higher than the highest literature value.

In the context of the average ion bond strength of 3.98 eV, the value of 3.7 eV assigned here as the endothermicity of the first dissociation (eq 1), seems entirely reasonable as an order of magnitude. We may go further and try to understand why the energy of the first dissociation of the ion, determined here to be 3.7 eV, can be less than that of the second dissociation

$$Fe(Cp)^+ \rightarrow Fe^+ + Cp \qquad (5)$$

which must be 4.3 eV by subtraction. Ion solvation effects can account for this difference and explain the fact that the average bond energy is larger in the ion than in the neutral species. The argument is that the electronic aspects of the ring–metal bonding are probably similar for the different cases but that an additional degree of stabilization (a solvation energy) is gained from electrostatic forces when a Cp ring attaches to a gas-phase ion. The greatest solvation energy will be expected when the bare metal ion is solvated, as in eq 5; thus the dissociation energy of eq 5 should be exceptionally large. An additional but smaller stabilization will be expected in eq 1 from the solvation of the $Fe^+(Cp)$ ion by the second Cp ring, so we expect the endothermicity of eq 1 to be less than that of eq 5 but greater than the metal–ring bond strength in the neutral ferrocene which gains nothing from charge solvation stabilization. These predictions are exactly in line with what is observed.

Since the heats of formation of the other species in eq 1 are known, the present assignment of the energy of this reaction is equivalent to a heat of formation value for $Fe(C_5H_5)^+$. Subject to the same assumptions as were outlined for the bond strength assignment, we can assign a ΔH_{f298} value of 1009 ± 30 kJ mol^{-1} to $Fe(C_5H_5)^+$.

Kinetic Shift. The conventional kinetic shift can be defined[7,9] as the internal energy (in excess of the activation energy) that must be supplied to give a fragmentation rate of 1000 s^{-1} or more. It is expected to be large for ions such as this one that have a large number of vibrational modes. The rate–energy curves in Figure 2 show that the internal energy content must be at least 6 eV for the fragmentation rate to be greater than 1000 s^{-1}, corresponding to a kinetic shift of at least 2.3 eV. It is not surprising that our value for E_0 is at least 2 eV lower than the threshold of 6–7 eV based on electron impact appearance energies taken from the literature.[14,15]

Radiative Relaxation. These results represent the first attempt to measure the radiative relaxation rate of an organometallic cation in the near-thermal internal energy regime (0.25–0.75 eV). In terms of internal temperature, the range of cooling observed in these experiments was from approximately 600 to 375 K. The radiative cooling rate constant (0.28 s^{-1}) is the lowest yet measured for polyatomic ion cooling in this energy regime but is not very different from those of other slow-cooling ions, notably the *n*-butylbenzene ion[16] (0.5 s^{-1}) and the chlorobenzene ion[1] (0.4 s^{-1}). The slow observed cooling of the ferrocene ion suggests that the tendency of its relatively large heat capacity in this temperature region to depress IR-radiative cooling outweighs the IR-radiative strength of its numerous low-frequency IR-active vibrational modes.

Note Added in Proof. Prof. Amster has called to our attention a recent determination of the heat of formation of $FeCp^+$ by Huang and Freiser, uisng a very different route. (Huang, Y.; Freiser, B. S. *J. Am. Chem. Soc.* **1990**, *112*, 5085.) Their value of 1045 ± 29 kJ mol^{-1} is in gratifying agreement with our result.

Acknowledgment. Support for this research is acknowledged from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Dicoordinated Boron Cations Dehydrate Organic Ethers in the Gas Phase

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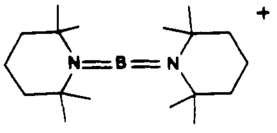
Abstract: Condensed-phase studies of two-coordinated boron cations are limited to ions with conjugatively stabilizing substituents; the reactions of these ions are dominated by simple addition. We have investigated the gas-phase reactions of two simple, dicoordinated boron cations, $CH_3OBOCH_3^+$ and $CH_3BCH_3^+$, in a dual-cell Fourier-transform ion cyclotron resonance device. These ions are found to undergo a bimolecular reaction with no well-known precedent in the gas phase or in solution: facile abstraction of a water molecule from organic ethers (the efficiency, or k_{obsd}/k_{ADO}, is measured to be 0.5–0.8). The mechanism of the reaction was investigated by using different neutral ethers, deuterium labeling, collision-activated dissociation of the ionic reaction products and the proposed ionic intermediates, bimolecular reactions of the proposed intermediates, and generating the intermediates using independent routes. On the basis of these data, dehydration of organic ethers by the boron cations is proposed to occur via consecutive 1,2-elimination of two alkene molecules from the ether. The overall reaction is estimated to be highly exothermic.

Introduction

Two-coordinated boron cations are proposed to exist as transient intermediates in solution reactions of boranes.[1] Studies of these highly electrophilic species are hampered by a rapid recombination with solvent molecules and counterions. Consequently, solution studies have predominantly focused on ions with at least one nitrogen-containing substituent (usually an amino group) which effects good electronic shielding at the boron through π-back-bonding; in addition, the substituents are typically bulky and provide steric restriction for nucleophilic attack (see an example below).[1] Reactions of these borylium ions are dominated by simple addition.[1]



Very few gaseous dicoordinated boron cations have been studied thus far;[2-5] besides addition,[2b,3,4] only simple atom[2b] and group

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[1] For recent reviews, see: (a) Nöth, H.; Rasthofer, B.; Narula, Ch.; Konstantinov, A. *Pure Appl. Chem.* **1983**, *55*, 1453. (b) Kölle, P.; Nöth, H. *Chem. Rev.* **1985**, *85*, 399.

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Table I. Rate Constants and Product Distributions Obtained for Ion–Molecule Reactions of $CH_3OBOCH_3^+$ (*m/z* 73) and $CH_3BCH_3^+$ (*m/z* 41) with Organic Molecules

reactant ion (*m/z*)	neutral reagent	ionic products (*m/z*)	branching ratio[a] (%)	k^b	k_{ADO}^b
$CH_3OBOCH_3^+$ (73)	C_4H_8O (THF)	$C_4H_8OH^+$ (73) $(CH_3O)_2BOC_4H_8^+$ (145)	*c*	*c*	1.7
	$C_2H_5OC_2H_5$	$(CH_3O)_2B(OH)_2^+$ (91)[d,e] $(CH_3O)_2BO(H)C_2H_5^+$ (119)[e] $(C_2H_5)_2OH^+$ (75)	95 5	0.7	1.5
	$C_2D_5OC_2D_5$	$(CH_3O)_2B(OD_2)^+$ (93)[e] $(CH_3O)_2BO(D)C_2D_5^+$ (125)[e] $(C_2D_5)_2OD^+$ (86)	90 10	0.9	1.5
	$CH_3(CH_2)_3OCH_3$	$C_4H_9^+$ (57)[e] $(CH_3O)_2BO(H)CH_3^+$ (105)[e] $CH_3O(H)CH_2CH_2CH_2CH_3^+$ (89) $(CH_3O)_2BO(CH_3)CH_2CH_2CH_2CH_3^+$ (161)	22 78	1.4	1.6
	$C_3H_7OC_3H_7$ (diisopropyl ether)	$(CH_3O)_2B(OH_2)^+$ (91)[e] $C_3H_7O(H)C_3H_7^+$ (103)	100	1.1	1.6
	$C_6H_5OCH_3$	$(CH_3O)_2BO(CH_3)C_6H_5^+$ (181)[e]	100	1.1	1.5
	C_2H_5OH	$(CH_3O)_2B(OH_2)^+$ (91)[e] $(CH_3O)(HO)BO(H)CH_2CH_3^+$ (105) $(CH_3O)_2BO(H)CH_2CH_3^+$ (119)	100	1.0	1.9
	CH_3OH	no products			1.9
$CH_3BCH_3^+$ (41)	$C_2H_5OC_2H_5$	$(CH_3)_2B(OH_2)^+$ (59)[e] $(CH_3)_2BO(H)C_2H_5^+$ (87)[e] $(CH_3CH_2)_2OH^+$ (75)	82 18	1.4	1.7
	$C_3H_7OC_3H_7$ (diisopropyl ether)	$(CH_3)_2B(OH_2)^+$ (59)[e] $(CH_3)_2BO(H)C_3H_7^+$ (101)[e] $C_3H_7^+$ (43) $C_3H_7O(H)C_3H_7^+$ (103)	84 16	1.1	1.9

[a] Branching ratios of primary products. [b] *k* in units of $\times 10^{-9}$ cm^3 molec^{-1} s^{-1}. [c] Reaction too slow for the measurement. [d] Reaction of the ion of *m/z* 91 with deuterium oxide yields the ions $(CH_3O)_2BOH(D)^+$ (*m/z* 92), and $(CH_3O)_2BOD(D)^+$ (*m/z* 93). [e] Denotes the primary products.

abstraction[2,3] and deprotonation[4,5] reactions have been observed. We report herein the first study on the solvent-free reactions of the strong Lewis acids $CH_3O-B^+-OCH_3$ and $CH_3-B^+-CH_3$ with organic ethers and alcohols. These ions are found to be exceedingly reactive toward oxygen lone pairs in organic substrates. Furthermore, they undergo an interesting reaction with no well-known precedent in the gas phase or in solution: *facile ionic dehydration of organic ethers*. On the basis of a variety of experimental evidence, the reaction is proposed to take place via consecutive 1,2-elimination of two neutral alkenes from the ether molecule.

Experimental Section

All the experiments were carried out in a prototype Extrel FTMS-2001 Fourier-transform ion cyclotron resonance mass spectrometer (FT-ICR) described in detail before.[6] The base pressure in this instrument is < 1 × 10^{-9} Torr. The instrument contains a differentially pumped dual-cell reaction chamber aligned collinearly in the magnetic field produced by a 2.9-T superconducting magnet. The cell consists of two cubic 2″ cells sharing one common wall (the conductance limit plate). Ions are transferred from one cell into another through a 2-mm hole in the middle plate by grounding this plate; at all other times, all the three trapping plates (plates parallel to the magnetic field lines) are kept at +2 V.

All the reagents were obtained commercially and used as received. Samples were introduced into the FT-ICR through a commercial leak valve, an Extrel-manufactured, heated batch inlet system equipped with a leak valve, or a set of pulsed valves. The uncorrected reagent pressures were 1.2 × 10^{-7} Torr, as measured by an ionization gauge on each side of the dual cell. For rate measurements, the ion gauges were calibrated by measuring apparent rates for reactions with known rate constants.[7] The precision of the rate measurements is better than ±5%; the accuracy is estimated to be better than ±50%. The reported reaction rates and the branching ratios for the primary products were found to be independent of the electron energy and the ionization time used, boron or deuterium substitution, and the method used to cool the reactant ions (see below). All the primary reaction products (products arising directly from the boron cations) are included in the illustrations and tables.

The neutral molecules were ionized by electron impact in one side of the dual cell. Electron energy, emission current, and the ionization time were optimized separately for each reaction. After transfer into the other side of the dual cell, the ions were relaxed internally and kinetically by many collisions (50–100) with argon pulsed into this chamber. A decay of the logarithm of the signal of the parent ion (see, for example, Figure 3) is linear over the entire time monitored (at least three half-lives). Collisional cooling using a number of different organic polyatomic targets resulted in the same ionic products, same branching ratios, and same rate constants as collisional cooling using argon.

After collisional cooling of the ions, the interesting ions were isolated by ejecting all the unwanted ions from the cell through the application of an appropriate combination of single frequency voltage pulses and radiofrequency sweeps to the excitation plates of the cell. During this process, special care was taken to avoid excitation of the ions to be isolated. After isolation, the ions were reacted with the desired neutral reagent for a variable reaction time.

All the collision-activated dissociation experiments were carried out using argon collision gas; this was the only neutral reagent in the cell during collisional activation. The isolated ions were kinetically excited by using an excitation pulse with a fixed amplitude (3 V_{p-p}) and a frequency equal to the cyclotron frequency of the ion to be activated. The duration of the pulse (usually <300 μs) determines the final laboratory ion kinetic energy, as described earlier.[8] A time period of 100 ms was allowed for collisional activation of the ions with argon (1.2 × 10^{-7} Torr) after the excitation pulse.

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(2) $CH_3BCH_3^+$: (a) Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 1433. (b) Kappes, M. M.; Uppal, J. S.; Staley, R. H. *Organometallics* **1982**, *1*, 1303.

(3) BF_2^+: Forte, L.; Lien, M. H.; Hopkinson, A. C.; Bohme, D. *Can. J. Chem.* **1990**, *68*, 1629.

(4) CH_3OBOH^+: Hettich, R. L.; Cole, T.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Processes* **1987**, *81*, 203.

(5) $HOBOH^+$: Attina, M.; Cacace, F.; Ricci, A.; Grandinetti, F.; Occhiucci, G. *J. Chem. Soc., Chem. Commun.* **1991**, 66.

(6) Farrell, J. T., Jr.; Lin, P.; Kenttämaa, H. I. *Anal. Chim. Acta* **1991**, *246*, 227.

(7) Ikezoe, Y.; Matsuoka, S.; Takebe, M.; Viggiano, A. *Gas-Phase Ion Molecule Reaction Rate Constants Through 1986*; Maruzen Co., Ltd.: Tokyo, Japan, 1987.

(8) For experimental details, see: Zeller, L. C.; Farrell, J., Jr.; Vainiotalo, P.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1992**, *114*, 1205.

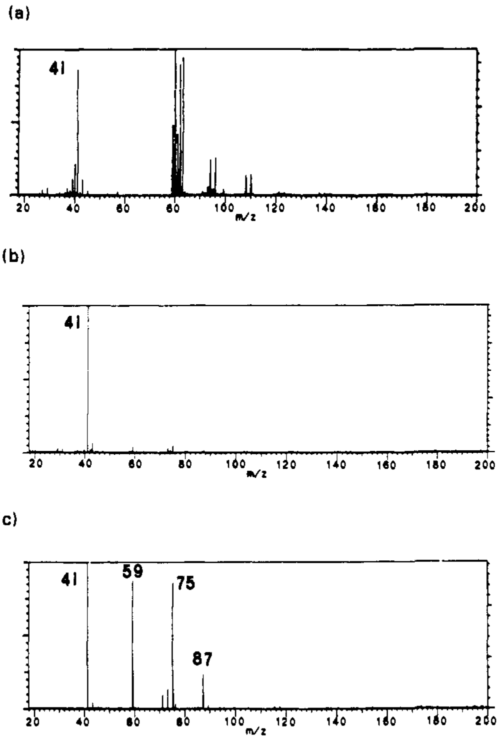

Figure 1. (a) Electron impact ionization of $(CH_3)_2BBr$. (b) Transfer of the ions into the other reaction chamber, followed by isolation of the fragment ion $CH_3{-}^{11}B{-}CH_3^+$ (*m/z* 41). (c) Reaction of the ion of *m/z* 41 with diethyl ether (uncorrected pressure 1.2×10^{-7} Torr) for 800 ms. The primary products were identified as the ion of *m/z* 59, $(CH_3)_2B{-}OH_2^+$, and the ion of *m/z* 87, $(CH_3)_2B{-}O(H)CH_2CH_3^+$. The ion of *m/z* 75 is protonated diethyl ether formed upon reaction of the primary products with neutral diethyl ether.

All the spectra shown are the average of at least 10 spectra acquired using an excitation sweep with 107-V (p–p) amplitude, 2.7-MHz bandwidth, and 3.2-kHz/μs sweep rate. The spectra were recorded as 32-K data points, and subjected to one zero fill before Fourier transformation.

Results and Discussion

The ions $CH_3{-}B^+{-}CH_3$ and $CH_3O{-}B^+{-}OCH_3$ were generated by dissociative electron ionization of $(CH_3)_2BBr$ (Figure 1a) and $(CH_3O)_3B$, respectively, added to one side of the dual-cell reaction chamber. The ions were transferred into the other reaction chamber and collisionally relaxed with argon, and all unwanted ions were ejected from the cell. The isolated ions $CH_3{-}B^+{-}CH_3$ (Figure 1b) and $CH_3O{-}B^+{-}OCH_3$ were allowed to react with neutral reagents for different time periods (for $CH_3{-}B^+{-}CH_3$, see Figure 1c). These ions undergo very fast reactions with organic molecules. For most of the neutral reagents studied, abstraction of water by the ion is the predominant exit channel for the collision complex (Table I). Proton-catalyzed dehydration of alcohols is a well-known[9] reaction in the gas phase. However, the observed very facile ionic dehydration of diethyl and diisopropyl ethers (more than every second collision[10] leads to a product) is a notable reaction with no well-known precedent.

The mechanism of the reaction leading to abstraction of water from diethyl ether by the ions $CH_3{-}B^+{-}CH_3$ and $CH_3O{-}B^+{-}OCH_3$ was examined by using different experimental approaches. The product ions obtained for ^{10}B-boron cations have a one unit lower *m/z* values than those obtained from the ^{11}B-boron cations, thus indicating the presence of boron in the product ions. When a perdeuterated ether, such as d_{10}-diethyl ether, is used as the reagent, abstraction of D_2O takes place (*m/z* 93, Figure 3); no scrambling of hydrogen and deuterium atoms within the ion-molecule complex is observed. Upon collisional activation, the product ion from the reaction of $CH_3O{-}^{11}B^+{-}OCH_3$ with diethyl ether (the ion of *m/z* 91; Table II)[8] readily loses water and

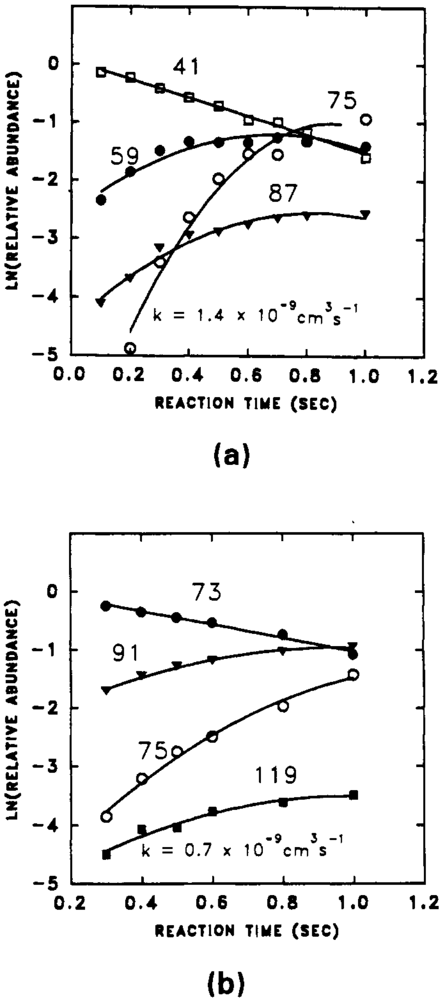

Figure 2. Temporal variation of the ion abundances for the reactions of (a) $CH_3{-}^{11}B^+{-}CH_3$ (*m/z* 41) and (b) $CH_3O{-}B^+{-}OCH_3$ (*m/z* 73) with diethyl ether (uncorrected pressure 1.2×10^{-7} Torr). Abstraction of ethanol and water yields the primary products which have the mass values of *m/z* 87 and 59, respectively, for $CH_3{-}B^+{-}CH_3$, and *m/z* 119 and 91, respectively, for $CH_3O{-}B^+{-}OCH_3$. The ion of *m/z* 75 is protonated diethyl ether formed upon reaction of the primary product ions with neutral diethyl ether.

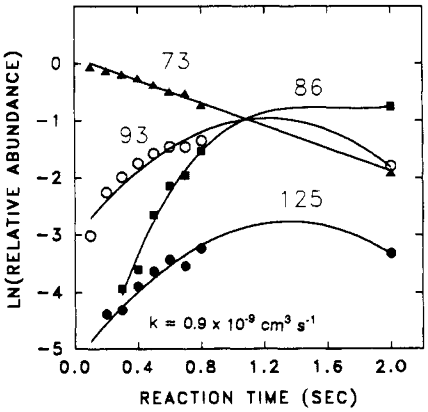

Figure 3. Temporal variation of the ion abundances for the reaction of $CH_3O{-}B^+{-}OCH_3$ (*m/z* 73) with d_{10}-diethyl ether (nominal pressure 1.2×10^{-7} Torr).

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[9] See, for example: (a) McAdoo, D. J. *Mass Spectrom. Rev.* **1988**, *7*, 363. (b) Harrison, A. G. *Org. Mass Spectrom.* **1987**, *22*, 637. (c) Bouchoux, G.; Hoppilliard, Y. *J. Am. Chem. Soc.* **1990**, *112*, 9110 and references therein. (d) Swanton, D. J.; Marsden, D. C. J.; Radom, L. *Org. Mass Spectrom.* **1991**, *26*, 227.

[10] Efficiency = k_{obsd}/k_{ADO}; k_{ADO} was calculated according to the following: (a) Chesnavich, W. J.; Su, T.; Bowers, M. *J. Chem. Phys.* **1980**, *72*, 2641. (b) Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183.

Table II. CAD Products of Selected Borocations

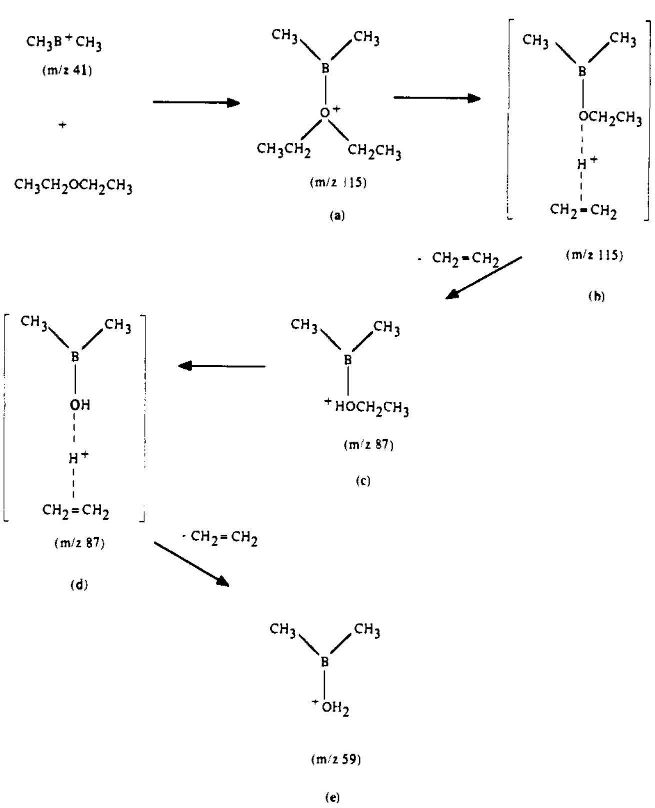
fragmenting ion (m/z)	kinetic energy (eV)	fragment ions, m/z (%)[a]
$(CH_3)_2BO(H)C_2H_5^+$ (87)	10	no fragments
	30	no fragments
	50	41 (35)[b], 59 (100)[c]
	100	41 (85), 59 (100)
	125	41 (93), 43 (25)[d], 59 (100)
	150	41 (100), 43 (52), 59 (100)
	200	41 (100), 43 (60), 59 (76)
$(CH_3O)_2B(OH_2)^+$ (91)	10	no fragments
	30	no fragments
	50	59 (25)[e], 73 (100)[f]
	60	59 (40), 73 (100)
	80	59 (100), 73 (87)
	100	59 (100), 73 (90)
$(CH_3O)_2BO(H)CH_3^+$ (105)	10	no fragments
	30	no fragments
	50	43 (7)[g], 72 (32), 73 (100)[h]
	75	43 (14), 72 (18), 73 (100)
	100	43 (7), 72 (10), 73 (100)

[a] Relative ion abundance normalized to the most abundant fragment. [b] $CH_3BCH_3^+$. [c] $(CH_3)_2B(OH_2)^+$. [d] CH_3BOH^+. [e] CH_3OBOH^+. [f] $CH_3OBOCH_3^+$. [g] $HBOCH_3^+$. [h] $(CH_3O)_2B^+$.

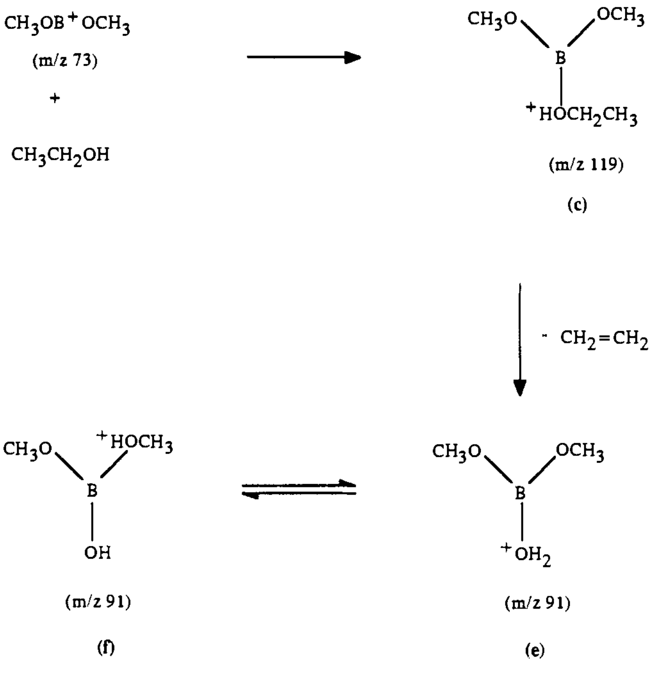
methanol, resulting in the ions $CH_3O{-}^{11}B^+{-}OCH_3$ (m/z 73) and $CH_3O{-}^{11}B^+{-}OH$ (m/z 59), respectively. Although rearrangement reactions may dominate the fragmentation of gas-phase ions at low excitation energies, highly excited ions usually preferentially fragment by direct bond cleavages.[11] Hence, the fragmenting ion is concluded to be a mixture of $(CH_3O)_2B{-}OH_2^+$ and $(CH_3OH)(CH_3O)B{-}OH^+$ (more stable). It is conceivable that these two structures may actually exist in a dynamic equilibrium. When the ion of m/z 91 is allowed to react with D_2O, a partial exchange of two hydrogen atoms with deuterium atoms occurs. The observation of nonlinear decay of the reactant ion supports the proposal that two different structures of m/z 91 are present, and that one of these structures, presumably $(CH_3OH)(CH_3O)B{-}OH^+$, does not undergo H/D exchange with D_2O.

Several bonds must be broken upon elimination of water from an ether. The mechanism presented in Scheme I for the reaction of $CH_3{-}B^+{-}CH_3$ with diethyl ether is thought to apply also for $CH_3O{-}B^+{-}OCH_3$. This mechanism is in agreement with all of our experimental results, including the fact that dehydration is observed for both the ions $CH_3O{-}B^+{-}OCH_3$ and $CH_3{-}B^+{-}CH_3$. Thus, the oxygen atoms in the former ion cannot play a crucial role in the reaction. The same applies to deprotonation of the latter ion (to give $CH_3B{=}CH_2$).[12,13] The proposed mechanism involves stepwise loss of two molecules of ethylene from the initial addition product (a: m/z 115, not directly observed). Direct cleavage of a C–O bond in the intermediate a would lead to an ethyl cation and $(CH_3)_2B{-}OCH_2CH_3$. Ethyl cation, however, is not observed. Hence, during or after the C–O bond cleavage, interaction between the ethyl cation and $(CH_3)_2B{-}OCH_2CH_3$ must occur within the ion–molecule complex, perhaps as depicted in Scheme I. Structure b is simply a bridged ethyl cation[14] interacting with an oxygen lone pair of $(CH_3)_2B{-}OCH_2CH_3$ through a hydrogen bond. This sort of an interaction could give rise to the observed products $CH_2{=}CH_2$ and $(CH_3)_2BO(H)CH_2CH_3^+$ (c). The intermediate c, if created with enough internal energy, is expected to eliminate ethylene through a process closely resembling proton-catalyzed dehydration of alcohols in the gas phase.[9,15]

Scheme I



Scheme II



Support for the proposed mechanism is obtained from a number of experimental results, including the observation of a minor product with a mass value corresponding to the intermediate c: an ion of m/z 119 is generated upon reaction of $CH_3O{-}^{11}B^+{-}OCH_3$ with diethyl ether (Figure 2b), and an ion of m/z 87 is obtained upon reaction of $CH_3{-}B^+{-}CH_3$ with diethyl ether (Figures 1c and 2a). Upon collisional activation, the ion of m/z

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(11) See, for example: (a) *Tandem Mass Spectrometry*; McLafferty, F. W., Ed.; John Wiley and Sons, New York: 1983. (b) Busch, K. L.; Glish, G. L.; McLuckey, S. A. *Mass Spectrometry/Mass Spectrometry*; VCH Publishers, Inc.: New York, 1988.

(12) Deprotonation of the ion $CH_3{-}B^+{-}CH_3$ cannot play an important part in the reaction involving this ion: the proton affinity of $CH_3{-}B{=}CH_2$ is too high (220 kcal/mol[4]) for a neutral ether to be able to deprotonate its conjugate acid, $CH_3{-}B^+{-}CH_3$, even within the ion–molecule complex.

(13) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, G. *J. Phys. Chem. Ref. Data* **1988**, 17.

(14) For the structure of ethyl cation, see, for example: *Ab Initio Molecular Orbital Theory*; Hehre, W. J., Radom, L., Schleyer, P. v. R., Pople, J. A., Eds; John Wiley and Sons, Inc.: New York, 1986; pp 384–385.

(15) For proton-catalyzed loss of an alkene from alkyl aryl ethers, see, for example: Kondrat, R. W.; Morton, T. H. *J. Org. Chem.* **1991**, *56*, 952 and references therein.

119 yields the final product of the dehydration reaction. The same is true for the ion of m/z 87 (Table II): at low excitation energies, this ion yields an abundant fragment ion of m/z 59 which further decomposes by loss of water to yield an ion of m/z 41 (a small amount of an ion of m/z 43 is also obtained at very high excitation energies). These findings suggest that some of the intermediates c are generated with an insufficient amount of energy for further reaction but that the reaction can be induced by collisional activation. Reaction of $CH_3O-{}^{10}B^+-OCH_3$ with diethyl ether yields an intermediate ion of m/z 118 instead of m/z 119. This demonstrates that the proposed intermediate contains boron. Further, reaction of $CH_3O-{}^{11}B^+-OCH_3$ with d_{10}-diethyl ether yields an ion corresponding to c with six deuterium atoms (m/z 125; Figure 3). Thus, all the hydrogen atoms in the first eliminated ethylene must originate from the ether. Finally, an ion corresponding to the intermediate c must be generated upon collisions of $CH_3O-{}^{11}B^+-OCH_3$ with ethanol (Scheme II). This ion decomposes spontaneously by loss of ethylene (Table I) to yield the ions e and/or f shown in Scheme II.

Alcohols that cannot lose an alkene according to Scheme II are not dehydrated by the boron cations. For example, methanol does not undergo any apparent reaction with $CH_3O-B^+-OCH_3$. Further, ethers that cannot lose two alkenes according to Scheme I are not dehydrated. Only slow condensation[2a] is observed for anisole and tetrahydrofuran (Table I). *n*-Butyl methyl ether undergoes a facile reaction (efficiency 0.9) with $CH_3O-{}^{11}B^+-OCH_3$ to yield an ion corresponding to the intermediate c: $(CH_3O)_2B-O(H)CH_3^+$ (m/z 105). Collision-activated dissociation of this product ion (Table II) is in agreement with the structural assignment: loss of methanol dominates the fragmentation.

The reaction of $CH_3O-B^+-OCH_3$ with *n*-butyl methyl ether yielding $(CH_3O)_2B-O(H)CH_3^+$ and neutral butene is analogous to the first elimination step in Scheme I. In order to obtain an estimate for the enthalpy change associated with this reaction, the proton affinity of trimethyl borate was determined. Protonated trimethyl borate was allowed to react with *n*-propanol (proton affinity 190.8 kcal/mol[13]), *sec*-butanol (proton affinity 195.0 kcal/mol[13]), tetrahydropyran (proton affinity 199.7 kcal/mol[13]), and diethyl ether (proton affinity 200.2 kcal/mol[13]). Proton transfer was observed to occur only to tetrahydropyran and diethyl ether. This brackets the proton affinity of trimethyl borate between that of *sec*-butanol and tetrahydropyran (195.0–199.7 kcal/mol). Hence, the elimination of butene from *n*-butyl methyl ether by the ion $CH_3O-B^+-OCH_3$ is estimated[16] to be exothermic by at least 50 kcal/mol. For diethyl ether, the elimination of two ethylenes by $CH_3O-B^+-OCH_3$ is estimated to be exothermic by at least 40 kcal/mol.[16,17]

The hydrogen-bonded structures b and d, if they occur as distinct intermediates on the reaction path, are not likely to be long-lived (they may actually correspond to transition states). This is indicated by results obtained upon investigation of the bimolecular reactions of an ion of m/z 93 corresponding to either c or b with six deuteriums (i.e., $(CH_3)_2B-O(D)CD_2CD_3^+$; from the reaction of $CH_3-{}^{11}B^+-CH_3$ with d_{10}-diethyl ether). The ion of m/z 93 is unreactive toward neutral ethylene. A facile exchange of deuterated ethylene with undeuterated ethylene is expected to take place for this ion if it had the structure d. Thus, the covalently bound structure c is more likely for the long-lived ion of m/z 93.

Conclusions

The B–O bond is among the strongest of all chemical bonds. Formation of this bond is likely to be the driving force for the observed abstraction of a water molecule from dialkyl ethers by dicoordinated boron cations. Initial addition of an ether molecule to the boron cation is highly exothermic, and some of this energy is used to eliminate first one and then a second alkene from acyclic ethers with alkyl groups that can be eliminated as alkenes. The high reactivity of the ions studied explains, in part, the difficulty to study simple dicoordinated boron cations in organic solvents. In sharp contrast, analogous carbon and phosphorus ions, e.g., $CH_3O-CH-OCH_3^+$ and $CH_3O-P-OCH_3^+$, were found to be unreactive toward diethyl ether in the gas phase. We are currently investigating reactions of gaseous dicoordinated boron cations with a variety of other organic substrates.

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[16] $(CH_3O)_3B$, $\Delta H_f = -215.7$ kcal/mol (ref 13); $CH_3(CH_2)_3OCH_3$; $\Delta H_f = -61.7$ kcal/mol (ref 13); $CH_3CH_2CH{=}CH_2$; $\Delta H_f = -0.1$ kcal/mol (ref 13); $CH_3O-B^+-OCH_3$, $\Delta H_f \simeq 66$ kcal/mol (AM1).

[17] $(CH_3O)_2BOH_2^+$, $\Delta H_f = -61$ kcal/mol, on the basis of $(CH_3O)_2B-OH$, $\Delta H_f = -251$ kcal/mol (estimated using Benson's method), proton affinity on OH 176 kcal/mol (proton affinity of $(HO)_3B$, ref 5); diethyl ether, $\Delta H_f = -60.1$ (ref 13); ethylene, $\Delta H_f = 12.5$ (ref 13).

The Identification of Distonic Radical Cations on the Basis of a Reaction with Dimethyl Disulfide

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Abstract: A novel bimolecular reaction selective for radical cations with spatially separated radical and charge sites (distonic ions) is reported. Gas-phase reactions of dimethyl disulfide with radical cations containing oxygen functionalities were studied in a dual-cell Fourier-transform ion cyclotron resonance mass spectrometer. Conventional radical cations (generated by removing an electron from a stable neutral molecule), as well as enol radical cations, undergo fast charge exchange with dimethyl disulfide. However, distonic radical cations abstract $CH_3S^\bullet$ from dimethyl disulfide (the reaction is often accompanied by charge exchange). Related even-electron cations are unreactive toward dimethyl disulfide. Hence, the observation of $CH_3S^\bullet$ abstraction is indicative of a distonic ion structure. This approach was used to identify two distonic ions formed in ion–molecule reactions involving other distonic ions. One of these product ions is a novel sulfur-containing distonic ion: $(CH_3)_2S^+-CH_2^\bullet$.

Introduction

Characterization of the structure of a gaseous radical cation is a difficult and time-consuming task. Various experimental strategies, usually based on a combination of different types of data, have been developed just for the determination of the connectivity of atoms in polyatomic ions.[1] The recognition of the stability[2] and generality[3] of *distonic ions*, ions with spatially

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[1] See, for example: (a) McLafferty, F. W. *Science* **1981**, *214*, 280. (b) Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169.

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