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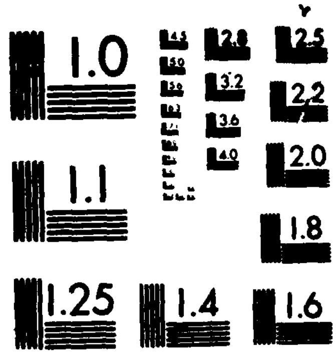

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Fast-atom bombardment mass spectra of vitreous boron trioxide (B_2O_3) has been obtained at sample temperatures below and above the melting point of B_2O_3 (450°C). The experiments utilized a new high-temperature sample holder that has been described in detail elsewhere (1). Spectra were obtained over a sample temperature range of 150-700°C. Boron trioxide is thermally stable over this temperature range and its low vapor pressure and high viscosity assure a long lived sample and a consistent surface geometry.

This technique enabled the first observation of high-molecular-weight, gas-phase boron oxides (see figure). Collision-induced dissociation of the boron oxide ions revealed structures composed of branched chains of alternating boron and oxygen atoms terminated by - B=O bonds. This observation is consistent with the structure of condensed-phase B_2O_3, which is composed of infinite chains of BO_3 units linked by -B-O-B- bonds.

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FAST-ATOM BOMBARDMENT OF MOLTEN BORON TRIOXIDE

BY

ROBERT J. DOYLE, JR.

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FAST-ATOM BOMBARDMENT OF MOLTEN BORON TRIOXIDE

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The structure of vitreous boron trioxide (B_2O_3) has been a topic of debate for several decades. The most recently proposed structure involves a random network of boroxol (B_3O_3) rings linked together by random numbers of BO_3 triangles. The extremely low vapor pressure of B_2O_3 has, until recently, limited the utility of mass spectrometry as a structural probe. However, the advent of fast-atom bombardment-mass spectrometry (FAB-MS) now enables the desorption of potentially structurally characteristic ions from the surfaces of intractable materials.

Vitreous boron trioxide is a very hygroscopic glass that is not easily purged of water. It reacts readily with ambient water vapor to form a surface coating of boric acid ($B(OH)_3$). Even at typical FAB operating pressures (10^{-6}-10^{-5} Torr), the residual water vapor is sufficient to provide a continuously renewable source of $B(OH)_3$ to the surface of the glass sample. Elevated sample temperatures are therefore required to both purge the sample of water and to prevent the formation of $B(OH)_3$.

Fast-atom bombardment mass spectra of vitreous boron trioxide have been obtained at elevated temperatures using a ZAB-2F mass spectrometer. The experiments utilized a new high-temperature sample holder that has been described in detail elsewhere (1). Spectra were obtained over a sample temperature range of 150-700^{0}C. Boron trioxide is thermally stable over this temperature range and its low vapor pressure and high viscosity assure a long lived sample and a consistent surface geometry.

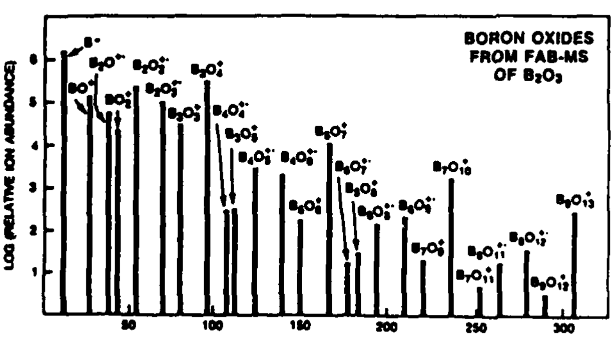

Figure 1. Boron oxide ion distribution from the FAB-MS of boron trioxide.

This technique enabled the first observation of high-molecular-weight, gas-phase boron oxides (Figure 1). The FAB-MS of vitreous B_2O_3 has yielded a complex distribution of boron oxide ions, most of which have been observed for the first time. Six groups of boron oxide ions have been identified and they may be described by six general formulae: $[B_{2n+1}O_{3n}]^+$, $[B_{2n+1}O_{3n+1}]^+$, $[B_{2n+2}O_{3n+1}]^{+\cdot}$, $[B_{2n+1}O_{3n+2}]^+$, $[B_{2n+2}O_{3n+2}]^{+\cdot}$, and

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$[B_{2n+2}O_{3n+3}]^{+\cdot}$, where n=0,1,2,3,... . The maximum values of n observed are 4,6,2,3,3, and 4 respectively. Local abundance maxima are observed for $[B_{2n+1}O_{3n+1}]^{+}$ ions which implies an enhanced stability for species such as $[B_3O_4]^+$, $[B_5O_7]^+$, $[B_7O_{10}]^+$, $[B_9O_{13}]^+$, etc.

The collision-induced dissociation (CID) mass spectra of mass-selected boron oxide ions show a remarkable similarity between the dissociation products of boron oxide ions within each group. For example, $[B_{2n+1}O_{3n+1}]^+$ ions, where n>0, all show the loss of B_2O_3 as the principal dissociation pathway (figure 2 a-c). On the other hand, $[B_{2n+2}O_{3n+3}]^{+\cdot}$ ions, where n>0, all show the loss of $\cdot BO_2$ as the principal dissociation pathway. Common dissociation losses can be explained in terms of structural features that are common to each group.

Although the numerous structural isomers of boron oxide ions cannot be distinguished by CID methods, the general form of boron-oxygen bonding can be deduced. For example, boron is always found 2-or 3- coordinated with oxygen. Boron oxide ions are composed of integral BO_3 triangles and terminal -B=O units. Figure 2d shows examples for the $[B_{2n+1}O_{3n+1}]^+$ series of ions.

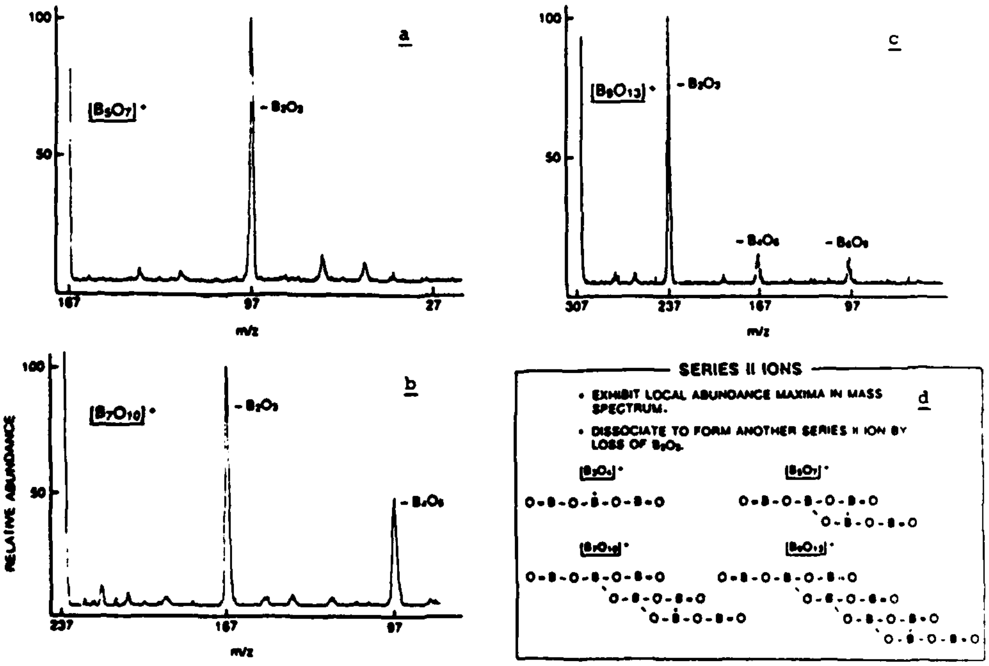

Figure 2. $^{a-c}$ CID spectra of $[B_{2n+1}O_{3n+1}]^+$ ions.
^{d} Proposed structures for this series of boron oxide ions.

1. Doyle, R.J., Jr, Anal. Chem. 1987, 59, 537-539.

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