Gas-phase Ion Chemistry of H_3BO_3. Protonated Orthoboric, Metaboric and Polyboric Acids, and their Anions in the Gas Phase

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Formation of protonated orthoboric, metaboric and polyboric acids, and of their anions has been demonstrated in the gas phase by mass spectrometric techniques, which have been used to measure the proton affinity of H_3BO_3, 175.6 kcal mol^{-1}, in fair agreement with the value of 181.2 kcal mol^{-1} from MO SCF *ab initio* calculations (1 cal = 4.184 J).

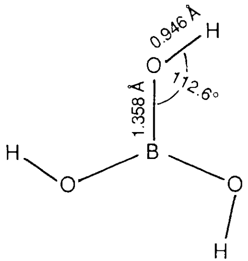
In contrast with the voluminous literature on boric acids in condensed media,[1,2] their gas-phase ion chemistry is still unexplored. This probably reflects the difficulty of applying mass spectrometric techniques to species that are particularly involatile, with the exception of orthoboric acid, H_3BO_3, which however is prone to facile decomposition in the ion source,[3] so that only recently has a mass spectrum of H_3BO_3 been reported.[4]

We have investigated the positive and negative ion chemistry of H_3BO_3 by a combination of chemical ionization (CI) and ion cyclotron resonance (ICR) mass spectrometry and of theoretical methods successfully used in the study of other inorganic acids.[5] Crystalline orthoboric acid introduced into the ion source in a thermostatically controlled direct-insertion probe emits vapour consisting of H_2O and H_3BO_3, whose partial pressures depend markedly on the temperature and change with time. Thus, at 20 °C one obtains a low ($\approx 10^{-8}$ Torr) H_3BO_3 pressure, which is nevertheless sufficient to record ICR spectra and persists for several hours. On raising the probe temperature to 70–80 °C one obtains the higher H_3BO_3 pressures required for conventional CI mass spectrometry at the expense, however, of the duration of the emission, which lasts only a few minutes.†

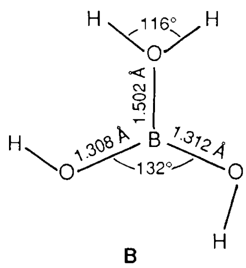
The electron-impact (EI) mass spectra of H_3BO_3, recorded using an electron energy of 12.0 eV, display only $H_3BO_3^+$ at *m/z* 61 and 62. At higher electron energies the $H_2BO_2^+$ fragment is formed as well, consistent with the published appearance potentials of $H_3BO_3^+$ and of $H_2BO_2^+$, respectively 10.8 and 13.8 ± 0.5 eV.[4] Protonated boric acid can be obtained *via* the general process in eqn. (1).

$$AH^+ + H_3BO_3 \leftrightarrows A + H_4BO_3^+ \qquad (1)$$

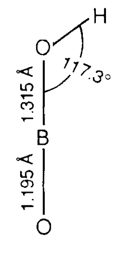
Following 'bracketing' experiments, $H_2C(CN)_2$ has been chosen as the most suitable reference base, and a van't Hoff plot has been constructed measuring the equilibrium constants of reactions (1), A = $H_2C(CN)_2$, in the range 20—70 °C. The results show that the reaction is thermoneutral, leading to a proton affinity (E_{pa}) of H_3BO_3 of 175.6 ± 1 kcal mol^{-1},[6] much of the estimated uncertainty reflecting the inaccuracy in the H_3BO_3 pressure measurements.‡ The experimental value is in



A



B



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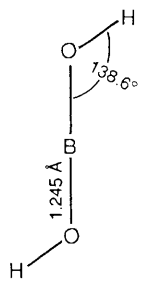

D

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† Most of the sample is recovered as a solid H_3BO_3 emission from which is prevented by the formation of involatile products, *e.g.* HBO_2 and B_2O_3.

‡ The H_3BO_3 pressure cannot be measured directly, since the acid is invariably accompanied by water. An approximate estimate can be based on the relative ionic abundances in the 75 eV mass spectrum of the mixture, corrected for the ionization cross sections of H_2O and H_3BO_3.[7] By combining the H_2O/H_3BO_3 ratio estimated in this way with the measured total pressure one can estimate the H_3BO_3 pressure.

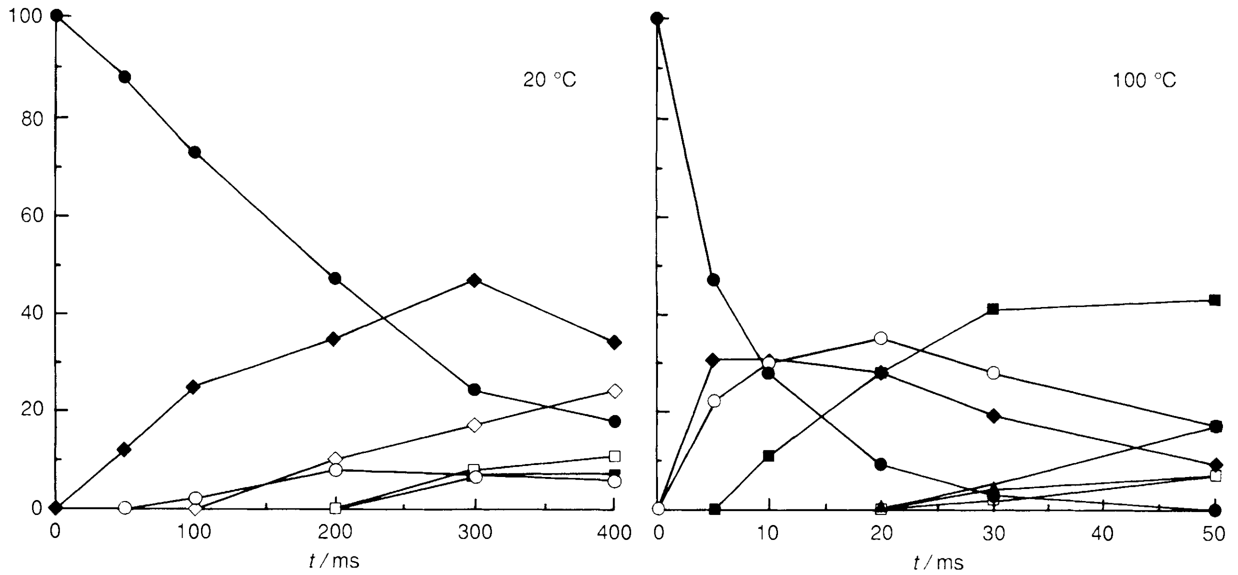

Fig. 1 Time dependence of the relative abundances of ions from the reaction of $H_4BO_3^+$ with H_3BO_3: $H_4BO_3^+$ (●), $H_5B_2O_5^+$ (◆), $H_6B_3O_7^+$ (◇), $H_4B_3O_6^+$ (○), $H_7B_4O_9^+$ (□), $H_6B_5O_{10}^+$ (▲), $H_5B_4O_8^+$ (■)

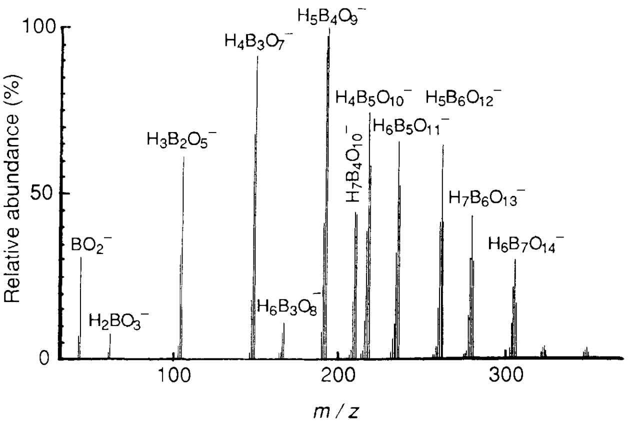

Fig. 2 Typical negative CI mass spectrum of H_3BO_3, showing the major anions of boric and polyboric acids; see text

fair agreement with the E_{pa} value of 181.2 kcal mol^{-1} from MO SCF calculations at the MP3/6-31-G**//6-31G* + ZPVE (6-31G*) level, that in addition give a value of 182.4 kcal mol^{-1} for the E_{pa} value of HBO_2, and the geometries in structures **A–D** of the species of interest. In the case of H_3BO_3 the calculated structural parameters agree remarkably well with the results of matrix-isolation IR spectroscopy.[4]

$H_4BO_3^+$ is the precursor of protonated polyboric acids of the general formula $H_{n+2}B_nO_{2n+1}$, formed *via* the stepwise sequence in eqn. (2), established by ion-ejection ICR techniques. Upon water loss the protonated polyboric acids give the protonated adducts of the corresponding $H_nB_nO_{2n}$ acids, whose abundances increase with temperature (Fig. 1). Species containing up to eight B atoms have been detected by CI and ICR spectrometry, and there are no reasons to exclude the presence of much higher homologues, which may be detectable by appropriate techniques. The $H_2BO_2^+$ ions do not evolve into polynuclear species, at least in ICR experiments where they are slowly converted into $H_4BO_3^+$, most likely *via* proton transfer.§ Illustration of other facets of the rich positive-ion chemistry of boric acids, *e.g.* their fast and extensive exchange with $H_2{}^{18}O$, the stepwise formation of protonated mono-, di- and tri-alkyl borates upon reaction with alcohols and glycols, *etc.*, is deferred to a forthcoming article.

$$H_4BO_3^+ \xrightarrow[-H_2O]{+H_3BO_3} H_5B_2O_5^+ \xrightarrow[-H_2O]{+H_3BO_3} H_6B_3O_7^+ \xrightarrow[-H_2O]{+H_3BO_3} H_7B_4O_9^+ \ldots \quad (2)$$

With regard to the negative ion chemistry of H_3BO_3, BO_2^- and $H_2BO_3^-$ ions can be obtained either *via* dissociative electron attachment, or *via* proton abstraction by gaseous bases, *e.g.* OH^-, F^-.

The stepwise addition of H_3BO_3 to the monomeric anions gives the anions of the same polyboric acids whose protonated adducts characterize the positive CI mass spectra, as well as the anions of a different class of polyboric acids of the general formula $H_{n+4}B_nO_{2n+2}$. The typical electron-attachment spectrum of Fig. 2 has been recorded in CH_4 at *ca.* 0.2 Torr, 150 °C. Analogous spectra are obtained from the reaction of H_3BO_3 with OH^-, in an N_2O–H_2–He mixture.¶ Using instead F^- reactant ions, produced upon ionization of 1% CF_4 in N_2, one obtains, in addition to the anions of $H_{n+2}B_nO_{2n+1}$ and of $H_nB_nO_{2n}$ acids ($n \leq 8$), fluorinated species including mononuclear, *e.g.* $H_3BO_3F^-$, and polynuclear ions, *e.g.* $H_3B_3O_6F^-$ and $H_4B_4O_8F^-$. These, and other interesting aspects of the negative ion chemistry of boric acids are currently being investigated.

In conclusion, this preliminary study demonstrates the existence of previously unknown inorganic ions, including protonated mononuclear and polynuclear boric acids, and of several polyborate anions, as well as the existence as discrete entities in the gas phase of other polyborate anions previously known only as solvated species in solution[8] or in the lattice of certain borates.[9]

The most salient feature of the positive and negative ion chemistry of H_3BO_3 that finds few analogies, if at all, in other inorganic systems, is the stepwise formation of polynuclear ions of steadily increasing size, even under unfavourable conditions, *e.g.* at pressures down to 10^{-8} Torr, as in typical ICR experiments.

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§ The slight endothermicity of process (1), A = HBO_2, is overcome by the much larger concentrations of H_3BO_3 than of HBO_2 in the gas phase.

¶ The CI spectra were recorded using either a ZAB-2F magnetic instrument or a TRIO quadrupolar spectrometer from VG Micromass Ltd. The ICR spectra were recorded using a Nicolet FTMS 1000 instrument. The gases were ultra high purity (>99.995 mol%) products from Matheson Inc.

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