

Studies on the mechanism of these rearrangements are in hand.

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The Reaction of the $B_{20}H_{18}^{-2}$ Ion with Hydroxide Ion

Sir:

A previous report¹ of the reaction of hydroxide ion with the $B_{20}H_{18}^{-2}$ ion¹⁻³ indicated the initial product to be apically substituted $B_{10}H_9OH^{-2}$ which subsequently rearranged to equatorially substituted $B_{10}H_9OH^{-2}$. We have reinvestigated this reaction and have found compelling evidence for other products.

The reaction of one formula weight of triethylammonium $B_{20}H_{18}^{-2}$ with aqueous potassium hydroxide or anhydrous potassium methoxide in methanol consumed four equivalents of base and liberated two moles of triethylamine. The product of the potassium methoxide reaction (I) exhibited a methoxyl group in its H^1 n.m.r. and infrared spectra. *Anal.* Calcd. for $K_4B_{20}H_{17}OCH_3 \cdot 2H_2O$: B, 47.36; H, 5.29; C, 2.63; mol. wt., 457. Found: B, 47.88; H, 4.98; C, 2.83; mol. wt., 429. The product of the hydroxide ion reaction (II) was characterized as $K_4B_{20}H_{17}OH \cdot 3H_2O$. *Anal.* Calcd.: B, 46.95; H_2O , 11.72; K/B, 0.200; mol. wt., 461. Found: B, 46.1; H_2O , 11.15; K/B, 0.198; mol. wt., 455. The salt II was converted on standing in neutral aqueous solution (25°, 12 hr.) to another salt (III) of apparently identical composition. *Anal.* Calcd. for $K_4B_{20}H_{17}OH \cdot 3H_2O$: B, 46.95; H_2O , 11.72; K/B, 0.200; mol. wt., 461. Found: B, 47.1; H_2O , 12.0; K/B, 0.202; mol. wt., 441. The salts II and III were easily distinguished by their characteristic B^{11} n.m.r. and infrared spectra. It is highly probable that the transformation of II to III accounts for the previously reported¹ $B_{10}H_9OH^{-2}$ rearrangement.

Potentiometric titration of I, II, and III with aqueous acid resulted in the consumption of one proton per formula weight. Equivalent weights and pK_a values were: I, 447 (theoretical 457), pK_a 6.1; II, 460 (theoretical 461), pK_a 5.8; III, 461 (theoretical 461), pK_a 5.8.

Protonation of II and III tetramethylammonium salts followed by rapid isolation produced the same tetramethylammonium salt (IV). *Anal.* Calcd. for $B_{20}H_{18}OH \cdot 3(CH_3)_4N$: B, 45.71. Found: B, 45.6. The salt IV gave an identical X-ray powder pattern and infrared spectrum (B-H-B bridge band near 5.60 μ) regardless of its source.

(1) A. Kaczmarezyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S. A.*, **48**, 729 (1962).

(2) W. N. Lipscomb, *ibid.*, **47**, 1791 (1961), proposed extensions of the valence theory which led to the satisfactory, although unproven, structure of $B_{20}H_{18}^{-2}$ shown in ref. 3. This structure is assumed throughout this discussion.

(3) A. R. Pitochelli, W. N. Lipscomb, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 3026 (1962).

Oxidation of II or III with hydrogen peroxide, ferric ion, or ceric ion in aqueous acid solution produced the same yellow $B_{20}H_{17}OH^{-2}$ anion (V) in 30–55% yield, λ_{max} 230 $m\mu$ (ϵ 12,000) and 300 $m\mu$ (ϵ 16,000). *Anal.* Calcd. for $B_{20}H_{17}OH \cdot 2(CH_3)_4N$: B, 54.26. Found: B, 54.0. The B^{11} n.m.r. spectrum of V clearly indicates the presence of equatorial -OH substitution on $B_{20}H_{18}^{-2}$, since the low field (apex) region of the hydroxyl derivative is identical with that found in $B_{20}H_{18}^{-2}$. A small difference is observed in the high field (equatorial) region. The infrared spectrum of V contains a sharp -OH band at 2.80. Similar oxidation of I produced $B_{20}H_{17}OCH_3^{-2}$.

These results suggest that the hydroxide ion cleavage of $B_{20}H_{18}^{-2}$ ion^{2,3} results in the cleavage of one B-H-B three-center bond and abstraction of a proton from the second bridge position. The resulting product is a substituted $B_{20}H_{18}^{-4}$ ion^{2,4} which gives reactions characteristic of $B_{20}H_{18}^{-4}$.

The kinetics of the hydroxide ion cleavage and certain structural considerations will be presented at a later date.

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(4) M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garrett, *ibid.*, **85**, 3704 (1963).

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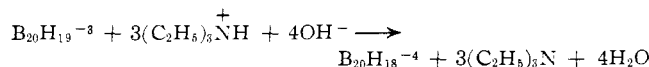
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The Isolation and Characterization of $B_{20}H_{19}^{-3}$ and $B_{20}H_{18}^{-4}$ Ions

Sir:

The ceric ion oxidation of $B_{10}H_{10}^{-2}$ was previously reported¹ to produce a second isomer of the $B_{20}H_{18}^{-2}$ ion.² Reinvestigation of this reaction has shown the product to be a double salt (I), $B_{20}H_{18}^{-2} \cdot B_{20}H_{19}^{-3} \cdot 5(C_2H_5)_3NH$, in which the $B_{20}H_{18}^{-2}$ ion is identical with that produced by the ferric ion oxidation² of $B_{10}H_{10}^{-2}$.³ *Anal.* Calcd. for $B_{20}H_{18} \cdot B_{20}H_{19} \cdot 5(C_2H_5)_3NH$: B, 44.12; C, 36.73; H, 12.01; N, 7.14. Found: B, 45.27; C, 37.17; H, 12.02; N, 6.41.

Treatment of I (m.p. 199–200°) with aqueous tetramethylammonium chloride precipitated a white tetramethylammonium salt which was converted by ion exchange to a triethylammonium salt (II), m.p. 163°. *Anal.* Calcd. for $B_{20}H_{19} \cdot 3(C_2H_5)_3NH$: B, 39.93. Found: B, 39.4. Crystallization of a 1:1 mixture of II and authentic² triethylammonium $B_{20}H_{18}^{-2}$ from water afforded I in 70% yield. The reaction of one formula weight of II with aqueous potassium hydroxide liberated 2.98 moles of triethylamine and consumed 4.05 moles of hydroxide ion.



(1) A. R. Pitochelli, W. N. Lipscomb, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 3026 (1962).

(2) A. Kaczmarezyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S. A.*, **48**, 729 (1962)

(3) This same conclusion was independently obtained by A. Kaczmarezyk, private communication, September, 1963.