Opening of the B$_{10}H_{10}^{2-}$ Cage to Give B$_{10}H_{14}$

H. Mongeot* and H. R. Atchekzai

Université Lyon 1, Laboratoire de Physicochimie Minérale, Associé au C.N.R.S. No. 118, 43, Boulevard du 11 Novembre 1918, F69622 Villeurbanne CEDEX

Z. Naturforsch. 36b, 313–314 (1981); received September 19, 1980

Decaborane, Bis(diethylsulphide)decaborane, Decahydrodecaborate Cage Opening

Decaborane B$_{10}H_{14}$ is formed by opening the B$_{10}H_{10}^{2-}$ cage in strong acidic medium. The reaction must be carried out in the presence of an inert solvent which dissolves B$_{10}H_{14}$. The best yields (28%) are obtained when zinc dust is added to the reaction mixture. The conversions of B$_{10}H_{10}^{2-}$ into B$_{10}H_{14}$ or B$_{10}H_{12}$(Et$_2$S)$_2$ probably obey the same mechanism.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution 4.0 International License.

The decahydrodecaborate anion B$_{10}H_{10}^{2-}$ and decaborane B$_{10}H_{14}$ belong to two different types of boron compound. The B$_{10}H_{10}^{2-}$ anion is a closo compound with a bi-capped Archimedean square antiprismonic structure, whereas B$_{10}H_{14}$ is a nido compound, the structure of which can be described as a fragment of an icosahedron with boron atoms at ten of the twelve vertices.

Decaborane or its derivatives are converted to B$_{10}H_{10}^{2-}$ by the action of amines [1, 2] or NH$_3$ [3]; the reverse conversion requires the opening of the very stable B$_{10}H_{10}^{2-}$ cage. The only example [4, 5], to our knowledge, is the transformation of B$_{10}H_{10}^{2-}$ to 6-9 bis (alkyl sulphide) decaborane [12]: B$_{10}H_{12}$(R$_2$S)$_2$.

In the present work, we have shown that reaction of B$_{10}H_{10}^{2-}$ with strong acids (i.e. H$_2$SO$_4$ or H$_2$PO$_4$) yields decaborane. The reaction occurs readily at room temperature, when pure acid is added dropwise to a suspension of a B$_{10}H_{10}^{2-}$ salt in an inert solvent such as hexane. Decaborane is dissolved as it is formed and thus, is not decomposed:

$$B_{10}H_{10}^{2-} + 2H^+ + H_2O \rightarrow B_{10}H_{14} \quad (1)$$

A part of the starting material also reacts with acid to give boric acid and hydrogen. Yields calculated according to equation (1) are 20%, but they may reach 28% when reducing agents, which give hydrogen in acidic medium, are added. Lower yields are observed when the acid contains water, and only boronic acid is formed when the water content reaches 20% w/w.

The reaction is very similar to that between strong acid and a B$_{10}H_{10}^{2-}$ salt in diethylsulphide suspension from which B$_{10}H_{12}$(Et$_2$S)$_2$ is obtained.

This suggests a mechanism involving the diethylsulphonium ion Et$_2$SH$^+$ [4, 5], in which protons, supplied by Et$_2$SH$^+$, attack the apical region of the B$_{10}H_{10}^{2-}$ cage. Cage-opening occurs when hydrogen-bridge bonds form and boron-boron bonds rupture; diethylsulphide coordinates with equatorial boron atoms.

Participation of the Et$_2$SH$^+$ ion in this mechanism is uncertain because of its low concentration; we were unable to identify it by Raman spectroscopy in the H$_2$SO$_4$-Et$_2$S mixtures used.

We believe that the formation of B$_{10}H_{14}$ and B$_{10}H_{12}$(Et$_2$S)$_2$ obey the same mechanism. In the first step, due to the presence of a strong acid, the protons attack the apical boron atoms of the cage (these boron atoms are generally involved in electrophilic reactions) [6]. In a second step, the most active species formed reacts very rapidly with diethyl sulphide. In the absence of sulphide, the active species reacts slowly with some of the hydrogen produced by the reaction of B$_{10}H_{10}^{2-}$, or reducing agents, with acid. This different behaviour towards Et$_2$S and hydrogen is due to the much lower concentration of hydrogen in the medium and, perhaps also, to its lower reactivity.

A possible mechanism of formation of B$_{10}H_{14}$ is shown in Fig. 1. Numbering of boron atoms is as for decaborane; terminal hydrogen atoms are omitted. The intermediate H$_2$B$_{10}H_{14}$ is very unstable in anhydrous media [3], and proton attack occurs on boron atoms 7 and 10.

Attempts to reproduce the opening of the B$_{10}H_{10}^{2-}$ cage in basic or neutral media have been unsuccessful. For instance reduction of the cuprous salt Cu$_2$B$_{10}H_{10}$ in solution in acetonitrile by NaH does not yield the known compound Na$_2$B$_{10}H_{12}$:

$$Cu_2B_{10}H_{10} + 2NaH \rightarrow Na_2B_{10}H_{12} + 2Cu + H_2 \quad (2)$$

* Reprint requests to Dr. H. Mongeot.

0340–5087/81/0300–0313/$ 01.00/0
These results confirm the role played by acids in the opening of the $\text{B}_{10}\text{H}_{16}^{2-}$ cage.

**Experimental**

To a stirred suspension of 1.6 g (4.22 mmol) of $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{16}$ in hexane at room temperature was added dropwise pure sulfuric acid (2 cm$^3$ in 30 mn). A yellow gummy material formed and the solution was decanted and filtered. Hexane was removed in a vacuum and white needles of decaborane recovered (0.104 g, 0.86 mmol).

Decaborane was characterized by its infrared [7, 8] and $^{11}$B NMR [9] spectra. Thin layer chromatography was performed on silufol sheets [10] using hexane as eluent. Only the white spot of decaborane was detected with iodine.

Hydrogen was evolved during the reaction, and no volatile borane was detected in the gas phase by infrared analysis.

Decaborane was also titrated with iodine [11] after dilution of the hexane solution with methanol. Yields were consistent with those determined from the weight of decaborane recovered.

Several syntheses were carried out in the presence of reducing agents: Hydrogen was bubbled through the mixture, Raney nickel, potassium borohydride or zinc dust were added. Decaborane was produced with a 28% yield in the presence of zinc dust, but no significant effect was observed with the other species (20% yields).

$(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{16}$ was synthetized by the pyrolysis [5] of tetraethylammonium tetrahydroborate, $\text{Et}_4\text{NBH}_4$.

---