

Electrophilic Substitution of Gaseous Borazine

Barbara Chiavarino, Maria Elisa Crestoni, and
Simonetta Fornarini*

Dipartimento di Chimica e
Tecnologia delle Sostanze Biologicamente Attive
Università di Roma "La Sapienza",
P.le A. Moro 5, I-00185, Roma, Italy

Received November 2, 1998

Borazine ($B_3N_3H_6$) is isoelectronic with benzene, having six π electrons which, although formally located on the nitrogen atoms, may be partially delocalized, conferring aromatic stabilization. Indeed, borazine is similar in physical properties to benzene and has often been termed "inorganic benzene".¹ Chemically, however, borazine is quite different from benzene, being much more reactive and decomposing slowly on storage. Unlike benzene, $B_3N_3H_6$ readily undergoes addition reactions, whereas thus far no electrophilic substitution has ever been reported. Thus, it appears that even if borazine may be endowed with some aromatic character, its reactivity behavior is not driven toward reassembling the π -ring system. Several experimental² and theoretical³ studies have been reported, aimed at assessing the degree of aromaticity of borazine with respect to benzene and other inorganic analogues. Diamagnetic susceptibility exaltation has been suggested as the unique criterion for aromaticity.^{3a,4} Recent computational data predict an aromatic stabilization energy of 10 kcal/mol and a negligible magnetic susceptibility anisotropy, showing that π electrons are localized on the nitrogen atoms.

Borazine has been successfully used as a precursor of boron nitride, a widely studied material with valuable properties, by photolysis, pyrolysis, and chemical vapor deposition procedures.⁵ The current interest in the fundamental properties of borazine and in its use as a starting material for the preparation of B–N ceramics has stimulated our study of the gas-phase reactivity of borazine with ionic electrophiles. It was expected that a nonnucleophilic medium such as the dilute gas-phase, where naked ionic electrophiles may be formed, could establish favorable conditions to direct the reactivity of borazine toward a formal electrophilic aromatic substitution reaction rather than an addition process.

The unambiguous identification of an electrophilic substitution reaction should rely on the recovery of substitution products, $B_3N_3H_5E$, where an E group from an attacking electrophile, $E(Y)^+$, has replaced a hydrogen atom. To this end, a radiolytic methodology has been exploited which allows the formation of well-characterized cations in a gaseous environment at atmospheric pressure.⁶ Representative $E(Y)^+$ ions were formed by γ -irradiation at 40 °C of an inert bath gas (600–700 Torr) in the presence of a radical scavenger (O_2 , 10 Torr) and borazine. All of the results summarized in Table 1 have been checked against a blank where

the same system was not submitted to γ -irradiation under otherwise identical conditions. The control experiments ensured that the reaction products did not arise from thermal reactions, and at the same time they enabled checking the thermal stability of the substrate. As previously known, borazine was found to decompose in the presence of certain additives such as amines or methyl nitrate.⁸ In particular, the thermal reaction of borazine with $MeONO_2$ presented a limitation because methyl nitrate is used as a convenient precursor of the nitrating ion $MeONO_2H^+$. As a consequence, the nitration reaction, a prototypical electrophilic reaction, was precluded to our study. Remarkably, however, the alkylating ions Me_2F^+ , Me_2CH^+ , and Me_3C^+ ($E = Me$, Me_2CH , and Me_3C , respectively) performed an efficient electrophilic substitution reaction, yielding the corresponding alkylated borazines with fair radiochemical yields. The regiochemistry of the substitution is directed to the nitrogen atoms, the expected nucleophilic sites of the molecule.⁹ This result is based on the direct identification of the methylated product by comparison with an authentic sample of 1-methylborazine and was extrapolated to the other alkylborazines. As the finding of 1-alkylation products conforms to the product pattern of the $E(Y)^+$ reactions with benzene,¹⁰ we suggest Scheme 1 to account for the observed electrophilic substitution reaction.

The ionic intermediate **2** may be viewed as an ammonium ion or, alternatively, as an inorganic analogue of an arenium ion, evolving to the neutral end product by deprotonation by a base, which may be excess neutral borazine itself, rather than by an addition process. Among the selected reagent ions, the reaction of Me_2F^+ is inherently different. Whereas Me_2CH^+ and Me_3C^+ can only react by electrophilic addition and, possibly, by protonation, alkylation by Me_2F^+ occurs by nucleophilic displacement at the methyl group with MeF as the leaving group. A more or less concerted mechanism could conceivably be envisioned, where methyl transfer occurs simultaneously with the transfer of a proton from the nucleophilic nitrogen to the leaving group. This pathway, avoiding the formation of intermediate **2**, is however highly unlikely, in view of the large difference in proton affinity (PA) between MeF and borazine (143.1 and 191.8 kcal/mol, respectively).¹¹ Furthermore, the intermediacy of a distinct species **2** ($E = Me$) has been directly observed by FT-ICR mass spectrometry, where a product ion corresponding to [borazine + Me]⁺ is formed from the highly efficient reaction of Me_2F^+ with neutral borazine ($k = 1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$).¹²

Whereas a common reaction scheme qualitatively accounts for the electrophilic substitution of both borazine and benzene, their reactivity is quantitatively different. Me_3C^+ , a mild electrophile,

(1) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1988. (b) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Benjamin/Cummings: New York, 1993.

(2) Doering, J. P.; Gedanken, A.; Hitchcock, A. P.; Fisher, P.; Moore, J.; Olthoff, J. K.; Tossell, J.; Raghavachari, K.; Robin, M. B. *J. Am. Chem. Soc.* **1986**, *108*, 3602.

(3) (a) Fowler, P. W.; Steiner, E. *J. Phys. Chem. A* **1997**, *101*, 1409. (b) Parker, J. K.; Davis, S. R. *J. Phys. Chem. A* **1997**, *101*, 9410. (c) Nelson, J. T.; Pietro, W. J. *Inorg. Chem.* **1989**, *28*, 544. (d) Cooper, D. L.; Wright, S. C.; Gerratt, J.; Hyams, P. A.; Raimondi, M. *J. Chem. Soc., Perkin Trans. 2* **1989**, 719. (e) Boyd, R. J.; Choi, S. C.; Hale, C. C. *Chem. Phys. Lett.* **1984**, *112*, 136.

(4) Schleyer, P. v. R.; Jiao, H.; v. Eikema Hommes, N. J. R.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669.

(5) (a) Paine, R. T.; Narula, C. K. *Chem. Rev.* **1990**, *90*, 73. (b) Mokhtari, M.; Park, H. S.; Roesky, H. W.; Johnson, S. E.; Bolse, W.; Conrad, J.; Plass, W. *Chem. Eur. J.* **1996**, *2*, 1269.

(6) Cacace, F. *Acc. Chem. Res.* **1988**, *21*, 215. Radiolytic experiments were performed using reagents from commercial sources. Borazine was prepared from sodium borohydride and ammonium sulfate, as described by Wideman, T.; Sneddon, L. G. *Inorg. Chem.* **1995**, *34*, 1002, and was stored in the dark at low temperature. 1-Methyl-, 1,3-dimethyl-, and 1,3,5-trimethylborazine were obtained as a mixture using the same procedure with a 1:3 ratio of methylamine hydrochloride and ammonium sulfate and were purified by trap-to-trap distillation. The radiolyses were performed at 40 °C in a 220 Gammacell from Nuclear Canada Ltd to the total dose of 2×10^4 Gy. The radiolytic products were analyzed by GC-MS using a 50-m long, 0.32-mm i.d. PONA fused silica capillary column mounted on a Hewlett-Packard 5890 gas chromatograph in line with a model 5989B quadrupole mass spectrometer.

(7) (a) Sandoval, I. B.; Ausloos, P. *J. Chem. Phys.* **1963**, *38*, 2452. (b) Ausloos, P.; Lias, S. G.; Gorden, R., Jr. *J. Chem. Phys.* **1963**, *39*, 3341.

(8) Meller, A. *Gmelin Handbuch der Anorganische Chemie, Boron Compounds*; Springer-Verlag: Berlin, 1988; 3rd Supplement, Vol. 3 and references therein.

(9) (a) Doiron, C. E.; Grein, F.; McMahon, T. B.; Vasudevan, K. *Can. J. Chem.* **1979**, *57*, 1751. (b) DeStefano, A.; Porter, R. F. *Inorg. Chem.* **1975**, *14*, 2882.

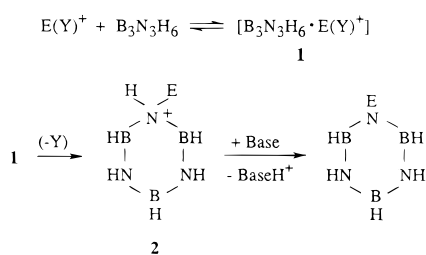
(10) Fornarini, S. *Mass Spectrom. Rev.* **1996**, *15*, 365.

(11) Hunter, E. P.; Lias, S. G. *Proton Affinity Evaluation in NIST Chemistry Webbook, NIST Standard Reference Database Number 69*, Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 20899 (<http://webbook.nist.gov>), 1998.

Table 1. Gas-Phase Reactions of Borazine and Methyl-Substituted Borazines with Charged Electrophiles

system composition (Torr) ^a	reagent ion	products (G_{+M}) ^b
borazine (10); MeF (650)	Me_2F^+	1-methylborazine (0.30)
borazine (10); C_3H_8 (640)	Me_2CH^+	<i>i</i> -propylborazine (0.24)
borazine (10); <i>i</i> - C_4H_{10} (640)	Me_3C^+	<i>t</i> -butylborazine (0.43)
borazine (8); <i>i</i> - C_4H_{10} (640)	Me_3C^+	<i>t</i> -butylborazine (0.30)
1-methylborazine (4)		<i>t</i> -butyl-1-methylborazine (0.13)
1-methylborazine (7.7); <i>i</i> - C_4H_{10} (605)	Me_3C^+	<i>t</i> -butyl-1-methylborazine (0.30)
1,3-dimethyl borazine (3.5)		<i>t</i> -butyl-1,3-dimethylborazine (0.09)
1,3,5-trimethylborazine (3); <i>i</i> - C_4H_{10} (620)	Me_3C^+	—
1,3,5-trimethylborazine (3.5); C_3H_8 (610)	Me_2CH^+	—
borazine (8); CH_4 (600)	$\text{CH}_5^+/\text{C}_2\text{H}_5^+$	—
borazine (10); CH_4 (620); MeOH (3)	$\text{CH}_5^+/\text{C}_2\text{H}_5^+$	methoxyborazine (0.05)

^a All systems contain O_2 (10 Torr) as free radical scavenger. Irradiations performed at 40 °C. ^b Number of molecules formed per 100 eV absorbed by the gas. The estimated uncertainty of the G_{+M} values is $\pm 20\%$. The radiochemical yields of the products, G_{+M} , can be compared with the G_{+M} values of the reagent ions, typically on the order of 2–3.⁷

Scheme 1

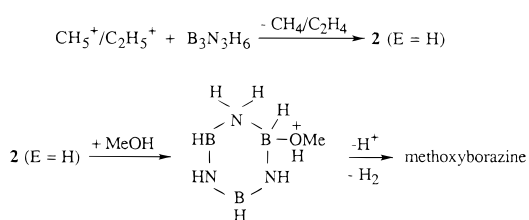
shows a remarkable substrate selectivity in the alkylation of benzene and toluene, corresponding to a reactivity ratio of ca. 1:50 at 40 °C.¹³ By contrast (Table 1), 1-methylborazine is less reactive than borazine by a factor of 1.5 and is in turn 1.5 times more reactive than 1,3-dimethylborazine. These ratios are obtained by assuming parallel, independent routes for the alkylation by Me_3C^+ in competition experiments. Such a reactivity order is nearly statistical, being conceivably related to the decreasing number of sites available for the electrophilic substitution reaction, namely, the unsubstituted nitrogen atoms. In the framework of Scheme 1, it follows that, once formed, the ion–neutral collision complex **1** statistically evolves into intermediate **2** with very limited back dissociation to the free reagents. The results suggest that **1** is more reactive with respect to the corresponding benzene complex and do not explain whether the electron-donating effect of a methyl group on nitrogen is transmitted through the π -system of borazine in a similar way as in benzene.

The formation of a single isomer from the alkylation of both 1-methyl- and 1,3-dimethylborazine further confirms the nitrogen atom as the nucleophilic site. Should the boron atoms be involved in the *tert*-butylation, formation of two isomeric products would be expected from both substrates. An additional piece of evidence is the failure of 1,3,5-trimethylborazine to undergo either *tert*-butylation or *i*-propylation.

The last entry in Table 1 shows that the radiolysis of borazine in methane does not yield alkylation products, although the C_2H_5^+

(12) FT-ICR experiments were performed using a Bruker Spectrospin Apex TM 47e spectrometer equipped with an external ion source and a cylindrical (60 mm diameter) “infinity” cell within a 4.7 T superconducting magnet. Me_2F^+ ions were generated by MeF-Cl in the external source and led into the cell, where they reacted with borazine at the pressure of 4×10^{-8} Torr.

(13) Cacace, F.; Ciranni, G. *J. Am. Chem. Soc.* **1986**, *108*, 887.

Scheme 2

ion is known to behave as both a Brønsted and a Lewis acid toward benzene and toluene.¹⁴ Rather, the methane ions CH_5^+ and C_2H_5^+ appear to react exclusively by a protonation route that is difficult to detect if **2** (E = H) is subsequently deprotonated. In the presence of methanol, however, methoxyborazine is formed. Although alternative pathways cannot be excluded, it is tempting to ascribe its formation to the reaction of methanol with **2** (E = H, Scheme 2). Both the protonation and the nucleophilic attack by MeOH are highly exothermic, based on the low PA of CH_4 and C_2H_4 (129.9 and 162.6 kcal/mol, respectively)¹¹ and on the high stability of the B–O bond. It is thus conceivable that loss of H_2 will follow, restoring the π -electron system.

Once again, independent support on the proposed ionic intermediates is obtained from FT-ICR experiments. Protonated borazine yields an ion of elemental composition consistent with $[\text{B}_3\text{N}_3\text{H}_6(\text{OMe})]^+$, formally corresponding to protonated methoxyborazine, upon reaction with methanol. Thus, although methoxyborazine is not a product of electrophilic substitution, still the addition–elimination pathway of Scheme 2 may be viewed as driven by the stability of the end product.

In conclusion, the first example of electrophilic substitution on the borazine ring has been reported, a result that is relevant in the context of the current debate on the extent of aromatic character of this fundamental inorganic ring.

Acknowledgment. We gratefully acknowledge support of this research by the Italian Ministero dell’Università e della Ricerca Scientifica e Tecnologica and by the Consiglio Nazionale delle Ricerche. We are grateful to Professor Fulvio Cacace for many helpful discussions and to Dr. Annito Di Marzio for invaluable experimental help.

JA983799B

(14) Cerichelli, G.; Crestoni, M. E.; Fornarini, S. *J. Am. Chem. Soc.* **1992**, *114*, 2002.