

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 report<sup>1</sup> of the reaction of hydroxide ion with the  $B_{20}H_{18}^{-2}$  ion<sup>1-3</sup> 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  $H^{11}$  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 reported<sup>1</sup>  $B_{10}H_9OH^{-2}$  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  $\mu$ ) 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,  $\lambda_{max}$  230  $m\mu$  ( $\epsilon$  12,000) and 300  $m\mu$  ( $\epsilon$  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<sup>2,3</sup> 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<sup>2,4</sup> 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).

(5) (a) Alfred P. Sloan Foundation Research Fellow; (b) National Science Foundation Undergraduate Research Assistant, Summer, 1962.

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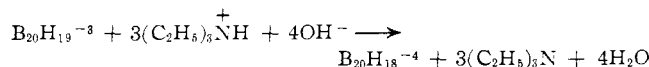
RECEIVED AUGUST 21, 1963

### 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 reported<sup>1</sup> to produce a second isomer of the  $B_{20}H_{18}^{-2}$  ion.<sup>2</sup> 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 oxidation<sup>2</sup> of  $B_{10}H_{10}^{-2}$ .<sup>3</sup> *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 authentic<sup>2</sup> 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.

The resulting potassium salt (III) accepted one proton upon potentiometric titration with aqueous acid. *Anal.* Calcd. for  $K_4B_{20}H_{18} \cdot 2H_2O$ :  $H_2O$ , 8.44; B, 50.7; K/B, 0.200; equiv. wt., 427; mol. wt., 427. Found:  $H_2O$ , 8.3; B, 50.5; K/B, 0.200; equiv. wt., 432; mol. wt., 435. Addition of tetramethylammonium ion to an acidified solution of III produced a salt identical with that obtained directly from I. The  $B_{20}H_{19}^{-3}$  ion exhibits a  $pK_a$  of 6.3.

The previously reported<sup>1</sup> isomerization of the "second isomer" of  $B_{20}H_{18}^{-2}$  to authentic  $B_{20}H_{18}^{-2}$  in aqueous acid was actually an air oxidation (perhaps catalyzed by a trace of ferric ion) of  $B_{20}H_{19}^{-3}$  to  $B_{20}H_{18}^{-2}$ . Thus, a solution of III in 1 M mineral acid at 25° was stable indefinitely in a nitrogen atmosphere, while an 18% conversion to  $B_{20}H_{18}^{-2}$  was observed after 72 hr. in an oxygen atmosphere. Furthermore, the oxidation of  $B_{20}H_{19}^{-3}$  to  $B_{20}H_{18}^{-2}$  was accomplished with hydrogen peroxide (42% yield) and ferric ion (68% yield) in acidic aqueous solution.

The  $B^{11}$  n.m.r. spectrum of III contained a singlet (area 2) at lowest field, a symmetrical low field doublet (area 2), and a symmetrical high field doublet (area 16). This spectrum is in agreement with that of a  $B_{10}H_{10}^{-2}$  ion substituted at one apex. On this basis, III may be formulated as two  $B_{10}H_{10}^{-2}$  polyhedra joined by a two-center bond at their apices.<sup>4</sup>

Protonation of  $B_{20}H_{18}^{-4}$  to produce  $B_{20}H_{19}^{-3}$  may proceed by proton addition to this B-B two-center bond.<sup>4</sup> The  $B^{11}$  n.m.r. spectrum of an acidified solution of III is not sufficiently well defined to permit a firm decision to be made on this point. However, the spectra thus far obtained suggest that the acidic proton exists in an unsymmetrical environment. A B-H-B bridge band is observed at 5.40  $\mu$  in the infrared spectrum of  $B_{20}H_{19}^{-3}$ .

Assuming that the proposed structures<sup>4</sup> of  $B_{20}H_{18}^{-2}$  and  $B_{20}H_{18}^{-4}$  are correct, the oxidation of  $B_{20}H_{18}^{-4}$  to  $B_{20}H_{18}^{-2}$  in acidic solution requires the intervention of a molecular rearrangement<sup>5</sup> (apex-apex to apex-equatorial interactions).

**Acknowledgments.**—The research reported in this publication was generously supported by the Advanced Research Projects Agency through Army Research Office (Durham) and the Naval Ordnance Laboratory (Corona). The authors thank Mr. Donald Young for several boron analyses and thermogravimetric water determinations.

(4) A structure first suggested for a then unknown  $B_{10}H_{10}^{-2}$  ion by W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **47**, 1791 (1961). It was further postulated that a  $B_{20}H_{19}^{-3}$  could be formed by protonation of the B-B two-center bond in this  $B_{20}H_{18}^{-4}$  and that  $B_{20}H_{18}^{-2}$  contained two such bridge bonds, each of which joins two  $B_{10}H_{10}^{-2}$  units by apex-equatorial interaction.

(5) Such rearrangements were previously suggested by Kaczmarczyk-Dobrott and Lipscomb (ref. 2) and were described as polyhedral isomerizations in which apical and equatorial positions in  $B_{10}H_{10}^{-2}$  interconvert. Other reaction paths are also available.

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### Neighboring Group Participation in Phosphate Ester Hydrolysis

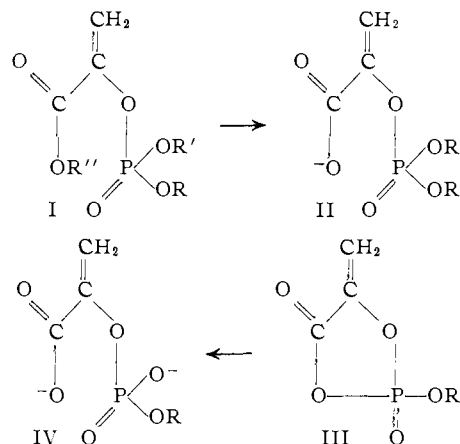
Sir:

We wish to report the rapid hydrolysis of the P,P-dimethyl ester (I,  $R = R' = CH_3$ ;  $R'' = H$ ) to free phosphoenol pyruvate under mildly acidic conditions.

Whereas in bicarbonate buffer (pH 8.0) at 100° this dimethyl ester undergoes quantitative hydrolysis in 6.5 hr. to the P-monomethyl ester<sup>1</sup> (IV,  $R = CH_3$ ), in initially neutral solution both methyl groups are lost at room temperature, the pH falling to 2.5, with hydrolysis to free phosphoenol pyruvate<sup>2</sup> (IV,  $R = H$ ) being complete within 72 hr.

Both stages of the hydrolysis involve nucleophilic attack on phosphorus since the P,P-diphenyl (I,  $R = R' = C_6H_5$ ,  $R'' = H$ ) and P-methyl, P-phenyl (I,  $R = CH_3$ ,  $R' = C_6H_5$ ,  $R'' = H$ ) esters also give free phosphoenol pyruvate under these conditions, the latter by way of the monomethyl ester (identified by paper chromatography).

The hydrolysis of the methyl group of IV ( $R = CH_3$ ) is much faster than that observed with simple dialkyl phosphates under acidic conditions.<sup>5</sup> Moreover, it is complete before detectable hydrolysis of the enol-ester linkage of the product occurs. These observations indicate a reversal of the usual order of relative reactivity of the mono- and dialkyl phosphates under similar conditions,<sup>5,6</sup> even though in this case the monoester is an enol phosphate. We suggest that the neighboring carboxyl group participates in the hydrolysis.<sup>7</sup> One possible mechanism involves nucleophilic attack on phosphorus by carboxylate oxygen.



At least one proton must be associated with the displacement, since the dianion (IV,  $R = CH_3$ ) is stable at pH 8. This implies that the molecular species displaced is methanol rather than methoxide ion. A concerted displacement is indicated by the specificity of both steps. In each case a methyl group is hydrolyzed preferentially, notwithstanding the fact that enol-ester linkages are usually more labile under acidic conditions.<sup>8</sup> Such selectivity is normally observed in the acid and base-catalyzed hydrolyses of trialkyl and dialkyl phosphate esters bearing vicinal hydroxyl functions.<sup>9,10</sup>

(1) Isolated as the barium salt, having a correct analysis, and consistent n.m.r. and infrared spectra.

(2) Phosphoenol pyruvic acid can be isolated as the monocyclohexylammonium salt in 50% yield. *Anal.* Found: C, 40.7; H, 6.9; N, 5.2.  $C_9H_{15}PO_3N$  requires C, 40.5; H, 6.7; N, 5.2. This is superior to previous methods for the synthesis<sup>3</sup> of this ester and we are reporting details of the preparation elsewhere.<sup>4</sup>

(3) F. Cramer and D. Voges, *Chem. Ber.*, **92**, 952 (1959).

(4) V. M. Clark and A. J. Kirby, *Biochim. Biophys. Acta*, in press.

(5) F. H. Westheimer, Special Publication No. 8, The Chemical Society, London, 1957, p. 1; C. A. Vernon, *ibid.*, p. 17.

(6) J. Kumamoto and F. H. Westheimer, *J. Am. Chem. Soc.*, **77**, 2515 (1955).

(7) Significantly the P-methyl, C-ethyl ester (I,  $R = H$ ,  $R' = CH_3$ ,  $R'' = C_2H_5$ ) is stable in aqueous solution at pH 5.

(8) F. W. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961).

(9) D. M. Brown in "Advances in Organic Chemistry. Methods and Results," Vol. 3, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience, Publishers, Inc., New York, N. Y., 1963, p. 75.