

Chemical characterization of boron radical anions by studying gas-phase ion-molecule reactions in a mass spectrometer

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**Abstract:**

Many highly reactive and short-lived ions cannot be studied in the solution phase. The chemistry of these reactive ions can be explored by studying gas-phase ion-molecule reactions in a mass spectrometer. Electronically and structurally stable *closo*-dodecacarborate anions  $[B_{12}X_{12}]^{2-}$  (X=halogen, CN) undergo cleavage of stable B-X bond on collision-activated dissociation in mass spectrometer yielding fragment ions of exceptional reactivity. This work aims at exploring the special binding properties of these electrophilic anions. The gas-phase reactivity of doubly charged *closo*-dodecacarborate anion,  $[B_{12}I_{11}]^{2-}$  towards allyl iodide and di-*tert*-butyl nitroxide was explored and compared to that of the singly charged anion,  $[HCB_{11}I_{10}]^{\bullet-}$ . Despite similar structural conditions of the radical binding site, the kinetics of these ion-molecule reactions differed due to different physical charge states of the reacting boron radical anions. Furthermore, to understand the influence of the localized radical binding site, the gas-phase reactivity of two singly charged derivatives,  $[HCB_{11}I_{10}]^{\bullet-}$  and  $[CB_{11}I_{11}]^{\bullet-}$ , towards oxygen and allyl iodide was studied and compared. The electrophilic nature of the boron binding site in  $[HCB_{11}I_{10}]^{\bullet-}$  was found to be greater than that of the carbon binding site in  $[CB_{11}I_{11}]^{\bullet-}$ .