405 originating from $[M+H]^+$ ions. This is direct evidence that $[M+H]^+$ ions formed under FAB conditions result in CI-like fragmentation.

It is clear from a tandem B/E FAB mass spectrum of the $[M+H]^+$ ion of **1** that the ion $M^{+\cdot}$ cannot originate from the $[M+H]^+$ ion. This result suggests that the $M^{+\cdot}$ and the $[M+H]^+$ ions of the compound are formed independently of each other under FAB conditions. The ion $M^{+\cdot}$ may be formed by the charge-transfer mechanism proposed by Bojesen *et al.*[5] in the gas phase and/or a selvedge region between the liquid matrix surface and the vapour phase. As discussed by Renner *et al.*[6] this is a hard ionization rather than a soft ionization by FAB. On the other hand, the ion $[M+H]^+$ may be formed by a CI-like process, such as ion/molecule reaction, in a matrix/plasma gas phase or a selvedge region.[2,3]

The evidence obtained here that both EI-like and CI-like fragmentations occur in a FAB mass spectrum has not previously been reported. This result can offer important information for analysing the fragmentations produced in FAB mass spectrometry, to which we can possibly apply the fragmentation rules of EI and CI mass spectrometry to elucidate the structure of organic compounds. On the basis of the results obtained here, further comparative studies will be carried out and reported on the fragmentations in EI, FAB and CI mass spectrometry of prenylated flavonoids.

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Ionization and Fragmentation of BF_3 and BF_2 Molecules by Electron Impact

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Although the chemistry of the BF_3 and BF_2 molecules has received much attention recently, there have been no extensive electron impact studies of these molecules. Photoelectron spectra have been used to study BF_3,[1,2] the results of a photoionization study[1] and some mass spectroscopic data[3–6] reported, but no attempt has been made to clarify the fragmentation mechanisms following electron ionization. Here, we report the results of a mass spectrometric study of ionization and fragmentation of both BF_3 and BF_2 molecules under electron impact.

EXPERIMENTAL

Threshold electron ionization efficiency curves were measured for BF_3^+, BF_2^+, BF^+ and B^+ from BF_3. The BF_2 radical was generated by reaction of SF_6 with B(s) under equilibrium conditions. Molecular effusion beams containing BF_2 radicals were also generated by admitting BF_3(g) over the elemental boron. In both cases identical ionization energies of the BF_2 radical were obtained. When BF_3(g) was admitted to the molybolenum cell containing B(s) at room temperature, appearance energies of different electronic states of the observed ions from BF_3 were determined. The signal at *m/z* 49 was clearly due to BF_2^+ formed from BF_3 by a dissociative ionization process. When the cell temperature was raised, a weak low energy tail with a threshold appearance energy corresponding to the BF_2^+ ion was observed. Probable ion fragmentation pathways in both the BF_3 and BF_2 systems were proposed, the heats of formation of some positive ions and the bond-dissociation energies were determined.

RESULTS

Electron ionization and fragmentation studies performed on the BF_3 and BF_2 molecules gave appearance energies for BF_3^+, BF_2^+, BF^+ and B^+ ions produced in the fragmentation process of:–

BF_3^+: 15.98 eV($^2A_2$), 16.70 eV($^2E_2$), 17.47 eV(^2E), 18.14 eV(?), 19.20 eV(A_2), 20.20 eV(E) and 20.73 eV(?).

The appearance energies (AE) of the processes (1) to (7) listed below were determined,

BF_2^+:	$BF_3 + e^- \rightarrow BF_2^+ + F + 2e^-$	(1)
	$BF_2 + e^- \rightarrow BF_2^+ + 2e^-$	(2)
BF^+:	$BF_3 + e^- \rightarrow BF^+ + F_2 + 2e^-$	(3)
	$\rightarrow BF^+ + 2F + 2e^-$	(4)
	$\rightarrow (BF^+)^* + 2F + 2e^-$	(5)
B^+:	$BF_3 + e^- \rightarrow B^+ + F_2 + F + 2e$	(6)
	$\rightarrow B^+ + 3F + 2e^-$	(7)

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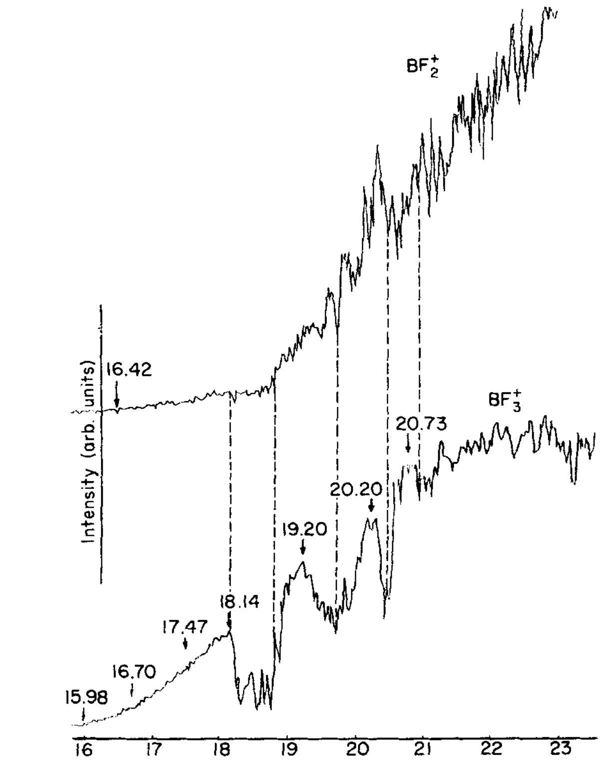

Figure 1. Ionization efficiency curves for BF_3^+ and BF_2^+ from BF_3.

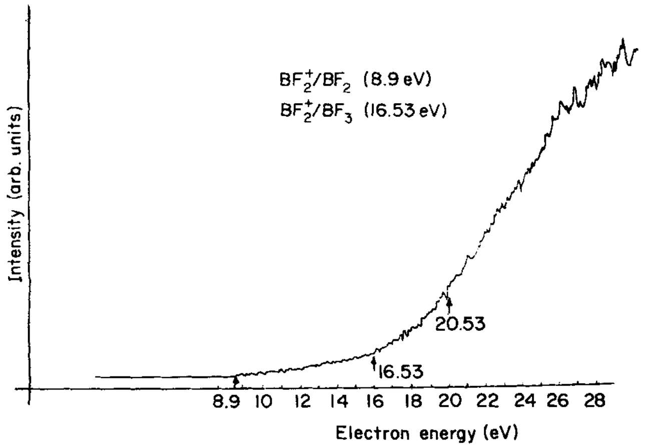

Figure 2. Ionization efficiency curves for BF_2^+ from BF_2 and for BF_2^+ from BF_3.

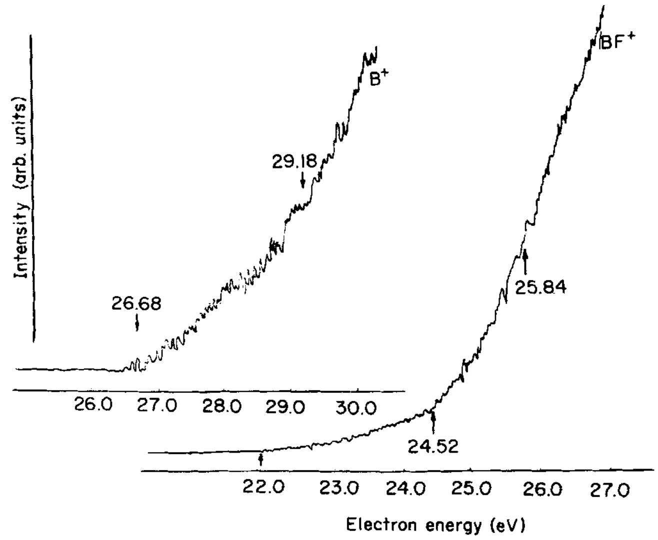

Figure 3. Ionization efficiency curves for BF^+ and B^+ from BF_3.

and the values obtained were

(1) AE = 16.4±0.1 eV
(2) AE = 8.9±0.1 eV
(3) AE = 22.0±0.1 eV
(4) AE = 24.5±0.1 eV
(5) AE = 25.8±0.1 eV
(6) AE = 26.8±0.1 eV
(7) AE = 29.2±0.1 eV

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