

Gaseous Borate and Polyborate Anions

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Borate and polyborate anions have been studied in the gas phase by an approach involving, instead of vaporization of preformed ions, gas-phase synthesis of increasingly complex polyanions by stepwise addition of H_3BO_3 , followed by H_2O loss, to $H_2BO_3^-$, obtained in turn from gaseous H_3BO_3 via dissociative electron attachment or by suitable ion-molecule reactions. Chemical ionization and ion-cyclotron resonance techniques demonstrate the formation, in addition to BO_2^- and $H_2BO_3^-$, of polyanions belonging to three different classes, $(H_{n-1}B_nO_{2n})^-$, $(H_{n+1}B_nO_{2n+1})^-$, and $(H_{n+3}B_nO_{2n+2})^-$, containing up to 11 B atoms. The results provide the first evidence for the existence as discrete entities in the gas phase of free polyanions, e.g., the triborate ion $H_4B_3O_7^-$ and the pentaborate ion $H_4B_5O_{10}^-$, whose salts exist in solid borates and in solution. Furthermore, previously unknown anions have been obtained, including gaseous $H_2BO_3^-$, $H_3B_2O_5^-$, $H_3B_4O_9^-$, etc. The character of the H_3BO_3 acidity changes in passing from solution to the gas phase. In solution H_3BO_3 behaves exclusively as a Lewis acid, giving $B(OH)_4^-$ upon ionization, whereas in the gas phase it behaves instead as a Brønsted acid, as shown by the formation of its conjugate base $H_2BO_3^-$ and by its gas-phase Brønsted acidity, 354 ± 4 kcal mol⁻¹, typical of a relatively weak gaseous acid whose strength is comparable to that of HClO.

The existence of borate and polyborate anions has been established by X-ray diffraction studies in ionic crystals¹⁻⁸ and in certain borate glasses.^{9,10} Several, but not all, of the anions identified in the solid phase exist in solution, where the complex equilibria among borates and polyborates have been extensively investigated by cryoscopy, IR, NMR, and Raman spectroscopy, and by pH, conductance, and temperature jump measurements.¹¹⁻¹⁶

The discrepancies noted between solid phases and solution reflect a general state of affairs, in that the existence of a given anion in a certain condensed system depends on many factors in addition to its intrinsic stability. Thus, the size and the charge of the cation contained in the lattice determine to a large extent which particular anion, or polyanion, exists in a crystalline borate, whereas the concentration, the pH, and the temperature of aqueous borate solutions determine the nature and the distribution of the anions.

The above considerations suggest that extension of the study to the gas phase could be useful in the area of borates and polyborates chemistry, allowing one to establish whether a given anion is capable of existence in isolation as a discrete entity, rather than just as a component of a complex system, and to

study its properties and reactivity unperturbed by the environmental factors typical of condensed media. Furthermore, only the study of free, gaseous ions can provide direct comparison terms to the increasingly sophisticated and accurate theoretical approaches.

Until recently, mass spectrometric studies have been severely limited by the low volatility and/or by the thermal instability of the species of interest. As a matter of fact, only BO^- and BO_2^- ions have been detected in the mass spectra of boron-containing flames,¹⁷ in the vapors from Knudsen cells heated up to 2100 K,¹⁸ and from hot filaments coated with boron compounds.¹⁹⁻²¹

We report here a different approach, stimulated by recent studies showing that concentrations of H_3BO_3 vapors adequate to mass spectrometric studies can be obtained by low-temperature sublimation techniques.²²⁻²⁴ Thus, instead of trying to vaporize preformed polyanions from solid borates heated to very high temperatures, we aimed at building up polyborate anions in the gas phase by the stepwise addition of H_3BO_3 to the $H_2BO_2^-$ anion, obtained in turn via dissociative electron attachment or by a suitable ion-molecule reaction from gaseous H_3BO_3 .

Experimental Section

Materials. The gases used, whose stated purity exceeded 99.99 mol %, were research-grade products from Matheson. The boric acid samples and the other chemicals were research-grade products from commercial sources and were used without further purification.

Instruments. The CI mass spectra were recorded using a QMD-1000 quadrupole instrument, equipped with a variable-temperature probe from C.Erba Instruments, or a ZAB-2F magnetic spectrometer, whose source was fitted with a specially built thermostatically controlled direct-insertion

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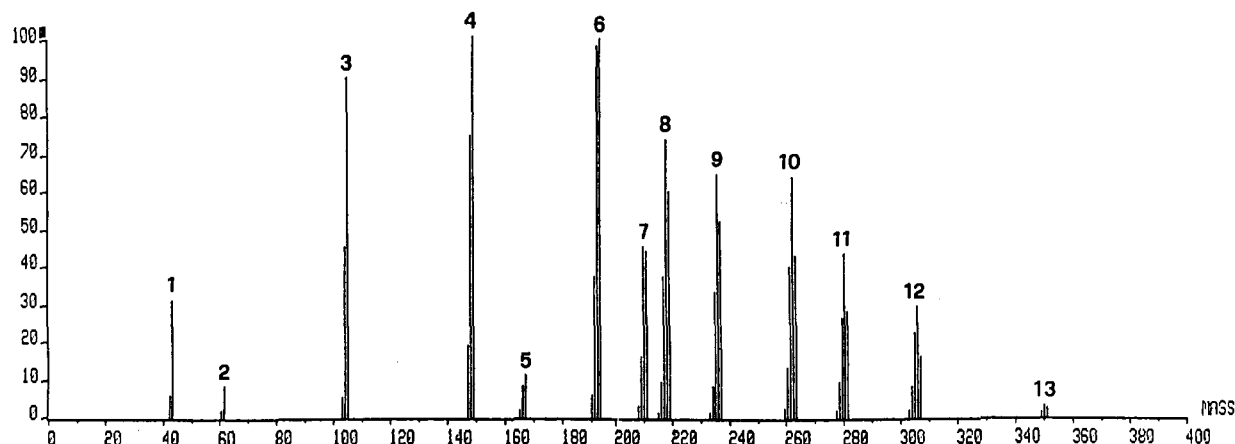


Figure 1. Negative-ion CH_4 mass spectrum of H_3BO_3 , recorded at 0.5 Torr, 150 °C, and solid probe temperature of 80 °C. Peaks of relative intensity below 1% are now shown: 1, BO_2^- ; 2, H_2BO_3^- ; 3, $\text{H}_3\text{B}_2\text{O}_5^-$; 4, $\text{H}_4\text{B}_3\text{O}_7^-$; 5, $\text{H}_6\text{B}_5\text{O}_9^-$; 6, $\text{H}_5\text{B}_4\text{O}_9^-$; 7, $\text{H}_7\text{B}_6\text{O}_{10}^-$; 8, $\text{H}_4\text{B}_5\text{O}_{10}^-$; 9, $\text{H}_6\text{B}_5\text{O}_{11}^-$; 10, $\text{H}_5\text{B}_6\text{O}_{12}^-$; 11, $\text{H}_7\text{B}_6\text{O}_{13}^-$; 12, $\text{H}_6\text{B}_7\text{O}_{14}^-$; 13, $\text{H}_7\text{B}_8\text{O}_{16}^-$.

probe and a MKS Baratron 221 A capacitance manometer. The ICR spectra were recorded using a Nicolet FTMS 1000 instrument, equipped with a manometer and a thermostatically controlled direct-insertion probe. The electron-capture negative-ion CI spectra were recorded in CH_4 , at a pressure range of ca. 0.5 Torr, whereas the OH^-/CI spectra were recorded using an equimolecular $\text{N}_2\text{O}/\text{N}_2/\text{H}_2$ reactant-gas mixture.

Results

Vaporization and Partial Pressure of H_3BO_3 . A recent study has shown that the vapors emitted from solid H_3BO_3 contained in a thermostated probe consist, at temperatures ranging from 20 to 100 °C, of a mixture of H_3BO_3 and H_2O , the latter arising from the partial dehydration of the sample.²⁴ The composition and the pressure of the vapors depend markedly on the temperature of the probe and change with time, which makes the accurate measurement of the H_3BO_3 pressure in the ion source difficult. Approximate values can be calculated by measuring the total pressure and taking into account the mole fraction of H_3BO_3 , deduced in turn from the abundances of the H_3BO_3^+ and H_2O^+ ions in the 75-eV electron impact (EI) mass spectrum of the vapors, corrected for the known ratio of the ionization efficiencies of boric acid and water.²⁵ The pressure estimated according to such an indirect and approximate procedure is affected by a large uncertainty, which however does not introduce intolerably large errors into the derived thermodynamic data. E.g., even the extreme and unrealistic assumption that the vapor consists exclusively of H_3BO_3 molecules would affect the estimated pressures by a factor <4 , introducing in turn an uncertainty of $<1 \text{ kcal mol}^{-1}$ into the ΔG°_{298} value deduced from the measured equilibrium constant of a proton-transfer reaction.

The results of the above outlined procedure show that at a probe temperature of 20 °C the partial pressure of H_3BO_3 is low ($\sim 10^{-7}$ Torr) but the emission of the vapor from the solid persists for hours. Raising the probe temperature increases the H_3BO_3 pressure, at the expense however of the emission time, e.g., $p(\text{H}_3\text{BO}_3) \sim 3 \times 10^{-5}$ Torr at 80 °C, with an emission time down to a few minutes. The spent sample consists largely of undecomposed H_3BO_3 , emission from which is prevented by a surface layer of involatile material, most likely HBO_2 .

Negative Ion CI Spectra. Closely similar spectra are obtained by electron attachment to H_3BO_3 and by proton abstraction from H_3BO_3 by OH^- ions. The abundances of the individual anions are influenced by the temperature of the H_3BO_3 sample, which affects the H_3BO_3 pressure and the $\text{H}_3\text{BO}_3/\text{H}_2\text{O}$ ratio in the vapor, as discussed in the previous section, as well as by the ion-source temperature and by the reactant-gas pressure. In general, increasing the temperature of the probe and of the source increases

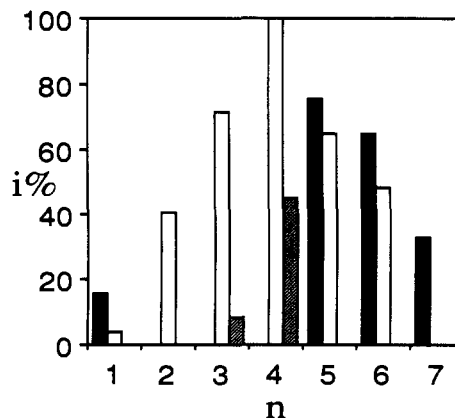


Figure 2. Relative abundances of borate and polyborate anions in the spectrum of Fig. 1 plotted as a function of the number of B atoms: ■ = $(\text{H}_{n-1}\text{B}_n\text{O}_{2n})^-$ ions; □ = $(\text{H}_{n+1}\text{B}_n\text{O}_{2n+1})^-$ ions; ▨ = $(\text{H}_{n+3}\text{B}_n\text{O}_{2n+2})^-$ ions.

the relative abundances of the higher polyanions. A typical spectrum, recorded in CH_4 (ca. 0.5 Torr, 150 °C) at a probe temperature of 80 °C displays the characteristic isotopic multiplets of borate and polyborate anions containing up to eight B atoms (Figure 1). We shall restrict the discussion to species containing up to seven B atoms, which appear in the spectra as isotopic clusters whose major peaks have intensities significantly higher than the background, in the correct ratios expected for the corresponding B_n multiplet. However, the spectra display low-intensity peaks at m/z ratios suggestive of the occurrence of higher polyanions, and there is little doubt that specifically designed experiments, carried out with appropriate techniques, will succeed in detecting species containing tens of B atoms. As a matter of fact, preliminary experiments based on the use of highly enriched $\text{H}_3^{10}\text{BO}_3$ have allowed detection of polyions containing up to 11 B atoms.

Owing to the increase in multiplicity of the isotopic clusters with increasing number of B atoms, raw mass spectra do not allow direct evaluation of the relative abundances of the various anions. A better representation is provided by a reconstructed graph, like the one reproduced in Figure 2, derived from the spectrum of Figure 1 by combining the intensities of all peaks belonging to the same multiplet.

In addition to the monomeric BO_2^- and H_2BO_3^- anions, the negative CI spectra display polyanions belonging to three distinct classes, which differ for the water content: class I, $(\text{H}_{n-1}\text{B}_n\text{O}_{2n})^-$ anions, detected only when $n > 4$; class II, $(\text{H}_{n+1}\text{B}_n\text{O}_{2n+1})^-$ anions, detected for n values up to 6, which are particularly abundant when $n = 3, 4$, and 5; class III, $(\text{H}_{n+3}\text{B}_n\text{O}_{2n+2})^-$ anions, detected only when $n = 3$ and 4.

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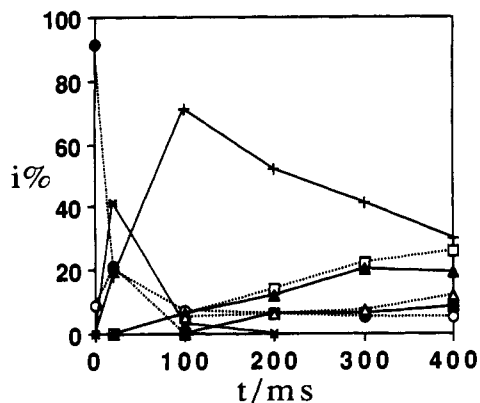


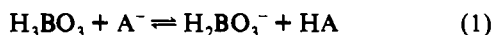
Figure 3. Growth of polyborate anions from H_2BO_3^- ions isolated by multiple resonance in $\text{H}_3\text{BO}_3/\text{H}_2\text{O}$ vapors at 35 °C and total pressure 7×10^{-7} torr: (O) BO_2^- ; (●) H_2BO_3^- ; (X) $\text{H}_3\text{B}_2\text{O}_5^-$; (+) $\text{H}_4\text{B}_3\text{O}_7^-$; (□) $\text{H}_5\text{B}_4\text{O}_9^-$; (■) $\text{H}_4\text{B}_5\text{O}_{10}^-$; (▲) $\text{H}_6\text{B}_5\text{O}_{11}^-$; (Δ) $\text{H}_5\text{B}_6\text{O}_{12}^-$.

ICR Mass Spectrometry. The problem of establishing the reaction sequences leading to formation of the polyanions detected in the CI experiments has been addressed by ICR spectrometry, utilizing in particular the multiple-resonance technique which allows isolation of a given precursor and determination of the charged products from its reactions with the neutral species present in the ICR cell.

Of the two monomeric anions BO_2^- is unreactive toward H_3BO_3 under ICR conditions, whereas H_2BO_3^- is the precursor of all polyborates via a sequence of steps, each of whose involves addition of H_3BO_3 and elimination of H_2O . Figure 3 illustrates the growth of polyborate anions from H_2BO_3^- , isolated by multiple resonance and allowed to react at 35 °C with $\text{H}_3\text{BO}_3/\text{H}_2\text{O}$ vapors at a total pressure of ca. 2×10^{-6} Torr. The plot, typical of consecutive reactions, shows the fast disappearance of H_2BO_3^- that yields $\text{H}_3\text{B}_2\text{O}_5^-$, rapidly converted into $\text{H}_4\text{B}_3\text{O}_7^-$, a considerably less reactive anion which slowly produces $\text{H}_5\text{B}_4\text{O}_9^-$, and so forth. A systematic study based on the isolation of all the B_1 – B_5 anions, has allowed us to establish the parent–daughter relationships illustrated in Figure 4, and to estimate the relative rate of several addition/elimination steps.

Taking as a reference the fastest process among such processes, namely the addition of H_2BO_3^- to H_3BO_3 , i.e. setting $k_{1,2} = 1.0$, one obtains $k_{2,3} \sim 0.5$ and $k_{3,4} \sim 0.1$, which reflects in quantitative terms the trends clearly apparent from Figure 3. As to the absolute values of the above rate constants, an accurate evaluation is prevented by the large uncertainty affecting the measurement of the H_3BO_3 pressure. A crude estimate leads to a $k_{1,2}$ value of the order of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which would characterize the addition/elimination reaction as a highly efficient process. As a final remark, it is worth noting that the ICR spectra recorded at sufficiently long storage times display all the anions observed in the CI mass spectra with the number of B atoms being <6 , with the exception of the $\text{H}_6\text{B}_5\text{O}_{11}^-$ and of the $\text{H}_7\text{B}_4\text{O}_{10}^-$ anions, both belonging to class III.

Gas Phase Acidity of H_3BO_3 . The application of the equilibrium method, based on the measurement of the equilibrium constant of the proton-transfer reaction



has in the present case two serious problems. First, the poor definition of the H_3BO_3 pressure introduces an unusually large uncertainty into the calculated values of K_1 . Even more seriously, the simultaneous occurrence of the proton-transfer (1) and of the H_2BO_3^- addition to H_3BO_3 complicates the interpretation of the data, making it difficult to ascertain whether reaction 1 has reached true thermodynamic equilibrium. The latter problem can be mitigated by working with the largest excess of the reference acid HA that is compatible with the instrumental parameters.

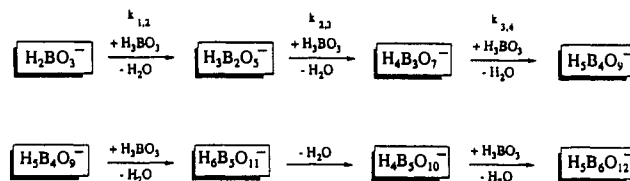


Figure 4. Reaction sequence promoted by H_2BO_3^- ions in $\text{H}_3\text{BO}_3/\text{H}_2\text{O}$ vapors (see text).

A number of experiments have been carried out at 308 K, using as the reference acid *m*-fluoroaniline, having a gas-phase acidity = $354 \pm 2 \text{ kcal mol}^{-1}$,²⁶ approaching the equilibrium from both sides and systematically changing the $[\text{H}_3\text{BO}_3]:[\text{HA}]$ ratio. Using the $p(\text{H}_3\text{BO}_3)$ values estimated as described in a previous section, we obtain $K_1 = 1.2 \pm 0.3$, and hence a gas-phase acidity (H_3BO_3) of $354 \text{ kcal mol}^{-1}$. This value has independently been confirmed by two additional sets of experiments carried out at 308 and 313 K, using as the reference acid $\text{CF}_3\text{CH}_2\text{OH}$, gas-phase acidity = $354 \pm 2 \text{ kcal mol}^{-1}$.²⁶ We conclude that the gas-phase acidity of H_3BO_3 amounts to $354 \text{ kcal mol}^{-1}$, with a cumulative uncertainty estimated to be 4 kcal mol^{-1} . Under the customary assumptions concerning the standard entropy change of proton transfer (1),²⁶ one obtains a $361 \pm 4 \text{ kcal mol}^{-1}$ value for the proton affinity (PA) of H_2BO_3^- , and combining the latter with the known heat of formation of gaseous H_3BO_3 ,²⁷ one arrives at $\Delta H_f^\circ(\text{H}_2\text{BO}_3^-) = -242 \pm 5 \text{ kcal mol}^{-1}$.

Discussion

Mononuclear Borate Anions. One of the two monomeric borate anions identified in the present study, BO_2^- , had previously been detected, and its heat of formation measured by high-temperature mass spectrometric techniques.^{17,18} The presence of a linear BO_2^- anion has also been established by X-ray diffraction in certain crystalline borates,⁸ as well as by Raman spectroscopy in solution.²⁸ On the other hand, the H_2BO_3^- anion has first been observed in this study, since its existence has not yet been proved in any solid borate nor in solution, where H_3BO_3 behaves not as a proton donor but as a Lewis acid,¹ undergoing ionization according to the equation



In this connection it is worth mentioning that, despite a specific search, we failed to detect $\text{B}(\text{OH})_4^-$ in the CI mass spectra of H_3BO_3 in a $\text{N}_2\text{O}/\text{N}_2/\text{H}_2$ mixture, where the abundant reactant ion OH^- promotes exclusively exothermic²⁹ proton abstraction from orthoboric acid



Thus, in contrast with its solution-chemistry behavior, H_3BO_3 acts in the gas phase as a Brønsted acid, yielding its conjugate base, H_2BO_3^- . From its gas-phase acidity, $354 \pm 4 \text{ kcal mol}^{-1}$, H_3BO_3 can be characterized as a gaseous acid of moderate strength, considerably weaker than HBO_2 (gas-phase acidity ca. $317 \text{ kcal mol}^{-1}$)²⁶ and comparable to gaseous HClO , gas-phase acidity = $353.5 \pm 2 \text{ kcal mol}^{-1}$.

Polyborate Anions. The existence of the only diborate anion observed in this study, $\text{H}_3\text{B}_2\text{O}_5^-$, has not previously been reported. Instead, a dinuclear anion $\text{H}_7\text{B}_2\text{O}_7^-$, indicated as the (2,1) anion in Ingri's notation,^{30,31} has been identified by X-ray diffraction

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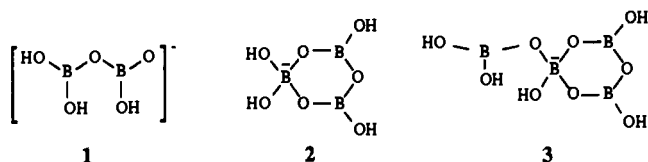
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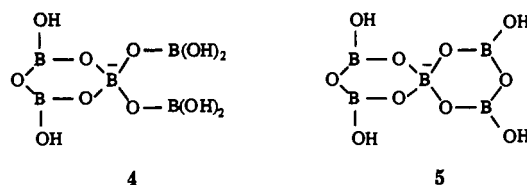
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in the mineral pinnoite³² and in aqueous solution on the basis of electrometric titrations³¹ and Raman spectroscopy.¹³ Taking into account the composition of the ion, its formation process, its reaction with H_3BO_3 to yield a cyclic trinuclear anion, and the general principles governing the structure of hydrated polyborates,³³ one can reasonably assign the gaseous $\text{H}_3\text{B}_2\text{O}_5^-$ anion the open structure **1**, consisting of two trigonal BO_3 groups sharing an oxygen atom. Among the anions containing three B atoms,



$\text{H}_6\text{B}_3\text{O}_8^-$, which is but a minor peak in the CI spectra and is not detectable at all in the ICR spectra, could be viewed as a mere cluster formed by $\text{H}_3\text{B}_2\text{O}_5^-$ and H_3BO_3 . However, considering that the corresponding cluster formed by H_2BO_3^- and H_3BO_3 is conspicuously absent, we are inclined to regard $\text{H}_6\text{B}_3\text{O}_8^-$ as an acyclic trimer of the $(\text{HO})_2\text{B}-\text{O}-\text{B}(\text{OH})_2-\text{O}-\text{B}(\text{OH})_2^-$ structure, whose dehydration, much favored under the low-pressure conditions typical of ICR spectrometry, leads to the $\text{H}_4\text{B}_3\text{O}_7^-$ anion **2**, which is predominant in both CI and ICR spectra. The triborate ion **2**, generally formulated as $\text{B}_3\text{O}_3(\text{OH})_4^-$ and indicated as the (3,1) anion in Ingri's notation, exists in many crystalline borates,¹ and predominates in aqueous solutions at concentrations of boric acid greater than 0.025 M.^{14,15,34} The stability conferred to **2** by a four-coordinated B atom contained in a cyclic structure, and by the relative delocalization of its charge, is consistent with the abundance of the ion in gaseous systems at widely different pressures, apparent from Figure 3 and its relatively low reactivity. As for the anions containing four B atoms, only $\text{H}_5\text{B}_4\text{O}_9^-$, abundant in the CI spectra, is detectable in ICR experiments, where it is formed from the addition of H_3BO_3 to **2**, suggestive of structure **3**. The existence of $\text{H}_5\text{B}_4\text{O}_9^-$ has not yet been reported, since the tetraborate anion identified in natural and synthetic borates and in aqueous solutions is instead $\text{H}_5\text{B}_4\text{O}_9^{2-}$. This ion, formulated as $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, (4,2) in Ingri's notation, is a tricyclic species containing two four-coordinated B atoms.^{1,15} Since the anion is doubly charged, its formation cannot occur under the conditions prevailing in our experiments, where only singly charged species are produced. As shown in Figure 4, addition of H_3BO_3 to **3**, followed by H_2O loss, yields $\text{H}_6\text{B}_5\text{O}_{11}^-$, whose further dehydration produces $\text{H}_4\text{B}_5\text{O}_{10}^-$. Such reaction sequence, established by

multiple-resonance ICR experiments, suggests the following structures



Of particular interest is the detection of anion **5** as a discrete species in the gas phase. This structure, which is characterized by two perpendicular rings fused by a common tetrahedral B atom, was first identified in potassium pentaborate, $\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$ ³⁵ and subsequently in various natural and synthetic pentaborates.¹ The anion, formulated as $\text{B}_5\text{O}_6(\text{OH})_4^-$, (5,1) in Ingri's notation, exists in solution, where its concentration increases at higher pH values.^{14,15,30,31} As to the structure of higher anions, in view of their increasing complexity and the lack of information on their formation pathways, any assignments must await additional data. In principle, pertinent information can be provided by extension of multiple-resonance ICR experiments and by collisionally activated dissociation (CAD) mass spectrometry, whose application requires, however, higher polyanions concentrations than are attainable in our experiments. Work in this direction is currently under way in this laboratory.

Conclusions

The first evidence has been obtained for the existence in the gas phase, as free, discrete entities, of several important polyborate anions whose salts have been identified in many natural and synthetic solid borates and in solution. Previously unknown borate and polyborate anions have been obtained, whose constitution is consistent with the general rules governing the structure of polyborates in condensed media. The only important difference is the limitation of the gas-phase study to singly charged anions. Another significant difference noted between the gas phase and solution concerns the different type of acidity displayed by orthoboric acid, which behaves in water exclusively as a Lewis acid giving upon ionization $\text{B}(\text{OH})_4^-$, rather than H_2BO_3^- . In the gas phase H_3BO_3 is instead a Brønsted acid, giving its conjugate base H_2BO_3^- , and is characterized by a gas-phase acidity of 354 ± 4 kcal mol⁻¹ comparable to that of other weak Brønsted acids, such as HClO.

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