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## Chemistry of Boranes. XXII.<sup>1</sup> Polyhedral Rearrangement of Derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$

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Individual isomers of bis(trimethylamine) decaborane (8),  $B_{10}H_8[N(CH_3)_3]_2$ , undergo isomerization at 300° to give an equilibrium mixture of isomers. Characterization of the rearrangement of C<sup>14</sup>-labeled 1,6-isomer yielded thermodynamic estimates; e.g., the enthalpy change for 1,10 ⇌ 2,7(8) isomerization is 0.77 kcal./mole. The 1,6-isomer is the sole product from 2,3-rearrangement at 220°. Activation parameters for this isomerization are  $\Delta H^* = 37$  kcal./mole and  $\Delta S^* = +2.4$  e.u. The 1,10-isomer of  $B_{10}H_8(CN)_2^{2-}$  rearranges above 350° to a predominantly equatorially substituted isomeric mixture. Rates of isomerization of the 1,2- and 1,6-isomers of  $(CH_3)_2SB_{10}H_8N(CH_3)_3$  are comparable. These structural interconversions are discussed in terms of an intramolecular "polyhedral rearrangement" mechanism. The vicinal isomer of  $B_{12}H_{10}[N(CH_3)_3]_2$  undergoes degradation at 325°. The 1,12-isomer does not isomerize at ~530° and the 1,7-isomer is mostly unchanged at 400°.

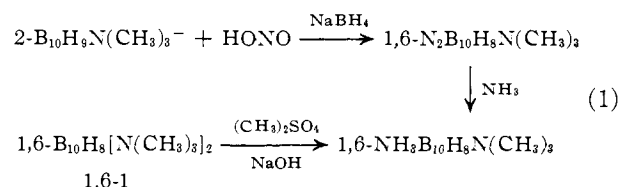
### Introduction

Rearrangement reactions have long provided intriguing and fruitful areas of research in both organic and inorganic chemistry. Of particular interest to us was the possibility of rearrangement of clovoboranes (closed polyhedral boranes). Recent work<sup>2</sup> has shown that icosahedral 1,2- $C_2B_{10}H_{12}$  undergoes rearrangement at ~500° to 1,7- $C_2B_{10}H_{12}$ . Hoffmann, Lipscomb, Kaczmarczyk, and Dobrott<sup>3a,b</sup> have discussed this and related hypothetical rearrangements in some detail in terms of stabilities of various isomers as estimated from LCAO-MO calculations.<sup>4</sup> A specific mechanism was proposed<sup>3a</sup> for the isomerization of  $C_2B_{10}H_{12}$ ,<sup>2</sup> and it was predicted that 1,2- and 1,7- $B_{12}H_{10}X_2^{2-}$  would undergo isomerization by the same mechanism. The proposed mechanism involves isomerization without breaking any bonds external to the polyhedral "cage." A cuboctahedron was proposed as an intermediate in the lowest energy pathway for isomerization of  $C_2H_{10}H_{12}$  or  $B_{12}H_{10}X_2^{2-}$ . However, a recent demonstration<sup>5</sup> of the thermal isomerization of neocarborane to *p*-carborane indicates that a rearrangement pathway which does not involve a cuboctahedron intermediate is also available in this system. Kaczmarczyk, Dobrott, and Lipscomb<sup>3b</sup> suggested that substituted derivatives of  $B_{10}H_{10}^{2-}$  should undergo polyhedral rearrangement and reported the isomerization of 1- $B_{10}H_9OH^{2-}$  to 2- $B_{10}H_9OH^{2-}$ . This work, however, has been shown to be erroneous.<sup>6</sup> Since earlier studies have made available to us four isomers of  $B_{10}H_8[N(CH_3)_3]_2$  (1),<sup>7-9</sup> all three isomers of  $B_{12}H_{10}[N(CH_3)_3]_2$  (2),<sup>7</sup> and a variety of other substituted derivatives of  $B_{10}H_{10}^{2-}$  of known configuration, a

study of polyhedral isomerizations in these systems was undertaken.

### Results

**Preparation of 1,6- $B_{10}H_8[N(CH_3)_3]_2$ .**—Methods for preparation of four of the seven possible isomers of  $B_{10}H_8[N(CH_3)_3]_2$  (1) have recently been published.<sup>7,8</sup> Thus, with 2,3-, 2,4-, 1,10-,<sup>7</sup> and 2,7(8)-<sup>8</sup> 1 in hand, only the 1,6-, 1,2-, and 2,6(9)- isomers remained unknown (see Fig. 1). In order to complete the collection of (four) nonvicinal isomers of 1 for our study of polyhedral rearrangement, the 1,6-isomer was synthesized as indicated in eq. 1. Nitrous acid has been shown<sup>10</sup> to react with  $B_{10}H_{10}^{2-}$  preferentially at the apical positions to give, after a reduction step, 1,10-



$B_{10}H_8(N_2)_2$ . Similarly 2- $B_{10}H_9N(CH_3)_3^-$  reacted with nitrous acid to give 1,6- $N_2B_{10}H_8N(CH_3)_3$ . Thin layer chromatography (t.l.c.) of the purified product on silica gel gave no evidence for the presence of more than one isomer.  $N_2B_{10}H_8N(CH_3)_3$  reacted with ammonia at 160° to give  $NH_3B_{10}H_8N(CH_3)_3$  which reacted with dimethyl sulfate to give 1,6- $B_{10}H_8[N(CH_3)_3]_2$  (see eq. 1). The assigned stereochemistry is confirmed by the B<sup>11</sup> n.m.r. spectrum (Fig. 2) which is discussed in detail in the Experimental section.

**Isomerization of  $B_{10}H_8[N(CH_3)_3]_2$ .**—All five of the available isomers of 1 underwent isomerization at 300° in the melt to give an identical mixture of isomers of 1 as determined by infrared spectroscopy. Thin layer chromatography (t.l.c.) of the isomerization mixture in each case showed the presence of 1,10-, 2,7(8)-, 2,4-, 1,6-, and 2,3-1 (in order of decreasing  $R_f$ ). No additional spots were apparent which means that if 1,2- and 2,6(9)-1 were components of the isomerization mixtures, their chromatographic behavior was similar to that of one or more of the observed components. Since the  $R_f$  values of the five available isomers of 1 are approximately inversely variable with the polarity of the isomers, the 1,2- and 2,6(9)- isomers

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(2) H. Schroeder and G. D. Vickers, *ibid.*, **2**, 1317 (1963); see also D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963).

(3) (a) R. Hoffmann and W. N. Lipscomb, *ibid.*, **2**, 231 (1963); (b) A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S. A.*, **48**, 729 (1962).

(4) (a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962); (b) R. Hoffmann and W. N. Lipscomb, *ibid.*, **37**, 2872 (1962); (c) R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 3489 (1962).

(5) S. Papetti and T. L. Heying, *J. Am. Chem. Soc.*, **86**, 2295 (1964).

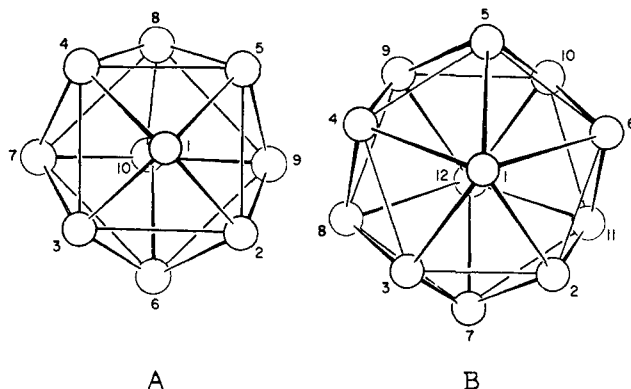
(6) M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garrett, *ibid.*, **85**, 3704 (1963).

(7) W. R. Hertler and M. S. Raasch, *ibid.*, **86**, 3661 (1964).

(8) W. R. Hertler, *Inorg. Chem.*, **3**, 1195 (1964).

(9) W. R. Hertler, *J. Am. Chem. Soc.*, **86**, 2949 (1964).

(10) W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *ibid.*, **86**, 115 (1964).

Fig. 1.— $B_{10}H_{10}^{2-}$  (A) and  $B_{12}H_{12}^{2-}$  (B).

might be expected to migrate on silica gel at about the same rate as the 2,3- isomer. The fact that identical isomeric mixtures were obtained from each of the five isomers indicates that equilibration is complete at  $300^\circ$  in 30 min.

**Isomerization of 1,6- $B_{10}H_8[N(CH_3)_3]_2$ - $C^{14}$ .**—Quantitative determination of the composition of the equilibrium isomerization mixture would permit calculation of the thermodynamic parameters for the various isomers. Accordingly, 1,6-1- $C^{14}$  was prepared by the reaction of 1,6- $NH_3B_{10}H_8N(CH_3)_3$  with dimethyl sulfate- $C^{14}$ . The labeled 1,6-1 was isomerized at two different temperatures, ( $300^\circ$  and  $325^\circ$ ), and the products were separated by t.l.c. on silica gel. The composition of the mixtures was determined by scintillation counting of the spots on the chromatogram. The results are summarized in Table I. Because chromatographic separation of 2,4-1 and 1,6-1 was only marginal, the individual equilibrium concentrations of these isomers in Table I are probably not as reliable as the combined concentrations (in brackets). It is apparent that 2,3-1 and/or other vicinally substituted isomers of 1 are present in considerably lower concentrations than the nonvicinally substituted isomers.

TABLE I

COMPOSITION OF THERMALLY EQUILIBRATED ISOMERIC MIXTURES OF  $B_{10}H_8[N(CH_3)_3]_2$ 

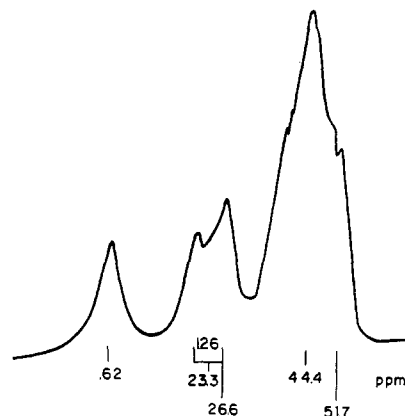
Isomer of 1	Relative concentration		Composition of a statistical mixture
	$300^\circ$	$325^\circ$	
1,10-	1.0	1.0	1
2,7(8)-	4.19	4.31	8
2,4-	[1.75]	[1.51]	4
1,6-	[3.90]	[4.85]	8
2,3- <sup>a</sup>	0.043	0.107	8 <sup>b</sup>

<sup>a</sup> This may be a mixture of the 2,3-, 1,2-, and 2,6(9)- isomers.

<sup>b</sup> This number should be 24 if 1,2- and 2,6(9)-1 are included here.

From the data of Table I we can calculate a plot of  $1/T$  vs.  $\ln K_{eq}$  for the equilibrium  $1,10-1 \rightleftharpoons 2,7(8)-1$ ,  $\Delta F = -1.63$  kcal.,  $\Delta H = +0.77$  kcal., and  $\Delta S = 4.19$  e.u. at  $300^\circ$ . Because of the rather narrow temperature range to which we are restricted by the nature of our materials, the reliability of the value of  $\Delta S$  is questionable. Nevertheless, it is interesting that essentially all of the entropy term is accounted for by the statistical factor (8, see Table I).

**Isomerization of 2,3- $B_{10}H_8[N(CH_3)_3]_2$ .**—The high ground-state energy of 2,3-1 relative to 1,10-, 2,4-, 1,6-

Fig. 2.— $B^{11}$  n.m.r. spectrum (19.2 Mc.) of 1,6- $B_{10}H_8[N(CH_3)_3]_2$  in acetonitrile-ethylene chloride ( $J$  in c.p.s.);  $\delta$  refers to external methyl borate.

and 2,7(8)-1, as indicated by the data in Table I, suggested that 2,3-1 might undergo isomerization at a lower temperature than the more stable isomers which would then permit identification of the initial product of isomerization. Solution studies in Dowtherm A and 1,1,2,2-tetrachloroethane showed that at  $230^\circ$ , 1,10-, 1,6-, 2,4-, and 2,7(8)-1 underwent no appreciable isomerization in 30 min. Under these conditions, however, 2,3-1 rearranged exclusively to 1,6-1. Attempts to find conditions under which 1,10-, 1,6-, 2,4-, and 2,7(8)-1 would undergo selective isomerization failed. In each case at least two additional isomers were formed.

A kinetic study showed that the isomerization of 2,3-1 to 1,6-1 in tetrachloroethane solution was cleanly first order in 2,3-1. The results, summarized in Table II, permit the calculation of the activation parameters,  $\Delta H^* = 37$  kcal. and  $\Delta S^* = +2.4$  e.u.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THERMAL ISOMERIZATION OF 2,3- TO 1,6- $B_{10}H_8[N(CH_3)_3]_2$  IN TETRACHLOROETHANE SOLUTION

Temp., $^\circ C.$	195.3	209.9	219.9
$k_1 \times 10^3$ , sec. <sup>-1</sup>	0.319	1.0	2.37
$\Delta H^* = 37$ kcal., $\Delta S^* = 2.4$ e.u. at $195.3^\circ$			

**Isomerization of  $B_{12}H_{10}[N(CH_3)_3]_2$ .**—Methods for the preparation of the three isomers of  $B_{12}H_{10}[N(CH_3)_3]_2$  (2) have been described.<sup>7</sup> 1,12-2, which does not melt up to  $\sim 530^\circ$ , also fails to undergo polyhedral isomerization up to this temperature within the detection limits of t.l.c. which showed only unchanged 1,12-2. Slow decomposition was also apparent. When 1,7-2 was heated in the melt at  $400^\circ$  for 5 min., there appeared to be little decomposition. Thin layer chromatography of the product showed it to consist primarily of unchanged 1,7-2 with indication of a small amount of 1,2-2 but no 1,12-2. Unfortunately, the amount of 1,2-2 formed was too small to permit its unequivocal identification by standard methods. Particularly disappointing was the observation that 1,2-2 underwent rapid decomposition to trimethylamine and as yet uncharacterized products at the melting point. No rearrangement products were identified by t.l.c. Similar results were encountered with solutions of 1,2-2 in Dowtherm A at  $325^\circ$ .

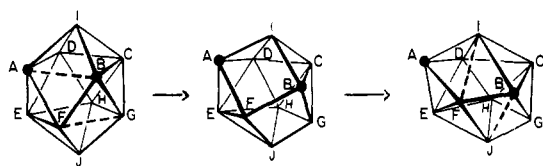


Fig. 3.—Polyhedral rearrangement of 2,3- $B_{10}H_8[N(CH_3)_3]_2$  to 1,6- $B_{10}H_8[N(CH_3)_3]_2$ .

**Isomerization of  $B_{10}H_8(CN)_2^{2-}$ .**—Thermal dehydration of the cesium salt of 1,10- $B_{10}H_8(CONH_2)_2^{2-}$  at 300–310° gave 1,10- $B_{10}H_8(CN)_2^{2-}$  without any observable isomerization. However, at higher temperatures (350–500°) an isomeric product was obtained,  $\xi$ - $B_{10}H_8(CN)_2^{2-}$ , which differs from the 1,10- isomer with respect to infrared, ultraviolet, and  $B^{11}$  n.m.r. spectra. The  $B^{11}$  n.m.r. spectrum of  $\xi$ - $B_{10}H_8(CN)_2^{2-}$  clearly shows the presence of unsubstituted apical boron atoms (low-field multiplet which can be decoupled on irradiation at 60 Mc.) which, of course, are absent in the 1,10- isomer. It has not been possible to determine the stereochemistry of  $\xi$ - $B_{10}H_8(CN)_2^{2-}$  but it is presumed to be a mixture of several isomers, perhaps all seven.  $\xi$ - $B_{10}H_8(CN)_2^{2-}$  also differs from 1,10- $B_{10}H_8(CN)_2^{2-}$ , in chemical reactivity. Nitrous acid, a reagent which has been shown to react with  $B_{10}H_{10}^{2-}$  preferentially at the apical positions,<sup>10</sup> failed to react with 1,10- $B_{10}H_8(CN)_2^{2-}$ . However  $\xi$ - $B_{10}H_8(CN)_2^{2-}$  which has some free apical positions, reacted with nitrous acid to give, after reduction with zinc dust,  $\xi$ - $N_2B_{10}H_7(CN)_2^{2-}$ .

Attempted thermal isomerization of 1,12- $B_{12}H_{10}(CN)_2^{2-}$  at 500° gave inconclusive results.<sup>10</sup> Although changes occurred at this temperature, it was not possible to demonstrate whether they were due to degradation, polymerization, or isomerization.

### Discussion

The thermal conversion of all of the five available isomers of  $B_{10}H_8[N(CH_3)_3]_2$  (**1**) to an identical mixture of isomers is consistent with a mechanism in which rupture of boron-substituent bonds does not occur<sup>3</sup> ("polyhedral rearrangement"<sup>11</sup>), but neither is a stepwise dissociation mechanism precluded whereby cleavage of a boron-ligand bond occurs followed by hydrogen migration and recombination. However, the observation that under limiting conditions 2,3-**1** can be isomerized exclusively to 1,6-**1** is more satisfactorily explained by a polyhedral rearrangement<sup>3</sup> than by a dissociation-recombination mechanism (see Fig. 3). Examination of models indicates that stretching of the  $B_2$ - $B_3$  (A-B in Fig. 3) bond of 2,3-**1** should be a potent factor in the smooth isomerization to 1,6-**1**, a process which has been said to require less than 0.5 Å. of motion by any boron atom.<sup>3b</sup>

Semiquantitative determination of the composition of the equilibrium mixture of isomers from rearrangement of 1,6-**1** (see Table I) shows that the differences in free energy among the various nonvicinal isomers of **1** are fairly small with 1,10-**1** being the most stable. However, the vicinal isomers of **1** appear to be appreciably

less stable than 1,10-, 2,7(8)-, 2,4-, and 1,6-**1** because of coulombic repulsions and nonbonded interactions of the substituents. The experimentally determined activation energy ( $\Delta H^*$ ), 37 kcal., for the thermal isomerization of 2,3-**1** to 1,6-**1** is consistent with major alterations of framework bonding in the transition state. This particular rearrangement certainly has a lower  $\Delta H^*$  than do rearrangements of nonvicinal isomers of **1** as evidenced by the higher temperatures required for appreciable isomerization of 1,6-, 2,7(8)-, 1,10-, and 2,4-**1**. Measurement of the energy of activation for rearrangement of nonvicinal isomers of **1**, however, has been hampered by the tendency for equilibration to occur at the required temperatures. The small positive value of  $\Delta S^*$  (+2.4 e.u.) for 2,3-**1**  $\rightarrow$  1,6-**1** probably reflects a modest relief of steric interaction in forming the transition state. The small numerical value may indicate that separation of  $B_2$  and  $B_3$  has not proceeded to its maximum extent in the transition state. In other words, the transition state may resemble 2,3-**1** more than it resembles 1,6-**1** as would be anticipated in an exergonic process. From the data in Table I, we can estimate a rough value of -4.5 to -6.4 kcal. for 2,3-**1**  $\rightleftharpoons$  1,6-**1**. An examination of scale models indicates that the maximum stretching of  $B_2$  and  $B_3$  during the transformation 2,3-**1**  $\rightarrow$  1,6-**1** is in the range 1.1 to 1.3 Å., a value slightly higher than the  $\sim 1$  Å. (0.5-Å. movement per boron atom) suggested earlier<sup>3b</sup> for polyhedral isomerization of derivatives of  $B_{10}H_{10}^{2-}$ . Our values are based on extrapolations of B-B separations as determined in X-ray studies of  $B_{10}H_{10}^{2-}$ <sup>12</sup> and 1,2-( $CH_3$ )<sub>2</sub>SB<sub>10</sub>H<sub>8</sub>NH( $CH_3$ )<sub>2</sub>.<sup>13</sup>

Examination of models indicates that the simplest mechanism (stretching of smallest number of B-B bonds) for isomerization of substituted derivatives of  $B_{10}H_{10}^{2-}$  is that depicted in Fig. 3 for the isomerization of 2,3-**1** to 1,6-**1**. In this mechanism, simultaneous extension of one nearest neighbor B-B bond in each of the equatorial belts (in the example, bonds A-B and F-G) produces an "intermediate" in which the boron framework has  $C_{2v}$  symmetry. Continuation of the bond extension then leads to formation of two new B-B bonds (I-F and B-J in Fig. 3). Note that the "intermediate" in Fig. 3 need not necessarily correspond to an inflection in the energy surface for polyhedral isomerization, although in some isomerizations it may be a reasonable approximation to the transition state. This mechanism appears to be essentially that suggested by Kaczmarczyk, Dobrott, and Lipscomb<sup>3b</sup> for polyhedral rearrangement of  $B_{10}H_9OH^{2-}$ . Application of this mechanism to the polyhedral rearrangement of various isomers of  $B_{10}H_8X_2^{2-}$  leads to the predictions of primary transformations listed in Table III.

Several interesting features are apparent from Table III. First, the only pathway for conversion of a vicinal isomer of  $B_{10}H_8X_2^{2-}$  to a nonvicinal isomer is *via* 2,3- $B_{10}H_8X_2^{2-}$ . Secondly, the proposed mechanism predicts that 2,3- $B_{10}H_8X_2^{2-}$  will undergo primary isomerization to 1,6-, 1,2-, 2,6(9)- and 2',3'- $B_{10}H_8X_2^{2-}$ . Yet isomerization of 2,3-**1** led exclusively to 1,6-**1**. The 2,3- $B_{10}H_8X_2^{2-} \rightarrow$  1,6- $B_{10}H_8X_2^{2-}$  conversion proceeds by extension of the B-B bond which joins the two X-substituted boron atoms (A-B in Fig. 3) and clearly in the case of 2,3-**1** this should be an especially favorable proc-

(11) "Polyhedral rearrangement" seems to be a reasonable term to designate rearrangement processes in polyhedral molecules where it is suspected that rearrangement involves intramolecular rearrangement of the framework rather than migration of substituents. This term has been applied to such processes by W. N. Lipscomb in "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p. 190.

(12) R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 1779 (1962).

(13) J. F. Whitney, unpublished results.

TABLE III

PATHWAYS FOR ISOMERIZATION OF  $B_{10}H_8X_2^{2-}$ 

Isomer	Products <sup>a</sup>
1,10-	2,7(8)-
1,2-	1',2', 2,3-, 2,6(9)- <sup>b</sup>
2,6(9)-	1,2-, <sup>b</sup> 2,3-, 2',6'(9')-
2,3-	1,6-, 1,2-, 2,6(9)-, 2',3'-
2,4-	2,7(8)-, 1,6-
2,7(8)-	2',7'(8')-, <sup>c</sup> 1,10-, 2,4-, <sup>b</sup> 1,6- <sup>b</sup>
1,6-	2,3-, 2,4-, 1',6'-, 2,7(8)-

<sup>a</sup> Primed numbers indicate interchange of substituents, observable only with  $B_{10}H_8XY^{2-}$ . <sup>b</sup> Statistical frequency of 2. <sup>c</sup> Statistical frequency of 3.

ess because of the size and charge of the substituents. Perhaps with other types of substituents, rearrangement of  $2,3-B_{10}H_8X_2^{2-}$  would produce isomers other than the 1,6. Finally, this mechanism predicts that  $1,10-B_{10}H_8X_2^{2-}$  will rearrange first to a single isomer.

Brief studies of the thermal requirements for polyhedral rearrangement of  $1,2-(CH_3)_2SB_{10}H_8N(CH_3)_3$  and  $1,6-(CH_3)_2SB_{10}H_8N(CH_3)_3$ <sup>14</sup> show that qualitatively the 1,2- isomer undergoes rearrangement no more readily than does the 1,6- isomer. This observation is consistent with the mechanism proposed for polyhedral rearrangement since this mechanism requires that  $1,2-B_{10}H_8X_2^{2-}$  undergo primary rearrangement only to 2,3-, 2,6(9)-, and 1',2'- $B_{10}H_8X_2^{2-}$ . Thus, starting material and products would all be expected to have high ground state energies relative to nonvicinal isomers. The energy of activation for polyhedral rearrangement of  $1,2-(CH_3)_2SB_{10}H_8N(CH_3)_3$  relative to that for  $1,6-(CH_3)_2SB_{10}H_8N(CH_3)_3$  should not be effectively diminished by a large favorable difference in enthalpy between starting material and product in marked contrast to the results for  $2,3-B_{10}H_8[N(CH_3)_3]_2 \rightarrow 1,6-B_{10}H_8[N(CH_3)_3]_2$ . If some other mechanism were operative in which attainment of the transition state involved appreciable extension of the B-B bond joining  $B_1$  and  $B_2$  of  $1,2-(CH_3)_2SB_{10}H_8N(CH_3)_3$ , then we should expect much greater thermal lability for this isomer relative to the 1,6- isomer in contrast to the experimental observations.

An especially important test of the proposed cuboctahedron<sup>3a</sup> intermediate in the rearrangement of substituted derivatives of  $B_{12}H_{12}^{2-}$  should be the rearrangement behavior of 1,2-, 1,7-, and 1,12- $B_{12}H_{10}[N(CH_3)_3]_2$ , since this intermediate places certain restrictions on the isomerization possibilities. Specifically 1,2- and 1,7- isomers should be interconvertible but should not isomerize to the 1,12- isomer, and the 1,12- isomer should not isomerize. The results obtained from the isomerization studies with 1,2-, 1,7-, and 1,12- $B_{12}H_{10}[N(CH_3)_3]_2$  (2) are consistent with this mechanism, but unfortunately do not provide the penetrating test which was hoped for because of competing decomposition of 1,2-2. Thus, under the conditions examined, 1,12-2 failed to isomerize, while 1,7-2 at 400° appeared to undergo slight isomerization to 1,2-2 but not to 1,12-2.

The thermal isomerization of  $1,10-B_{10}H_8(CN)_2^{2-}$  to an isomeric mixture, in which the substituents are to a

(14) W. H. Knoth, W. R. Hertler, and E. L. Muetterties, *Inorg. Chem.*, in press.

large extent equatorial, demonstrates that polyhedral rearrangements are not limited to nonionic derivatives. The higher reactivity of the rearranged dinitrile toward electrophilic substitution by nitrous acid than the 1,10-dinitrile provides an intriguing entry into studies of new polyfunctional clovoboranes.

Our results argue for characterization of intramolecular polyhedral rearrangements as relatively high energy processes. Rearrangement of  $2,3-B_{10}H_8[N(CH_3)_3]_2$  is without question one of the most favorable rearrangements in that coulombic and steric repulsions are quite large. Yet the activation energy for this favorable case is 37 kcal. The barrier to rearrangements of other isomers should be significantly higher—a situation qualitatively indicated by the higher temperatures required for isomerization of 1,10-, 2,7(8)-, 1,6-, and 2,4- $B_{10}H_8[N(CH_3)_3]_2$ . Again, from a qualitative assay of isomerization temperatures, rearrangements in the  $B_{12}H_{12}^{2-}$  series appear to be intrinsically higher energy processes than rearrangements in the  $B_{10}H_{10}^{2-}$  series. Delineation of the energy profile in polyhedral rearrangements was critical to our studies dealing with the mechanism and stereochemistry of substitution reactions of  $B_{10}H_{10}^{2-}$  and  $B_{12}H_{12}^{2-}$ . Since the isomerization barrier is relatively high, we now feel more secure in ascribing the resultant stereochemistry in substitution reactions effected at moderate temperatures for derivatives of  $B_{10}H_{10}^{2-}$  and  $B_{12}H_{12}^{2-}$  to largely kinetic factors relating to the attacking reagent and *in some cases* to the ground-state charge distribution in the polyhedron. Certainly, our experimental observations that specific geometries can be maintained through a series of replacement reactions<sup>15</sup> supports this contention.

### Experimental<sup>16</sup>

**1,6- $N_2B_{10}H_8N(CH_3)_3$ .**—A solution of 5 g. of  $(CH_3)_3N[2-B_{10}H_8N(CH_3)_3]^{7-}$  in water was passed through a sodium cation-exchange column, and the effluent was concentrated *in vacuo* to a volume of 50 ml. The resulting solution was added to a cooled solution of 15 g. of sodium nitrite and 20 ml. of acetic acid in 100 ml. of water. After a few minutes the resulting yellow precipitate was collected by filtration and transferred while still moist to a stirred slurry of 10 g. of sodium borohydride in 100 ml. of methanol. After 1 hr., 50 ml. of water was added, and the methanol was removed under reduced pressure. The resulting slurry was filtered to give 2.56 g. of tan solid. Recrystallization from acetone-ethanol and from acetonitrile gave pale orange crystals of  $1,6-N_2B_{10}H_8N(CH_3)_3$ , m.p. >400°. Satisfactory C and N analyses have never been obtained for this product although it is homogeneous to t.l.c. *Anal.* Calcd. for  $C_{10}H_{17}N_3$ : B, 53.3; H, 8.44; C, 17.7; N, 20.7. Found: B, 53.3; H, 8.29; C, 16.5; N, 18.2. The infrared spectrum of the product shows strong absorption at 2210  $cm^{-1}$  characteristic of the diazonium group. The ultraviolet spectrum of the product in acetonitrile has absorption at 392 ( $\epsilon$  46) and 258  $m\mu$  ( $\epsilon$  19,100).

**1,6- $NH_3B_{10}H_8N(CH_3)_3$ .**—A mixture of 4 g. of  $1,6-N_2B_{10}H_8N(CH_3)_3$  and 80 ml. of liquid ammonia was heated at 160° under autogenous pressure in a shaker tube for 4 hr. The crude product was dissolved in acetonitrile and filtered. The filtrate was evaporated, and the residue was suspended in water and filtered to give 3.84 g. of tan  $1,6-NH_3B_{10}H_8N(CH_3)_3$ . The product was purified by recrystallization from acetonitrile-benzene to give crystals of  $1,6-NH_3B_{10}H_8N(CH_3)_3 \cdot 0.5CH_3CN$ , m.p. 305–307° cor. *Anal.*

(15) Various displacement reactions with  $1,10-B_{10}H_8(N_2)_2^{10}$  have been tried. In all of these where reaction temperature is below ~200°, the 1,10-configuration is maintained. Moreover, as mentioned in this paper,  $1,10-B_{10}H_8(CONH_2)_2^{2-}$  is converted to  $1,10-B_{10}H_8(CN)_2^{2-}$  at ~300°. Rearrangement does not occur at a significant rate at these temperatures.

(16) All melting points are uncorrected unless otherwise indicated.  $B^{11}$  n.m.r. spectra were determined at 19.2 Mc. Decoupling experiments were performed with an NMR Specialties Model SD60 spin decoupler.  $H^1$  n.m.r. spectra were determined at 60 Mc.

Calcd. for  $B_{10}H_{20}C_8N_2 \cdot 0.5CH_3CN$ : B, 50.7; H, 10.2; C, 22.6; N, 16.5. Found: B, 50.6; H, 10.1; C, 22.5; N, 16.9, 17.1. The infrared spectrum of the product shows absorption at 3300, (N-H str.), 2500 (B-H str.), 2250 (C≡N), 1580 (N-H def.), and 1490  $cm^{-1}$  ( $Me_2N^+$ ).

**1,6- $B_{10}H_8[N(CH_3)_3]_2$ .**—A solution of 120 mg. of 1,6- $NH_3B_{10}H_8N(CH_3)_3$  and one pellet of sodium hydroxide in 15 ml. of water and 10 ml. of tetrahydrofuran was heated at reflux and treated three times with 5 ml. of 10% sodium hydroxide and 0.6 ml. of dimethyl sulfate. The resulting mixture was evaporated under reduced pressure, and the resulting slurry was filtered to give 145 mg. (99%) of 1,6- $B_{10}H_8[N(CH_3)_3]_2$ . Recrystallization from acetone-ethanol gave crystals with m.p. 250–252° cor. *Anal.* Calcd. for  $B_{10}H_{26}C_6N_2$ : B, 46.1; H, 11.2; C, 30.7; N, 12.0. Found: B, 46.4; H, 11.2; C, 31.1; N, 11.9. The  $H^1$  n.m.r. spectrum of the product in chloroform-*d* shows two peaks of equal intensity at  $\tau$  6.35 and 7.2 (external reference, tetramethylsilane) which can be assigned to apical  $N(CH_3)_3$  and equatorial  $N(CH_3)_3$ , respectively.

The  $B^{11}$  n.m.r. spectrum of 1,6- $B_{10}H_8[N(CH_3)_3]_2$  (Fig. 2) is consistent with a structure in which there is one substituted apical boron atom (single peak at 0.62 p.p.m.) and one substituted equatorial boron atom (single peak at 26.6 p.p.m.). The doublet corresponding to the unsubstituted apical boron atom appears at 23.3 p.p.m. ( $J = 126$  c.p.s.) with the high field half-coincident with the 26.6-p.p.m. peak. On irradiating at 60 Mc., the 23.3-p.p.m. doublet and the 26.6-p.p.m. singlet collapse to a single peak at 24 p.p.m. The 44.4-p.p.m. multiplet, which can also be decoupled to a single peak, represents the remainder of the unsubstituted equatorial boron atoms. The intensity ratios of the 0.62-p.p.m. peak:23.3 + 26.6-p.p.m. peaks:44.4 + 51.7-p.p.m. peaks = 1.2:2.4:6.5 (theory requires 1:2:7). The 51.7 peak presumably represents the high-field half of a doublet representing two equatorial boron atoms ( $B_2$  and  $B_3$ ) shifted about 7.3 p.p.m. to high field by the two adjacent substituted boron atoms. Since the 23.3-p.p.m. doublet is shifted to higher field than a normal apical boron atom in simple derivatives of  $B_{10}H_{10}^{2-}$  (usually 14–18 p.p.m.), we can conclude that the apical boron atom responsible for the 23.3-p.p.m. doublet is adjacent to a substituted boron atom which produces the high-field shift. Thus, the spectrum is more consistent with 1,6 than 1,2 stereochemistry.

**1,6- $B_{10}H_8[N(CH_3)_3]_2 \cdot C^{14}$ .**—To a refluxing solution of 76 mg. (0.396 mmole) of 1,6- $NH_3B_{10}H_8N(CH_3)_3$  in a mixture of 18 ml. of water and 0.5 ml. of 10% sodium hydroxide solution was added 50 mg. (0.396 mmole) of dimethyl sulfate (containing 500  $\mu c.$  of  $C^{14}$ ) together with enough tetrahydrofuran to ensure quantitative transfer. Then 1 ml. of 10% sodium hydroxide solution was added. After 5 min., 5 ml. of 10% sodium hydroxide solution and 0.6 ml. of ordinary dimethyl sulfate were added. Next, 6 ml. of tetrahydrofuran was added to aid in solubilizing the precipitate which was forming. The refluxing mixture was then treated three times with 5 ml. of 10% sodium hydroxide solution and 0.6 ml. of ordinary dimethyl sulfate.

The resulting mixture was concentrated *in vacuo*, and the resulting slurry was filtered to give 75 mg. of 1,6- $B_{10}H_8[N(CH_3)_3]_2 \cdot C^{14}$ . The infrared spectrum of the product was identical with that of authentic 1,6- $B_{10}H_8[N(CH_3)_3]_2$ .

**Isomerization of 1,6- $B_{10}H_8[N(CH_3)_3]_2 \cdot C^{14}$ .**—In a typical isomerization experiment, a small sample of 1,6-1- $C^{14}$  was placed in the bottom of a Pyrex sublimation tube under a nitrogen atmosphere. The tube was heated at the desired temperature by means of a thermostated sublimation-tube heater. The temperature remained constant to within  $\pm 1.5^\circ$ . At the end of the reaction period, the product was dissolved in a small volume of acetonitrile and applied to silica gel thin layer chromatography plates which were developed and detected as described earlier.<sup>7</sup> The spots were carefully scraped into vials for scintillation counting. The relative counts per minute are reported in Table I in which each entry is the average of at least two chromatograms. The results after 15 and 30 min. at 300° were essentially the same, which shows that equilibration is complete at 300° in this time range. At 275° (in the melt), however, equilibration was not complete after 30 min. as indicated by higher concentrations of 1,6- and 2,7(8)-1 than was observed at 300 or 325°.

**Isomerization of 2,3- $B_{10}H_8[N(CH_3)_3]_2$ .**—A small sample of 2,3-1 was heated in a tube at 230° for 30 min. with sufficient Dowtherm A to give a homogeneous solution. The resulting solution was diluted with pentane, and the resulting precipitate was collected

by filtration to give 1,6- $B_{10}H_8[N(CH_3)_3]_2$  identified by infrared spectrum and t.l.c. No other isomers were detected.

**Kinetics of Isomerization of 2,3- $B_{10}H_8[N(CH_3)_3]_2$  to 1,6- $B_{10}H_8[N(CH_3)_3]_2$ .**—In order to prepare solutions of 2,3-1 in 1,1,2,2-tetrachloroethane at room temperature, it was necessary to use an intimate mixture of 2,3- and 1,6-1 to increase solubility. The resulting solution was 0.1090 *M* in 1 (0.0664 *M* in 2,3-1 and 0.0426 *M* in 1,6-1 as determined by the  $H^1$  n.m.r. spectrum). No correction was made for expansion of solvent. Aliquots (0.5 ml.) of the solution were sealed in standard n.m.r. tubes and placed in a thermostated oil bath in which the temperature was controlled to within  $\pm 0.1^\circ$ . Tubes were removed from the bath at timed intervals, and disappearance of 2,3-1 and formation of 1,6-1 was followed by observing the 60-Mc.  $H^1$  n.m.r. spectrum in which  $N(CH_3)_3$  groups of 2,3-1 appeared as a single peak at  $\tau$  6.86, while the apical  $N(CH_3)_3$  group of 1,6-1 appeared as a single peak at  $\tau$  6.22, and the equatorial  $N(CH_3)_3$  group of 1,6-1 appeared as an equally intense single peak at  $\tau$  7.05. Straight-line plots of  $\ln$  (concentration of 2,3-1) *vs.* time were obtained at the three temperatures studied. The rate constants determined graphically agreed well with the average rate constants calculated from the integrated first-order rate equation. No deviation from first-order kinetics was found through >90% reaction. The results are summarized in Table II.

**Isomerization of  $B_{12}H_{10}[N(CH_3)_3]_2$ .**—Small samples of 1,2-, 1,7-, and 1,12-2' were placed in capillary tubes and heated in a melting point apparatus at the desired temperature. Products were identified by t.l.c. of the solid residue on silica gel.

**$Cs_2[1,10-B_{10}H_8(CN)_2]$ .**— $Cs_2[1,10-B_{10}H_8(CONH_2)_2]$ <sup>10</sup> (10.5 g., 22.4 mmoles) was heated to 300–310° at 0.1 mm. nominal pressure for 100 min. Conversion to  $Cs_2[1,10-B_{10}H_8(CN)_2]$  was quantitative as shown by infrared analysis. Recrystallization from water gave 6.2 g. (64%) of analytically pure product. *Anal.* Calcd. for  $Cs_2B_{10}H_8(CN)_2$ : B, 24.9; C, 5.5; H, 1.8; N, 6.4. Found: B, 24.8; C, 6.2; H, 2.6; N, 6.4. Ultraviolet showed  $\lambda_{max}^{H^2O}$  250 ( $\epsilon$  838) and 217  $m\mu$  ( $\epsilon$  54,800). The infrared spectrum in Nujol has absorption at 2470 (B-H str.) and 2175  $cm^{-1}$  (C≡N str.), and a moderately sharp band at 998  $cm^{-1}$ . The  $B^{11}$  n.m.r. spectrum consists of a broad singlet at 21.7 p.p.m. and a doublet at 42.8 p.p.m. ( $J = 127$  c.p.s.). The low-field singlet is not affected by decoupling irradiation; the high-field doublet collapses to a single peak.

In a small-scale preparation of  $Cs_2[1,10-B_{10}H_8(CN)_2]$ , the thermal dehydration was performed in air. The conversion was quantitative with no indication of decomposition being found by infrared analysis.

In a differential thermal analysis of  $Cs_2[1,10-B_{10}H_8(CN)_2]$ , (25–558°) in an evacuated system, an endotherm peaking at 338° (m.p.) was the only change noted. No thermal peaks were noted on cooling nor on reheating the sample. Infrared analysis of the recovered sample showed that it was  $Cs_2[\xi-B_{10}H_8(CN)_2]$ .

**$Cs_2[\xi-B_{10}H_8(CN)_2]$ .**— $Cs_2[1,10-B_{10}H_8(CONH_2)_2]$  (5.9 g., 12.4 mmoles) was heated under vacuum to 400° for 2 hr. Conversion to  $Cs_2[\xi-B_{10}H_8(CN)_2]$  was quantitative. *Anal.* Calcd. for  $Cs_2B_{10}H_8(CN)_2$ : B, 24.9; N, 6.4. Found: B, 25.1; N, 5.6. Ultraviolet showed  $\lambda_{max}^{H^2O}$  212  $m\mu$  ( $\epsilon$  18,100). The infrared spectrum in Nujol resembles that of  $Cs_2[1,10-B_{10}H_8(CN)_2]$  except that the absorption band at 998  $cm^{-1}$  is shifted to about 985  $cm^{-1}$  with accompanying broadening and development of shoulders. The  $B^{11}$  n.m.r. in water consists of a weak quadruplet at 9.4, 14.0, 21.8, and 27.0 p.p.m. and two stronger peaks at 42.0 and 48.3 p.p.m. The 48.3-p.p.m. peak is significantly stronger than the 42.0-p.p.m. peak. The 9.4-, 14.0-, and 21.8-p.p.m. peaks decouple to a fairly sharp peak at 17.5 p.p.m. The 27.0-p.p.m. peak is not affected by double irradiation. The 42.0- and 48.3-p.p.m. peaks decouple to a sharp peak with a high-field shoulder. This  $Cs_2[\xi-B_{10}H_8(CN)_2]$  is probably a mixture of isomers, and the  $B^{11}$  spectrum can be interpreted (since the  $B^{11}$  spectrum of  $Cs_2-B_{12}H_{10}(CN)_2$  shows that boron in these systems is shifted to high field when attached to CN) as follows. The 9.4-p.p.m. peak is one-half the doublet absorption due to an unsubstituted apical boron atom which is shifted to low field because of a neighboring equatorial B-CN group. The 14.0- and 21.8-p.p.m. peaks contain the other half of this doublet and also absorption due to unsubstituted apical boron atoms which are not adjacent to substituted equatorial boron atoms (e.g., the 10-boron of a 1,2-, 2,3- or 2,4- isomer). The 27.0-p.p.m. peak is due to apical boron atoms bearing CN groups, and the high-field doublet is due to unsubstituted equatorial boron atoms and, under the high-field peak of this doublet, equatorial boron atoms bearing CN groups.

$B_{10}H_7(CN)_2 \cdot N_2^-$ .—A solution of  $Cs_2[\xi-B_{10}H_7(CN)_2]$  (4.0 g., 9.2 mmoles, prepared at 400° in 400 ml. of water was chilled in a water-ice bath. Sodium nitrite (5.0 g., 72.5 mmoles) and 12 *M* hydrochloric acid (10 ml.) were added, resulting in formation of a dark color. After 2 min. of stirring, with continued cooling in the ice bath, zinc dust (15 g., 230 g. atoms) was added. The cooling bath was removed, and an additional 10-ml. portion of 12 *M* hydrochloric acid was added. A vigorous reaction ensued, and the mixture became quite hot. After the reaction subsided, a final 10-ml. portion of 12 *M* hydrochloric acid was added, and the mixture was stirred until the supernatant liquid was light yellow, almost colorless. The mixture was filtered. The addition of excess tetramethylammonium chloride precipitated a white solid which was recrystallized from water. The recrystallization caused the development of a light yellow color, and the final product,  $(CH_3)_4NB_{10}H_7(CN)_2 \cdot N_2$ , was obtained as 0.4 g. (16%) of well-formed, light yellow crystals. *Anal.* Calcd. for  $(CH_3)_4NB_{10}H_7(CN)_2 \cdot N_2$ : B, 40.0; C, 26.0; H, 7.1. Found: B, 39.8; C, 26.1; H, 7.6. Ultraviolet showed  $\lambda_{max}^{CH_3CN-H_2O}$  395 ( $\epsilon$  38.8), 258 ( $\epsilon$  15,400), 218  $m\mu$  ( $\epsilon$  24,400).

$Cs_2[1,12-B_{12}H_{10}(CN)_2]$ .— $Cs_2[1,12-B_{12}H_{10}(CONH_2)_2]^{10}$  (4.3 g., 8.7 mmoles) was heated at 35–375° at 0.1 mm. nominal pressure for 5 days. Infrared analysis indicated complete dehydration of the amide groups and conversion to  $Cs_2[1,12-B_{12}H_{10}(CN)_2]$ . A small amount was recrystallized from water for analysis and was obtained as a hydrate as shown by its infrared spectrum. *Anal.* Calcd. for  $Cs_2B_{12}H_{10}(CN)_2 \cdot H_2O$ : B, 27.3; C, 5.0; H, 2.5; N, 5.9. Found: B, 27.4; C, 5.0; H, 2.5; N, 5.4. There was no maximum in the ultraviolet region. The infrared spectrum of a Nujol mull has absorption at 2515 (B–H str.), 2200 (C≡N), 3640, and 1630  $cm^{-1}$  (water of hydration), as well as fairly sharp absorptions of medium intensity at 1040 and 955 (shoulder at 970  $cm^{-1}$ ) and a somewhat broader one at 725  $cm^{-1}$  (shoulder at 737  $cm^{-1}$ ). The  $B^{11}$  n.m.r. spectrum in water consists of two peaks at 28.6 and 36.2 p.p.m. The 36.2-p.p.m. peak is more intense than the 28.6-p.p.m. peak because of coincidence of the

resonance from the boron atoms attached to CN with the high-field peak of the doublet caused by borons bonded to hydrogen. This is demonstrated by the decoupled spectrum which has a sharp peak at 32.3 p.p.m. with a high-field shoulder.

$Cs_2[\xi-B_{12}H_{10}(CN)_2]$ .— $Cs_2[1,12-B_{12}H_{10}(CONH_2)_2]$  (14 g., 28.3 mmoles) was heated to 500° for 1 hr. at 0.1 mm. nominal pressure. At the end of this time, the product was a clear straw-colored liquid which set to a very brittle glass on cooling. The infrared spectrum showed complete conversion of the amide groups to CN groups. *Anal.* Calcd. for  $Cs_2[B_{12}H_{10}(CN)_2]$ : B, 28.4; C, 5.2; H, 2.2; N, 6.1. Found: B, 29.1; C, 4.7; H, 2.6; N, 5.4. There was no ultraviolet maximum. The infrared spectrum of a Nujol mull had absorption at 2470 (B–H str.), 2190  $cm^{-1}$  (C≡N), and also had broad absorptions of moderate to weak intensity centered at 1190, 1020, 960, and 720  $cm^{-1}$ . The  $B^{11}$  n.m.r. spectrum was similar to that of the 1,12-isomer. In a similar preparation, characterization of evolved gases showed that 0.2 mole equiv. of hydrogen was formed. Noticeable gas evolution began at 450°.

**Isomerization of 1,2- and 1,6- $(CH_3)_2SB_{10}H_8N(CH_3)_3$ .**—Small samples of 1,2- (m.p. 268°) and 1,6- $(CH_3)_2SB_{10}H_8N(CH_3)_3^{14}$  (m.p. 204°) were placed in melting point capillary tubes and heated at various temperatures in a melting point apparatus. The products were subjected to t.l.c. on silica gel using 2% acetonitrile in ethylene chloride. At 236–240° (20 min.), the 1,2-isomer showed mostly unchanged starting material ( $R_f$  0.24) and a small amount of material with  $R_f$  0.36. Under the same conditions the 1,6-isomer showed mostly unchanged starting material ( $R_f$  0.59) with a smaller spot at  $R_f$  0.65 and very small spots at  $R_f$  0.17 and 0.37. Similar results were obtained at 258–261° except that the same minor products in each case became more pronounced.

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## A Study on the Stability of Xenon Trioxide in Basic Solutions<sup>1</sup>

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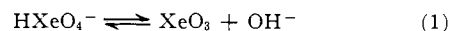
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The reaction of  $XeO_3(aq)$  with NaOH and KOH solutions in the range of 0.25 to 4.2 *M* and 2.0 to 3.6 *M*, respectively, at room temperature gives a 33% yield of the alkali perxenate. Higher  $[OH^-]$  and temperature increase the yield. Lowering the  $[OH^-]$  toward the neutral point leads to the direct decomposition of  $XeO_3$ . For comparable concentrations for LiOH, the yield of perxenate is 50% and higher. A yellow, mixed oxidation state complex with variable stoichiometry forms predominantly in the NaOH and KOH systems. It provides a mechanism by which Xe(VI) directly decomposes to  $Xe + 1.5O_2$ . In the KOH system, the complex is present as a solid during most of the course of the reaction. Subsequently,  $K_4XeO_6 \cdot 9H_2O$  has been isolated. The relative stabilities of the alkali and alkaline earth perxenates, a mechanism for the disproportionation-decomposition reaction of  $XeO_3$ , and the nature of the mixed oxidation state complex are presented.

### Introduction

The research of Appelman and Malm<sup>3</sup> has done much to elucidate the nature of the aqueous, oxygen-containing, xenon species. Since the earliest report on the preparation of Xe(VIII)<sup>4</sup> from the hydrolysis of  $XeF_6$  in NaOH solutions and with the observations at pH 7 that a secondary reaction interfered with the kinetic studies of the oxidation of iodide anion by aqueous xenon trioxide,<sup>5</sup> our interest in the disproportionation and de-

composition of Xe(VI) has been keen. Raman spectra in aqueous solution<sup>6</sup> have shown that xenon trioxide exists as a discrete, pyramidal molecule just as it does in the solid state.<sup>7</sup> From their titration experiments on aqueous xenon trioxide,<sup>3</sup> Appelman and Malm suggest that the Xe(VI) species that exists above pH 12 is  $HXeO_4^-$ . The end point that they and others have found is not well defined (see Fig. 2 in ref. 3), and we suggest that the change in slope of the graph need not be due entirely to<sup>3</sup>



Whether reaction 1 is fast or slow, the onset of the disproportionation reaction can complicate the titration

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