

## Mass Spectrometric Determination of Bond Dissociation Energies in $\text{BF}_3 \cdot \text{OEt}_2$

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**Summary** A reduction in the B-F bond dissociation energy is observed upon complexation of  $\text{BF}_3$  with ethyl ether.

BORON TRIFLUORIDE is a triangular planar molecule with F-B-F bond angles of  $120^\circ$  and B-F bond distances of  $1.295 \text{ \AA}$ .<sup>1</sup> Complex formation with a Lewis base results in alterations of the groups involved the changes being most appreciable in  $\text{BF}_3$ . In such complexes the planar configuration of the parent  $\text{BF}_3$  unit changes to a pyramidal configuration with an increase in the B-F bond length of *ca.*  $0.1 \text{ \AA}$ .<sup>2,3</sup>

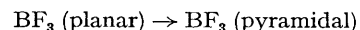
The B-F bond dissociation energy in  $\text{BF}_3$  can be calculated from the appearance potential of  $\text{B}^+$ ,  $A(\text{B}^+)$ , using the equation:

$$A(\text{B}^+) = 3D(\text{B-F}) + I(\text{B}) \quad (1)$$

Using  $8.29 \text{ eV}$  for  $I(\text{B})$ , and the appearance potential determined for  $\text{B}^+$ , given in the Table, one obtains a B-F

calculated using the equation (2). Using the value of  $0.50 \text{ eV}$ , as measured by McLaughlin and Tamres,<sup>6</sup> for  $D[\text{B-OEt}_2]$  and the appearance potential measured for  $\text{B}^+$  in the Table, one obtains for the average B-F bond dissociation energy a value of  $6.57 \text{ eV}$ .

From the bond energy data it is possible to calculate the energy for the rearrangement process:



This value is experimentally determined to be  $2.22 \text{ eV}$ . This compares quite well with the value of  $2.08 \text{ eV}$  calculated on the basis of MO theory.<sup>7</sup>

Equations (1) and (2) do not take into account the vibrational, electronic, and translational excitation energy resulting from a vertical transition to a potential-energy surface above that necessary for decomposition. In a study of n-butane, Inghram<sup>8</sup> showed that almost all of the excess excitation energy occurs as internal vibrational energy of the fragments amounting to  $0.20 \text{ eV}$ , the calculated "kinetic shift" being *ca.*  $0.02 \text{ eV}$ . Stevenson<sup>9</sup> has shown that kinetic shifts are for the most part all equal and quite small. The assumption made is that the kinetic shifts in the dissociation of  $\text{BF}_3$  and the corresponding etherate are nearly identical and cancel out in calculating the planar to pyramidal reorganization energy. The imparted vibrational energy is also assumed to be similar in both processes leading to the individual B-F bond dissociation energies whose effect cancels out in the calculation of the reorganization energy.

As a result of the fact that  $I(\text{B}) < I(\text{F})$  and  $I(\text{B}) < I(\text{Et}_2\text{O})$ , the effect of excitation energies on the individual bond dissociation energies is minimized but not eliminated.<sup>10</sup> In view of the possible nonadiabatic nature of the processes investigated, the calculated planar to pyramidal reorganization energy appears likely.

TABLE  
Determined appearance potentials

| Process  | Appearance potential        |
|--|-----------------------------|
| $\text{BF}_3 + e^- \rightarrow \text{BF}_3^+ + 2e^-$                                   | $15.71 \pm 0.10 \text{ eV}$ |
| $\text{BF}_3 \cdot \text{OEt}_2 + e^- \rightarrow \text{BF}_3^+ + \text{OEt}_2 + 2e^-$ | $15.00 \pm 0.10 \text{ eV}$ |

bond dissociation energy of  $7.32 \text{ eV}$ . This compares well with the value of  $7.4 \text{ eV}$  obtained by Marriott and Craggs<sup>4</sup> and that calculated from appearance potentials determined by Koski.<sup>5</sup>

For the etherate, the B-F bond dissociation energy can be

$$A(\text{B}^+) = 3D(\text{B-F}) + I(\text{B}) + D[\text{B-OEt}_2] \quad (2)$$

The appearance potentials were obtained using the RPD (retarding potential difference) method, that is the electron accelerating voltage at the point where the difference in ion current becomes zero. To calculate the energy scale, Xe was added in sufficient quantity to match the source sample pressure, the energy scale being adjusted to the first ionization potential of Xe, 12.129 eV.<sup>11</sup>

Mono-energetic electron impact studies on trivalent boron compound complexes can thus be used to obtain planar to pyramidal rearrangement energies and to investigate the nature of complex formation.

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