeq$ pK_a for HNO_2. Results are consistent with a mechanistic model involving preequilibration protonation of molecular nitrous acid followed by rate-limiting hydride attack on H_2ONO^+ or free NO^+ to produce nitrosyl hydride as a reactive intermediate.

Introduction

Previous studies have revealed a high sensitivity of the kinetic stability of amine−boranes to changes in structure. Indeed, substitution in the coordination spheres of nitrogen and/or boron in compounds of the type $R_nNH_{3-n}{\cdot}BH_yX_{3-y}$, where R may be an alkyl, aryl, or heterocyclic group, *n* and *y* have possible values of 0, 1, 2, and 3, and X represents a hydride, halide, cyanide, or azide ligand, has been shown to have profound effects on both the rate and mechanism of hydride oxidation.[1−15] In addition, recent studies have shown differences in the *stoichiometry* of reaction of BH_3 adducts of secondary and tertiary amines with hypochlorous acid wherein secondary amine−boranes are found to undergo hydride oxidation and tertiary amine−boranes to be subject to B-chlorination.[16−18]

The effectiveness of amine−boranes as hydridic reducing agents in hydrolytic solvents is necessarily dependent on their hydrolytic stability. A dominant pathway for amine−borane hydrolysis has been shown to involve acid catalysis.[2,5] Since nonaromatic tertiary amine−BH_3 adducts display relatively high kinetic stability in aqueous solution, they have been widely employed in synthesis as well as for the study of mechanisms of selected redox reactions in acidic media. Trimethylamine−borane has proven particularly suitable for such investigations, which include previously reported studies of borane reactivity with oxyanions and the present investigation of the acid-catalyzed amine−borane reduction of nitrite ion.

Experimental Section

Materials and Methods. Trimethylamine−borane (99%), sodium nitrite (97%), deuterium oxide (99.9% D), sodium tetrahydroborate (98%), sodium tetradeuterioborate (98% D), tetrahydrofuran (99%), 1,4-dioxane (99+%), sodium, benzophenone, and 95+% calcium hydride were obtained from Aldrich Chemical Co. Lithium tetrahydroaluminate was obtained as a 47.2% protected oil dispersion from Johnson Matthey Electronics.

Trimethylamine−borane was sublimed *in vacuo* and $NaNO_2$ was dried several hours *in vacuo* prior to use. Tetrahydrofuran was refluxed under an N_2 atmosphere over CaH_2 for several hours. After decantation, the solvent was boiled under reflux with a mixture of sodium and benzophenone, again under N_2, until a deep blue color appeared, indicating an O_2-free solution. It was then collected by distillation. 1,4-Dioxane was refluxed with aqueous HCl (ca. 20 mL of 12 M HCl/dm^3 of solvent) for several hours to hydrolyze trace quantities of acetals and ketals. The cooled solution was then heated with KOH pellets (ca. 20g of KOH/dm^3 of solution) as a preliminary drying step. After cooling and decantation, the dioxane was refluxed and fractionally distilled under an N_2 atmosphere from a CaH_2 slurry or an $LiAlH_4$ solution.

Inorganic salts used for the preparation of buffers, for analyses, and for adjustments of the ionic strengths of solutions were obtained as reagent grade materials from Mallinckrodt, Fisher Scientific Co., J. T. Baker Chemical Co., and/or Aldrich Chemical Co. Vitex starch was obtained from GFS Chemicals. Stock solutions of HCl and H_2SO_4 were prepared by dilution of the respective concentrated acids, which were acquired from Mallinckrodt. All solutions were prepared using deionized H_2O that was redistilled or passed through a Barnstead mixed-bed ion-exchange column to produce effluent of conductance corresponding to <0.01 ppm of total salt measured as NaCl.

pH measurements were carried out using a Corning Model 130 pH meter. At pH <4, kinetic studies involved measurement of the time-dependent decrease in nitrite absorbance at 209−217 nm using a Dionex D-110 stopped-flow spectrophotometer in conjunction with a Tektronix 5103N storage oscilloscope. For slower reactions at pH >4, higher concentrations were employed and the reaction was followed in the lower extinction region for nitrite at 350−360 nm. In most cases, pseudo-first-order conditions were maintained using excess amine−

[†] Present address: Westinghouse Hanford Co., Richland, WA 99352.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

(1) Hawthorne, M. F.; Lewis, E. S. *J. Am. Chem. Soc.* **1958**, *80*, 4296.
(2) Ryschkewitsch, G. *J. Am. Chem. Soc.* **1960**, *82*, 3290.
(3) Ryschkewitsch, G.; Birnbaum, E. R. *J. Phys. Chem.* **1961**, *65*, 1087; *Inorg. Chem.* **1965**, *4*, 575.
(4) Lewis, E. S.; Grinstein, R. H. *J. Am. Chem. Soc.* **1962**, *84*, 1158.
(5) Kelly, H. C.; Marchelli, F. R.; Giusto, M. B. *Inorg. Chem.* **1964**, *3*, 431.
(6) Davis, R. E.; Kenson, R. E. *J. Am. Chem. Soc.* **1967**, *89*, 1384.
(7) Kelly, H. C.; Underwood, J. A., III. *Inorg. Chem.* **1969**, *8*, 1202.
(8) Weidig, C.; Uppal, S. S.; Kelly, H. C. *Inorg. Chem.* **1974**, *13*, 1763.
(9) Heaton, G. S.; Riley, R. N. K. *J. Chem. Soc. A* **1966**, 952.
(10) Lowe, J. R.; Uppal, S. S.; Weidig, C.; Kelly, H. C. *Inorg. Chem.* **1970**, *9*, 1423.
(11) Weidig, C.; Lakovitz, J. M.; Kelly, H. C. *Inorg. Chem.* **1976**, *15*, 1783.
(12) Skillern, K. R.; Kelly, H. C. *Inorg. Chem.* **1977**, *16*, 3000.
(13) Kelly, H. C.; Marriott, V. B. *Inorg. Chem.* **1979**, *18*, 2875.
(14) Minter, D. E.; Kelly, C. R.; Kelly, H. C. *Inorg. Chem.* **1986**, *25*, 3291.
(15) Bell, K. E.; Kelly, H. C. *Inorg. Chem.* **1992**, *31*, 2665.
(16) Wilson, I.; Kelly, H. C. *Inorg. Chem.* **1982**, *21*, 1622.
(17) Kelly, H. C.; Yasui, S. C.; Twiss-Brooks, A. B. *Inorg. Chem.* **1984**, *23*, 2220.
(18) Bell, K. E.; Kelly, C. R.; Minter, D. E.; Kelly, H. C. *Inorg. Chim. Acta* **1993**, *211*, 187.

S0020-1669(96)00154-1 CCC: $12.00

borane with $[H_3O^+]$ maintained essentially constant though the use of buffers or by "swamping" with excess hydronium ion. Infrared spectra were obtained using a MIDAC FT-IR spectrophotometer. A Finnegan OWA 1020 GC-MS spectrometer was used to obtain mass spectra, and NMR data were obtained on a Varian XL-300 spectrometer.

Stoichiometric Studies. The molar equivalence of trimethylamine−borane to total nitrite in acidic solution was determined by iodometric analysis. In a series of experiments, different volumes of an $NaNO_2$ solution of known concentration were added to solutions containing the same known amount of amine−borane. In each case, the amine−borane was in stoichiometric excess. Each solution was acidified with H_2SO_4 and allowed to stand for about 1 min to ensure completion of the reaction. The solution was then treated with 1 g of KI and a sufficient volume of standard KIO_3 solution to generate I_2 in excess of the amount required to oxidize all hydridic hydrogen of the remaining amine−borane, i.e., that in stoichiometric excess of nitrite, according to $H^- + I_2 \rightarrow 2I^- + H^+$. The excess I_2 was then determined by titration with standard $Na_2S_2O_3$ to the starch end point.

The measurement of gaseous products was performed by conducting the reaction in a high-vacuum line designed and constructed in our laboratories, into which was inserted a Toepler pump obtained from Delmar Corp. of Maywood, IL. The reaction was carried out at room temperature in aqueous dioxane as solvent. Volatile materials were allowed to pass into the vacuum manifold. The condensable gas product, along with traces of solvent, was trapped in a liquid-nitrogen-cooled U-tube. Non-condensable product (H_2) was collected through the repetitive cycling action of the Toepler pump. On each cycle, a vacuum was applied to an external mercury reservoir causing a mercury column within the Toepler pump to be lowered, thereby allowing H_2 to expand into an evacuated region. Through the subsequent slow application of atmospheric pressure to the reservoir, the interior mercury column was then raised, sealing off that fraction of the contained H_2 and transferring it, by compression, through a mercury float valve into a chamber of previously calibrated volume. Following collection of all measurable noncondensable gas, its molar quantity was determined from a measure of the pressure at known volume and temperature.

The hydrogen then was expelled from the system, following which condensable gaseous product was separated from trace solvent by fractional condensation and collected by Toepler pump action. After determination of the molar yield, its molecular weight was determined by condensing and isolating the product in a calibrated vessel of known mass, which was then warmed to room temperature and weighed.

In a specific study, a mixture of 0.531 g (7.28 mmol) of $(CH_3)_3N{\cdot}BH_3$ and 0.559 g of 97% $NaNO_2$ (7.86 mmol) was dissolved in 20 mL of 50% dioxane−50% H_2O in a round-bottom flask which was attached to the vacuum line. Air was removed through a series of freeze−thaw cycles using liquid nitrogen. The solution was then warmed and stirred while aqueous HCl was added in small increments *via* a dropping funnel. After addition of a solution composed of about 12 mL of 1 N HCl diluted to 40 mL with H_2O, the product gases were collected as described above. A total of 4.1 mmol of H_2 and 3.55 mmol of N_2O were produced (stoichiometric $NaNO_2/N_2O$ ratio 1.92). Residual solubility of N_2O in H_2O may account for an experimental $NaNO_2/N_2O$ ratio somewhat greater than 2. The small excess of H_2 was due to slow hydrolysis of $(CH_3)_3N{\cdot}BH_3$, which was kept in stoichiometric excess. In a similar experiment, a 0.1173 g sample of the condensable gas produced was found to exert a pressure of 364 Torr in a volume of 0.135 L at 24.5 °C: MW found 44.2, calcd for N_2O 44.0.

Results and Discussion

Stoichiometry. Results of the iodometric analysis of hydride remaining in acidic solutions following the addition of $NaNO_2$ to a stoichiometric excess of trimethylamine−borane are illustrated in Figure 1, where the negative of the slope of the line represents the molar equivalence of nitrite to amine−borane (2:1). The reaction results in the evolution of H_2 and a condensable gas identified as nitrous oxide from its mass spectrum, which includes a parent ion peak (N_2O^+) of *m*/*e* 44, a gas-phase molecular weight determination (found 44.2; calcd for N_2O 44.0), and its gas-phase infrared spectrum, which was comparable to that of an authentic sample of N_2O obtained from Matheson Co. Equimolar amounts of H_2 and N_2O are produced, and the stoichiometric ratio of $NaNO_2$ reacted to N_2O produced is 2:1. Results are consistent with the overall stoichiometric relation

$$(CH_3)_3N{\cdot}BH_3 + 2HNO_2 + H_3O^+ \rightarrow (CH_3)_3NH^+ + B(OH)_3 + N_2O + H_2 + H_2O \quad (1)$$

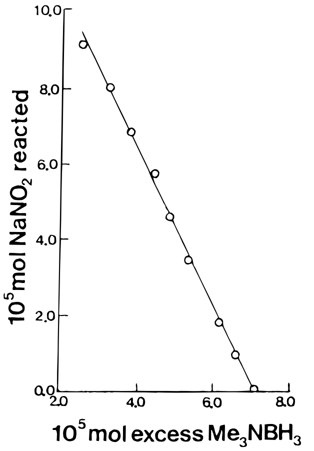

Figure 1. Determination of the stoichiometric ratio of sodium nitrite to trimethylamine−borane ($t = 25$ °C). In each experiment, a designated amount of $NaNO_2$ was added to 7×10^{-5} mol of $(CH_3)_3N{\cdot}BH_3$. Each point represents the amount of $(CH_3)_3N{\cdot}BH_3$ remaining after reaction with the specified amount of $NaNO_2$. $[NaNO_2]/[(CH_3)_3N{\cdot}BH_3] = -(\text{slope}) = 2.02$.

Kinetics. In the presence of a large excess of amine−borane and at constant hydrogen ion concentration, the decrease in absorbance characterizing loss of nitrite follows first-order kinetics. At a given pH, the pseudo-first-order rate constant shows direct proportionality to the concentration of trimethylamine−borane, leading to the "pseudo-second-order" relation

$$-d[NO_2^-]_0/dt = k_2[(CH_3)_3N{\cdot}BH_3][NO_2^-]_0 \quad (2)$$

where $[NO_2^-]_0$ denotes the total stoichiometric concentration of nitrite. A first-order dependence on $[H_3O^+]$ is found in the range pH 0.7−2.7, and at higher acidity, a linear correlation of k_2 with the Hammett acidity function, h_o,[19,20] is observed (Figure 2). The k_2 term is also subject to a pronounced *inverse* solvent isotope effect (Table 1). Although an exchange of boron-bonded hydrogen of trimethylamine−borane with solvent has been shown to be significant in highly acidic solutions,[22] the inverse effect observed here is clearly due to an effect of solvent which is relatively uncomplicated by hydrogen-deuterium exchange in the substrate. Indeed, as seen in Table 2, a small *normal* substrate isotope effect is apparent from a comparison of reactivities of trimethylamine−borane and trimethylamine−borane-d_3 in aqueous HCl.

The correlation of rate with h_o and the observed solvent isotope effect strongly suggest a mechanistic scheme involving preequilibrium protonation of a substrate prior to its rate-determining reduction by amine−borane. In regions of high

---

(19) Hammett, L. P.; Deyrup, A. J. *J. Am. Chem. Soc.* **1932**, *54*, 2721.

(20) Paul, M. A.; Long, F. A. *Chem. Rev.* **1957**, *57*, 1.

(21) Covington, A. K., Paabo, M.; Robinson, R. A.; Bates, R. G. *Anal. Chem.* **1968**, *40*, 700.

(22) Davis, R. E.; Brown, A. E.; Hopmann, R.; Kibby, C. L. *J. Am. Chem. Soc.* **1963**, *85*, 487.

(23) A lower value based on thermodynamic calculations ($pK_a = 3.14$) and ionic strength dependent values ($pK_a = 2.9{-}3.0$ at $I = 0.2$ M) has been reported: Tummavuori, J.; Lumme, P. *Acta Chem. Scand.* **1968**, *22*, 2003.

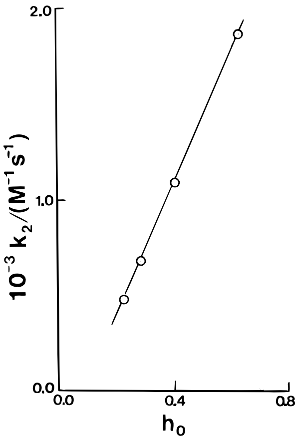

Figure 2. Correlation of the rate of reaction of trimethylamine−borane with $NaNO_2$ with the Hammett acidity function in 1% dioxane−99% aqueous HCl ($t = 25$ °C). $k_2 = -\mathrm{d}\ \ln[NO_2^-]_0/([(CH_3)_3N\cdot BH_3]\mathrm{d}t)$. Data are taken from the first four entries of Table 3 ($r = 0.999$).

Table 1. Solvent Isotope Effect for the Reaction of Trimethylamine−Borane with Nitrite in 2% Dioxane−98% H_2O ($t = 25$ °C)

$[H_2SO_4]$/M in H_2O	$[D_2SO_4]$/M in D_2O	pH (pD)^a	$k_{obs}{}^b$/s^{-1}	$k_2{}^c$/M^{-1} s^{-1}	k_{D_2O}/k_{H_2O}
	0.0970	(1.05)	3.03	456	2.83
0.0995		0.96	1.31	161^d	
	0.0530	(1.25)	1.57	235	2.63
0.0535		1.21	0.668	89.6^e	

[a] pD = pH + 0.41.[21] [b] $k_{obs} = -\mathrm{d}\ \ln[NO_2^-]_0/\mathrm{d}t$. [c] $k_2 = k_{obs}/[(CH_3)_3N\cdot BH_3]$. [d] Value extrapolated to pH 1.05. [e] Value extrapolated to pH 1.25.

Table 2. Substrate Isotope Effect for the Reaction of Trimethylamine−Borane with Nitrite in 1% Dioxane−99% H_2O ($t = 25$ °C; $\mu = 0.2$ M)

[HCl]/M	pH	k_H/M^{-1} s^{-1a}	k_D/(M^{-1} s^{-1b}	k_H/k_D
0.010	2.00	24.5	17.9	1.37
0.10	1.00	261	194	1.35
0.20	0.70	548	406	1.35

[a] $k_H = -\mathrm{d}\ \ln([NO_2^-]_0)/(\mathrm{d}t[(CH_3)_3N\cdot BH_3])$. [b] $k_D = -\mathrm{d}\ \ln([NO_2^-]_0)/(\mathrm{d}t[(CH_3)_3N\cdot BD_3])$.

acidity corresponding to pH ≪ pK_a (=3.4 for HNO_2),[23] there is no significant concentration of free NO_2^- ion, indicating molecular nitrous acid to be the species undergoing protonation. The substrate isotope effect, albeit small, is not out of line with numerous other substrate effects observed in reactions proposed to involve rate-determining B−H bond cleavage[1,4,18,24] and is consistent with an activated complex involving B−H bond scission through attack of amine−borane on the conjugate acid of nitrous acid, $H_2NO_2^+$ (or nitrosonium ion, NO^+).[25] Such a sequence is shown in Scheme 1 with a proposed rate-determining step (eq 4) leading to the formation of nitrosyl hydride, HNO. Equations 5−9 represent conjecture on the nature and possible sequence of subsequent rapid steps. Presumably a $-BH_2$-containing species is produced in (4). Consistent with the stoichiometry, it is proposed that one of these boron-bonded hydrogens will be involved in attack on $H_2NO_2^+$, producing a second nitrosyl hydride, followed by bimolecular association of HNO to N_2O with the other B−H linkage undergoing hydrolysis to produce H_2. Formation of nitrosyl hydride has been proposed in numerous studies of nitrosation mechanisms, some of which involve the dynamics of HNO dimerization and decomposition to N_2O.[31,32] Neither the nature of reactive hydridic intermediates nor the sequence of fast processes is known; however, from previous studies of the redox chemistry of boranes in solution, it seems reasonable to propose early cleavage of the B−N bond with possible formation of hydrated borane species.[33,34]

Scheme 1

$$HNO_2 + H^+ \rightleftharpoons H_2NO_2^+ \text{ (fast)} \tag{3}$$

$$\begin{gathered} H^- \text{ (from } (CH_3)_3N\cdot BH_3) + H_2NO_2^+ \rightarrow HNO + H_2O \\ \text{(slow, and leading to release of } (CH_3)_3N + H_2OBH_2^+) \end{gathered} \tag{4}$$

$$H_2OBH_2^+ \rightarrow (HO)BH_2 + H^+ \text{ (fast)} \tag{5}$$

$$(HO)BH_2 + H_2NO_2^+ \rightarrow HNO + (HO)_2BH + H^+ \text{ (fast)} \tag{6}$$

$$2HNO \rightarrow N_2O + H_2O \text{ (fast)} \tag{7}$$

$$(HO)_2BH + H_2O \rightarrow B(OH)_3 + H_2 \text{ (fast)} \tag{8}$$

$$(CH_3)_3N + H^+ \rightleftharpoons (CH_3)_3NH^+ \text{ (fast)} \tag{9}$$

The kinetic consequences of Scheme 1 are given in eq 10, where $[NO_2^-]_0$ denotes the total stoichiometric concentration of nitrite in all forms, i.e., $[H_2ONO^+] + [HONO] + [NO_2^-]$, and K_a and K_a' represent the respective acid dissociation constants of HONO and H_2ONO^+. As previously noted, a first-order dependence of rate on $[H_3O^+]$ is observed at relatively high acidity. This would correspond to the limiting case $[H_3O^+] \gg K_a$. Consistent with and, indeed, demanded by the proposed mechanism is a transition from first-order to second-order dependence on $[H_3O^+]$ at low acidity corresponding to $K_a \gg [H_3O^+]$. As seen in Figure 3, which shows a range in k_2 of over 9 orders of magnitude, such a transition does indeed occur, as expected, in the vicinity of pH ≈ pK_a.

$$\frac{-\mathrm{d}[NO_2^-]_0}{\mathrm{d}t} = \frac{k_r[(CH_3)_3N\cdot BH_3][NO_2^-]_0[H_3O^+]^2}{K_a'[K_a + (H_3O^+)]} \tag{10}$$

Relating the empirical second-order rate equation (2) to the derived expression shown in eq 10, one obtains

---

[24] White, S. S., Jr.; Kelly, H. C. *J. Am. Chem. Soc.* **1970**, *92*, 4203.

[25] Whether the H^+, HNO_2 interaction leads to nitrosoacidium ion, $H_2NO_2^+$, free nitrosonium ion, NO^+, or an equilibrium mixture ($H_2NO_2^+ \rightleftharpoons NO^+ + H_2O$) is a matter of speculation. Williams has suggested this to be a function of the acidity of the medium,[26] and the question has been addressed by numerous investigators.[27−30] In either event, the kinetic pattern for nitrite reduction by amine−borane is unaffected. For purposes of discussion here, the species is represented as $H_2NO_2^+$.

[26] Williams, D. L. H. *Adv. Phys. Org. Chem.* **1983**, *19*, 381.

[27] Bayless, N. S.; Dingle, R.; Watts, D. W.; Wilkie, R. J. *Aust. J. Chem.* **1963**, *16*, 933.

[28] Seel, F.; Winkler, R. Z. *Phys. Chem.* **1960**, *25*, 217.

[29] Prakash, G. K. S.; Heiliger, L. P.; Olah, G. A. *Inorg. Chem.* **1990**, *29*, 4965.

[30] Ko, Y.; Bonner, F. T.; Crull, G. B.; Harbison, G. S. *Inorg. Chem.* **1993**, *32*, 3316.

[31] Kohout, F. C.; Lampe, F. W. *J. Chem. Phys.* **1967**, *46*, 4075.

[32] Bazylinski, D. A.; Hollocher, T. C. *Inorg. Chem.* **1985**, *24*, 4285.

[33] Jolly, W. L.; Schmidt, T. *J. Am. Chem. Soc.* **1966**, *88*, 4282; *Inorg. Chem.* **1967**, *6*, 344.

[34] White, S. S., Jr.; Kelly, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 2009.

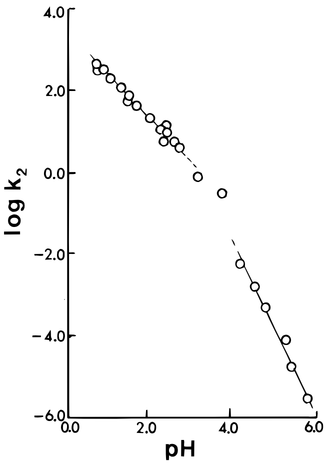

Figure 3. Variation of log k_2 with pH (solvent 1% dioxane−99% H_2O (by volume); t = 25 °C; $\mu = 0.2$ M). For pH 0.70−2.74, slope = −1.03 ($r = 0.999$); for pH 4.25−5.85, slope = −2.05 ($r = 0.992$). $k_2 = -\mathrm{d}\ \ln[NO_2^-]_0/([(CH_3)_3N{\cdot}BH_3]\mathrm{d}t)$.

$$k_2 = k_r[H_3O]^2/(K_a'[K_a + [H_3O^+]]) \qquad (11)$$

Data obtained in the region of pH ∼0.7−2.7 lead to the value ∼2.5 × 10^3 M^{-2} s^{-1} for the third-order rate constant represented here as k_r/K_a'. This is approximately the value of rate constants obtained in a series of nitrosation reactions thought to involve a near-diffusion-controlled attack of selected substrates by NO^+.[35] In a previous study, Bayless and co-workers[27] described nitrous acid protonation in terms of eq 12, with K_{eq} calculated

$$\mathrm{HONO} + \mathrm{H}^+ \rightleftharpoons \mathrm{H_2O} + \mathrm{NO}^+ \qquad (12)$$

to be on the order of 3 × 10^{-7}. If this is the nature of the preequilibrium step, and if the rate-determining step is viewed as an attack of amine−borane on NO^+, then taking $1/K_a' = 3 \times 10^{-7}$, one obtains from eq 11 and the data of Table 3 the value $k_r = (2-8) \times 10^9$ M^{-1} s^{-1}, which implies a near-diffusion-controlled reaction of amine−borane with nitrosonium ion. This conclusion is subject to question, however, on the basis of the observed substrate isotope effect as well as the fact that faster steps are proposed to occur subsequent to this rate-limiting step. In addition, one might reasonably expect hydride transfer from a molecule such as $(CH_3)_3N{\cdot}BH_3$ to involve a steric or orientational barrier for hydride transfer over and above an encounter requirement that may suffice for reaction of NO^+ with structually simpler nucleophiles. On these grounds, we suggest the calculated value of k_r to be high perhaps by an order of magnitude. This high level of hydride reactivity with nitrite has prompted additional studies related to the possible use of amine−boranes as denitrosation agents in the decomposition of nitrosamines.

Table 3. pH Dependence of the Rate of Reduction of Nitrite by Trimethylamine−Borane[a]

pH[b]	h_o[c]	$10^3[(CH_3)_3N{\cdot}BH_3]_0$/M	k_2/M^{-1} s^{-1}	log k_2
0.30[d]	0.63	6.43	1870	3.27
0.45[e]	0.41	6.43	1090	3.04
0.60[f]	0.28	2.71	659	2.82
0.70	0.23	4.65	473	2.67
0.73[g]		4.63	394	2.60
0.83		2.71	355	2.55
1.06		4.28	230	2.36
1.35		4.28	117	2.07
1.55		2.71	636	1.80
1.57		20.7	62.7	1.80
1.74		2.71	45.5	1.66
2.05		2.71	22.0	1.34
2.34[h]		29.8	8.92	0.950
2.35[h]		2.71	9.96	0.998
2.35[h,i]		30.0	5.81	0.764
2.43		4.90	8.91	0.950
2.67		4.90	4.81	0.682
2.74[h]		5.62	3.40	0.531
3.17[h]		1.36	0.733	−0.135
3.82[j]		2.71	0.255	−0.593

pH[k]	$[(CH_{3)3}NBH_{3]0}$/M	10^3k_2/M^{-1} s^{-1}	log k_2
4.25	0.0770	6.05	−2.22
4.62	0.0856	1.55	−2.81
4.89	∼0.08	0.444	−3.35
5.38	0.0733	0.074	−4.13
5.56	0.0676	0.014	−4.86
5.85	0.0770	0.0031	−5.52

[a] Conditions: t = 25 °C; $\mu = 0.2$ M; $[NaNO_2]_0 = (2-3) \times 10^{-4}$ M at pH <4 and (6−7) × 10^{-3} M at pH >4. [b] Source of H_3O^+ was HCl(aq) unless otherwise indicated. [c] Interpolated from ref 20. [d] $\mu = 0.5$ M. [e] $\mu = 0.35$ M. [f] $\mu = 0.25$ M. [g] H_2SO_4(aq). [h] $H_3PO_4/H_2PO_4^-$ buffer. [i] $\mu = 0.08$ M. [j] HF/F^- buffer. [k] HOAc/OAc^- buffer.

Acknowledgment. We acknowledge Lu Kelly for analytical and spectral studies and Dr. Geoffrey Stedman (University of Wales, Swansea, Wales) for helpful discussions. This work was partially supported by the Welch Foundation (Grant No. P-161) and the TCU Research Fund.

IC9601549

---

(35) Ridd, J. H. *Adv. Phys. Org. Chem.* **1978**, *16*, 1.