corresponding reactions of the undeuteriated radical cations, $k_h > k_d$.

Of particular interest is the effect of selective isotopic substitution. As shown in Table II, for toluene and *p*-xylene, ring deuteriation leads to no or insignificant isotope effect, whereas methyl deuteriation results in almost the same isotope effect as perdeuteriation. These remarkable specific isotope effects are similar to others observed previously in charge-transfer complex absorption spectra[9a] and in the nonradiative decay of exciplexes in the gas phase.[9b–g] The methyl-specific isotope effect is consistent with significant changes in the methyl carbon–hydrogen and ring carbon–methyl carbon bond lengths upon ionization of the substituted benzene.[9] These specific bond length changes are consistent with significant hyperconjugative stabilization of the substituted benzene radical cations by the ring methyl groups.[9a,d–g]

The observed kinetic isotope effect (Table I) seems to depend on the reaction exothermicity and on the number of methyl groups on the benzene ring. Thus, isotope effects per methyl group, $(k_h/k_d)_{\mathrm{perMe}}$, are calculated with eq 2 in which n is the number of methyl groups on the donor.

$$(k_h/k_d)_{\mathrm{perMe}} = (k_h/k_d)^{1/n} \qquad (2)$$

In Figure 1 are plotted (k_h/k_d) and $(k_h/k_d)_{\mathrm{perMe}}$ as a function of reaction free energy. The plots clearly show that the magnitude of the isotope effect increases with increasing reaction exothermicity ($\Delta G_{-\mathrm{et}}$). Previously, we have shown that the maximum rate of return electron transfer for the undeuteriated donors, i.e., the rate for which the Franck–Condon factors are maximized and the reaction activation energy is minimized, occurs for a reaction exothermicity of 1.9 eV. According to the figure, at this value of ΔG, the k_h/k_d ratio approaches a value of unity. This observation is in clear agreement with the theoretical predictions of Jortner et al. for isotopic quantum effects.[4] The Franck–Condon factors for the electron-transfer process are reduced as a result of changes in the frequencies of the rearranged vibrational modes. In addition to the frequency changes, the extent of hyperconjugation should decrease with deuteriation due to the stronger C–D bond, and thus the internal reorganization could decrease. Thus, the isotope effects observed here could also contain contributions from changes in the internal reorganization energy, λ_v.

Many treatments of electron-transfer reactions assume that the rearranged vibrational modes can be approximated by a single average vibrational frequency, often ca. 1500 cm^{-1} which is typical of carbon–carbon skeletal stretching modes.[6,7] However, the present deuterium isotope effects suggest that higher frequency modes may have to be taken into account. Indeed, in the radiationless transitions of the triplet states of aromatic hydrocarbons in the gas phase, the role of high-frequency (ca. 3000 cm^{-1}) carbon–hydrogen modes is well established, although for these processes, isotope effects are observed upon deuteriation of the ring hydrogens.[11] Although the present results do not say anything about lower frequency modes, they suggest that contributions of the high-frequency carbon–hydrogen modes to the single averaged frequency in single mode models should not be underestimated, at least for the reactions of alkyl-substituted aromatic radical cations, in which hyperconjugation can be significant.

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(9) (a) Martens, F. W.; Verhoeven, J. W.; De Boer, T. J. *Tetrahedron Lett.* **1979**, *31*, 2919. (b) Dresner, J.; Prochorow, J.; Sobolewski, A. *Chem. Phys. Lett.* **1978**, *54*, 292. (c) Prorochow, J.; Deperasinska, I.; Sobolewski, A. *J. Lumin.* **1979**, *18/19*, 105. (d) Lim, B. T.; Okajima, S.; Chandra, A. K.; Lim, E. C. *J. Chem. Phys.* **1982**, *77*, 3902. (e) Okijama, S.; Lim, E. C. *J. Phys. Chem.* **1982**, *86*, 4120. (f) Lim, B. T.; Okijama, S.; Chandra, A. K.; Lim, E. C. *Chem. Phys. Lett.* **1981**, *79*, 22. (g) Okijama, S.; Lim, B. T.; Lim, E. C. *J. Chem. Phys.* **1980**, *73*, 3512.

(10) Howell, J. O.; Gonclaves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

(11) Henry, B. R.; Siebrand, W. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: New York, 1973; p 153.

Hydrogen–Deuterium Exchange of Diborane in Superacid Solution through Diboranonium ($B_2H_7^+$) and Diboranium ($B_2H_5^+$) Ions[1a,b]

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The gaseous positive ion chemistry of diborane **1** was studied by mass spectrometry, including ICR studies.[2] Aside from the preparation of simple carborane cations,[3,4] the behavior of diborane **1** in superacidic media has not been previously explored, although the interaction of B_2H_6 with HF(DF) was the subject of theoretical[5] and spectroscopic studies.[6] We report herein the slow proton/deuterium exchange of B_2H_6, **1**, in the superacidic $FSO_3D{\cdot}SbF_5$ (deuterio Magic acid)/SO_2ClF medium at low temperatures involving the corresponding isotopomeric diboranonium ions (protonated diborane) $B_2H_7^+$ ions. The structure of the $B_2H_7^+$ ion has also been probed by ab initio theoretical calculations.

When triply distilled diborane, (B_2H_6) **1**,[7] was mixed with 1:1 $FSO_3D{\cdot}SbF_5$ (deuterio Magic acid)/SO_2ClF at −78 °C, most of the diborane dissolved with no detectible gas evolution, and a colorless solution was obtained. An immediate ^{11}B and ^2H NMR[8] analysis did not reveal any initial proton–deuterium exchange. After 24 h, however, at −78 °C, such analysis showed proton–deuterium exchange. Direct NMR study of the superacidic solution of diborane did not reveal the presence of any observable cation and was indicative only of a complex mixture of exchanged boranes. After warming to room temperature analysis of the products also showed the formation of some BF_3 and H_2 as well as SO_2 and SbF_3. By using standard vacuum line techniques, a portion of diborane was removed and condensed onto frozen THF. Upon warming, the thawed THF solution was subjected to ^2H NMR spectroscopic analysis. The proton decoupled ^2H NMR showed a peak at 2.5 ppm indicating proton–deuterium exchange in B_2H_6. The peak at 2.5 ppm is identical with that of $THF{\cdot}BD_3$ obtained by reacting B_2D_6 with THF. Partially exchanged diboranes (B_2H_5D to B_2HD_5) which form $THF{\cdot}BD_2H$ and $THF{\cdot}BDH_2$ adducts also show similar ^2H NMR spectra. In a further experiment a gas-phase sample was also subjected to FT-infrared analysis.[9] The spectrum obtained is complex as would be expected from a B_2H_6, B_2H_5D, etc. mixture wherein the deuterium is at

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(1) (a) Onium Ions. 37. At the the University of Southern California. For Part 36, see: Olah, G. A.; Prakash, G. K. S.; Marcelli, M.; Lammertsma, K. *J. Phys. Chem.* **1988**, *92*, 878. (b) Dedicated to Professor Heinz Nöth on occasion of his 60th birthday.

(2) Dunbar, R. C. *J. Am. Chem. Soc.* **1968**, *90*, 5676.

(3) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L.; Wade, K. *Hypercarbon Chemistry*; Wiley Interscience: New York, NY, 1987.

(4) Williams, R. E.; Prakash, G. K. S.; Field, L. D.; Olah, G. A. *Advances in Boron and the Boranes*; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; VCH Publishers, Inc.: New York, 1988, p 191.

(5) Rowlands, T. W.; Somasundram, K. *Chem. Phys. Lett.* **1987**, *135*, 549.

(6) Gutowsky, H. S.; Emilsson, T.; Keen, J. D.; Klots, T. D.; Chang, C. *J. Chem. Phys.* **1986**, *85*, 683.

(7) Diborane was prepared from the reaction of sodium borohydride (or deuteride) and sulfuric acid (or deuteriosulfuric acid) by Weiss and using the procedure described by Shapiro (Weiss, H. G.; Shapiro, I. *J. Am. Chem. Soc.* **1959**, *81*, 6167).

(8) The NMR spectra was recorded on a Varian Associates VXR 200 MHz NMR spectrometer equipped with variable temperature broad band probe.

(9) The infrared spectra was recorded on a Perkin-Elmer 1500 FT-IR instrument. The gas cell used was 10 cm long.

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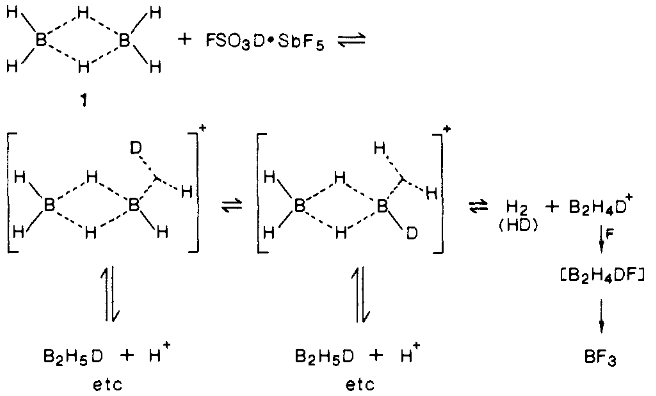
both terminal and bridged positions. A strong band was observed at 1100 cm^{-1} (characteristic of a BHD deformation in B_2H_5D) as well as the BH_2 deformation band at 1200 cm^{-1}. Peaks due to partially exchanged diboranes (from B_2H_6D to B_2HD_5) were also observed. These experiments confirm proton/deuterium exchange of diborane (B_2H_6) in the deuteriated superacidic medium.

The H/D exchange can be best rationalized by the following pathway: Deuteriation occurs exclusively on an unbridged (terminal B–H) bond resulting in a $B_2H_6D^+$ ion which is expected to undergo polytopal (bond-to-bond) rearrangement scrambling all hydrogens and deuteriums followed by proton loss leading to the exchanged product.



Alternatively diborane, B_2H_6, in equilibrium with monomeric BH_3 could react through deuteriation of the latter resulting in a $[BH_3D]^+$ which would subsequently undergo proton loss. This pathway, however, is highly unlikely since $[BH_4]^+$ is isoelectronic with the thermodynamically highly unstable $[CH_4]^{2+}$.[10]

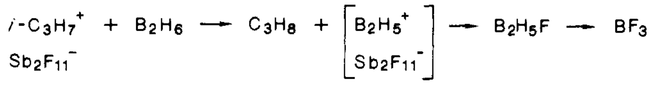
Boron trifluoride, as well as some H_2, SO_2, and SbF_3 observed as byproducts are indicative that $B_2H_7^+$ can also lose H_2 according to the equilibrium (vide infra)

$$B_2H_7^+ \rightleftharpoons H_2 + B_2H_5^+$$

The diboranium ion (i.e., $BH_2^+{\cdot}BH_3$) is immediately quenched by the counterion ($Sb_2F_{10}FSO_3^-$ or its analogues) giving B_2H_5F (or $B_2H_5OSO_2F$). Although these species were not directly observed, it is known that they readily disproportionate further eventually giving the thermodynamically stable BF_3. Boron fluorosulfates are also not stable and known to decompose to BF_3 and SO_3 (which is reduced to SO_2 under the reaction conditions). Formation of SbF_3 is also in accord with the reductive cleavage process.

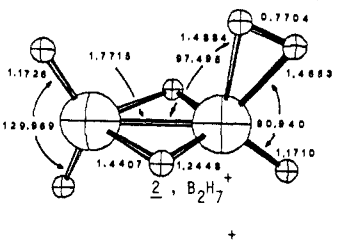
The amount of H_2 formed although small is indicative of the observed accompanying reductions. HD formation is also expected in 1/7 of the amount due to the polytopal equilibrium but was not determined. In any case exchange of B_2H_6 with HD under the present reaction conditions cannot be considered to cause the observed HD exchange in a significant way.

The diboranium ion, $B_2H_5^+$, is also readily formed when alkyl cations, such as the isopropyl cation, $i\text{-}C_3H_7^+$ prepared as a stable long-lived ion from their corresponding fluoride with SbF_5 in SO_2ClF solution, is reacted with diborane. Reduction to propane occurs, as shown by GC–MS and NMR analysis of the worked up reaction mixture, with BF_3 formed as the byproduct. Other carbocations, such as the triphenylmethyl cation are also readily reduced by diborane, and the reaction seems to be a general one.

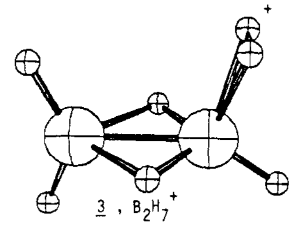


$$\underset{Sb_2F_{11}^-}{i\text{-}C_3H_7^+} + B_2H_6 \longrightarrow C_3H_8 + \left[\begin{matrix} B_2H_5^+ \\ Sb_2F_{11}^- \end{matrix}\right] \longrightarrow B_2H_5F \longrightarrow BF_3$$

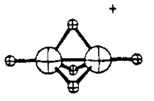
To further probe the structure and energetics of $B_2H_7^+$ and $B_2H_5^+$ ions their potential energy surfaces were investigated with ab initio theory.[11] The $B_2H_7^+$ ion proves to be a kinetically stable species. Structure **2** is at all levels of theory (HF/3-21G, HF/6-31G*, HF/6-31G**, and MP2/6-31G**) the global $B_2H_7^+$ minimum; only positive vibrational frequencies are obtained from diagonalization of the Hessian matrices. The calculated (isolated ion) protonation energy of diborane **1** → **2** is strongly exothermic (147 kcal/mol, HF/6-31G*).[12,13] The C_s geometry of **2** reflects dihydrogen coordination to one of the boron atoms; the BHB bridging hydrogens lay in a plane orthogonal to the one carrying both borons and all other hydrogens. In essence one terminal B–H bond of diborane **1** has been protonated to give a BHH three-center, two-electron bond. A 90° rotation of this BHH bond results in the 0.8 kcal/mol (MP4/6-31G**) less stable HF/6-31G** transition structure **3**. This latter species was the focus of earlier MNDO and HF/3-21G calculations.[14]



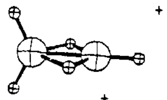
2, $B_2H_7^+$



3, $B_2H_7^+$



5, $B_2H_5^+$



4, $B_2H_5^+$

The geometries of **2** and **3** represent loose H_2–$B_2H_5^+$ associations, similar to those in neutral BH_5 (H_2–BH_3)[15] and the common hypercoordinated carbomono- and -dications.[16] The thermodynamically controlled dehydrogenation of **2** to the global $B_2H_5^+$ minimum, the triply bridged structure **5**, is exothermic by 6.9 kcal/mol at MP2/6-31G**//MP2/6-31G**. The doubly bridged $B_2H_5^+$ ion **4**, which is structurally more reminescent to **2**, is a transition structure at this level for H-scrambling in $B_2H_5^+$ with a barrier of 20.6 kcal/mol. At the Hartree–Fock level of theory isomer **4** represents a minimum. Interestingly, **4** is only 13.6 kcal/mol higher in energy than its "hydrogenated" isomer **2**; hydrogenations of classical carbocations typically give a stabilization of ca. 40 kcal/mol.[17] In earlier studies,[18] the single hydrogen bridged $B_2H_5^+$ isomer was found even less stable than **4** and **5**.

In contrast to the dehydrogenation of **2**, its dissociation into BH_3 and BH_4^+ is endothermic by 32 (HF) and 50 kcal/mol (MP4/6-31G**), which compares rather well with the dimerization energy of BH_3 of 40 kcal/mol (MP4/6-31G**). Consequently, a dissociation/recombination route would seem less probable for the acidic H/D exchange observed in diborane **1** than a direct protonation/deprotonation equilibrium.

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(10) Lammertsma, K. *J. Am. Chem. Soc.* **1984**, *106*, 4619. Pople, J. A.; Tidor, B.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1982**, *88*, 533. Siegbahn, P. E. M. *Chem. Phys.* **1982**, *66*, 443.

(11) The GAUSSIAN 86, Release C, series of programs was used: Frisch, M.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Martin, R.; Steward, J. J. P.; Bobrowicz, F.; DeFrees, D.; Seeger, R.; Whiteside, R.; Fox, D.; Fluder, E.; Pople, J. A. Carnegie-Mellon University.

(12) B_2H_6 values were taken from the following: Whiteside, R. A.; Frish, M. N.; Pople, J. A. *The Carnegie-Mellon Chemistry Archive*; Carnegie-Mellon University: Pittsburgh, PA, 1983.

(13) The HF/6-31G*, HF/6-31G**, and MP4SDTQ/6-31G** energies (in au) for the optimized geometry of **4** are −53.04670, −53.06237, and −53.29135, respectively.

(14) Pierce, R. C.; Porter, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 3849. DeKock, R. L.; Lasperse, C. G. *Inorg. Chem.* **1983**, *22*, 3843.

(15) Pepperberg, I. M.; Halgren, T. A.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1976**, *98*, 3442. Collins, J. C.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A.; Radom, L. *J. Am. Chem. Soc.* **1976**, *98*, 3446. Hoheisel, C.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1975**, *97*, 6970.

(16) Lammertsma, K. *Rev. Chem. Intermediates* **1988**, *9*, 141.

(17) Lammertsma, K.; Olah, G. A.; Barzaghi, M.; Simonetta, M. *J. Am. Chem. Soc.* **1982**, *104*, 6851.

(18) Sana, M.; Leroy, G. *J. Mol. Struct.* (*THEOCHEM*) **1987**, *151*, 307. Rastogi, R. C.; Ray, N. K. *Int. J. Quantum Chem.* **1977**, *40*, 435.