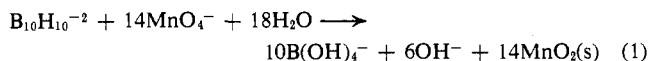


## Oxidative Degradation of Polyhedral Boranes<sup>1</sup>

Sir:

While exploring the chemistry of the  $B_{10}H_{10}^{-2}$  and  $B_{20}H_{18}^{-2}$  ions, we found the oxidation of these ions by potassium permanganate to be unique in that: (a) even at pH 7 it proceeds readily to completion at room temperature and (b) it results in quantitative conversion to boric acid. All the oxidation reactions of  $B_{10}H_{10}^{-2}$  so far reported<sup>2-4</sup> require acidic conditions and yield primarily varying amounts of  $B_2O_3$  and  $B_2O_4$ . Even concentrated nitric acid, which reacts explosively with  $B_{10}H_{10}^{-2}$ , fails to convert the ion quantitatively to boric acid. Yet a conductometric titration of a dilute aqueous solution of  $B_{10}H_{10}^{-2}$  with neutral dilute  $KMnO_4$  gives an end point satisfying the equation



In view of the remarkable thermal and hydrolytic stabilities of many of the recently synthesized boranes, carboranes, and haloboranes, which have changed boron analyses from a trivial into a complicated problem and forced some workers to resort to such esoteric methods as combustion in a fluorine atmosphere or oxidation on a platinum electrode,<sup>5</sup> the analytical possibilities of this reaction became immediately apparent. We have therefore examined the yield of boric acid from the oxidation of  $B_{10}H_{10}^{-2}$  (I),  $B_{12}H_{12}^{-2}$  (II),  $B_{20}H_{18}^{-2}$  (III),  $B_{20}H_{18}^{-4}$  (IV), and  $B_{20}H_{17}OH^{-4}$  (V) ions and their organic and halo derivatives by dilute permanganate. Except in conductometric titrations the boric acid content was determined by the standard analytical procedure after a 15-min. treatment of the salts with a 10% excess (over stoichiometric amount) of  $KMnO_4$ . One set of data was collected without pH control, another in weakly acidic to neutral solutions. The results are summarized below.

At pH 5-7 and room temperature the reaction was 100% complete for ion I and 96-99% complete for ions III, IV, and V; at 80° ions I-V were oxidized quantitatively. Without pH control at 80° ions I and II still underwent 99-100% oxidation; ions IV and V, 98-99%; but ion III, only 94-97%. At room temperature the extent of oxidation was 98-99% for I, 92-96% for IV and V, and 87-92% for III. Only ion I reacts fast enough to give an exact conductometric end point at room temperature; for ions III, IV, and V titration at pH 5-7 yielded end points corresponding to 96-99% of oxidation. The oxidation of  $B_{12}H_{12}^{-2}$  is too slow for conductometric titration at room temperature. Completely halogenated ions react very

(1) Research sponsored by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

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

(3) M. F. Hawthorne, R. L. Pilling, P. F. Stockely, and P. M. Garrett, *J. Am. Chem. Soc.*, **85**, 3704 (1963); A. R. Pitochelli, W. N. Lipscomb, and M. F. Hawthorne, *ibid.*, **84**, 3026 (1962).

(4) B. L. Chamberland and E. L. Muetterties, *Inorg. Chem.*, **3**, 1450 (1964).

(5) N. E. Miller, H. C. Miller, and E. L. Muetterties, *ibid.*, **3**, 866 (1964).

slowly, but the rate increases rapidly with increasing hydrogen:halogen ratio.

In dealing with more stable ions, the pH control was necessary because, despite the formation of a borate buffer, the pH of the reaction mixture rapidly rises in the course of reaction to about 9-10, which markedly reduces the reaction rate. To promote oxidation at room temperature one can either buffer the reaction system with a nonoxidizable salt (a fixed amount of  $MgSO_4$  introduced into the initial solution was found to be ideal for the conductometric titrations) or, if the boric acid is to be later determined by acid-base titration, add with the permanganate enough acid to keep the pH close to 7. We found it inadvisable to permit the pH to drop below 4 since frequently the oxidation may be incomplete owing to the formation of intermediate oxidation products requiring more rigorous reaction conditions. Moreover, at lower pH values partial reduction of the permanganate ion to  $Mn^{2+}$  will render the conductometric end point ambiguous and the ion, if not removed, will subsequently interfere with the boric acid determination.

In dealing with an unknown compound dilute (0.1-0.2 M)  $KMnO_4$  is added until the purple color persists for 15 min. at room temperature, then to ensure complete oxidation the mixture is heated for 30 min. on a steam bath and more permanganate added if necessary. Subsequently, unchanged permanganate is destroyed with oxalic acid and the boric acid is determined in the usual way. Conductometric titration can be used to get an accurate  $MnO_4^-:B$  ratio and establish the reaction stoichiometry from which, through an equation such as eq. 1, the correct formula of the oxidized ion can be deduced. This method, however, is only applicable to cases where the cation and the cage substituent, if any, either resist oxidation or are oxidized completely to a known oxidation state. With many organic cations and substituents this is not a serious problem at room temperature since they will react with neutral permanganate much more slowly than will the boron cages.

It is noteworthy that at 25° and pH >4  $K_2Cr_2O_7$  does not react at a measurable rate with  $B_{10}H_{10}^{-2}$ , while at pH <2  $B_{20}H_{18}^{-2}$  is produced quantitatively. Use of acidic permanganate and dichromate in the synthesis of  $B_{20}H_{18}^{-2}$  has already been reported.<sup>4</sup> To explain why neutral permanganate succeeds where  $Ce^{+4}$  and acidic dichromate fail, we had undertaken a study of the oxidation mechanism and the detailed results will be published at a later date. However, preliminary work indicates that the permanganate ion replaces the cage hydrogens by hydroxyls and after two to three hydroxyls are introduced the ion undergoes extensive decomposition.

(6) National Science Foundation Undergraduate Research Assistant, 1963-1964.

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Received January 11, 1965