

Fig. 2.—Comparison of Raman spectra of potassium tantalate in solution with crystalline  $K_3Ta_6O_{19} \cdot 16H_2O$ . Left traces, double slit width; right traces, single slit width; all  $10 \text{ cm}^{-1}$ . Top spectra (crystalline): sensitivity settings,  $1 \times 100RD4$ ; period controls, left trace, 0.5; right trace, 0.3. Bottom spectra (solution): left trace sensitivity,  $1.6 \times 100RD4$ ; period, 5.0; right trace sensitivity,  $1 \times 100RD4$ ; period, 0.

likely that the lines at  $170$  and  $145 \text{ cm}^{-1}$  may not correspond to genuine vibrations for the tantalate ion. With our spectrometer spurious lines in this region are sometimes observed in the spectra of crystals, although in solution these lines, if observed at all, are usually much weaker. The close correspondence of the two spectra, with each of the seven lines (excluding  $145$  and  $170 \text{ cm}^{-1}$ ) observed in the solution having its counterpart in the solid within about  $4 \text{ cm}^{-1}$ , strongly supports the conclusion that the same hexatantalate anions present in the crystal are also present in solution. The simplicity of the spectra, compared with those of less symmetrical ions (for example,<sup>10</sup>  $Mo_7O_{24}^{6-}$ ) provides further qualitative evidence for the octahedral arrangement of tantalum atoms proposed by Lindqvist. However, for the ion  $Ta_6O_{19}^{8-}$  with  $O_h$  point group symmetry, there is a center of symmetry, which means there should be no coincidence between the Raman lines and infrared bands. The infrared spectrum of  $K_3Ta_6O_{19} \cdot 16H_2O$  has been observed<sup>4</sup> and one of the four bands ( $822 \text{ cm}^{-1}$ ) has a frequency close to the  $825 \text{ cm}^{-1}$  Raman line. Our infrared measurements covering this region and below indicated lines at  $843$  (sharp),  $694$  (broad),  $535$  (medium),  $402$  (broad), and  $355$  (weak)  $\text{cm}^{-1}$ . We checked the region of primary interest here with a Nujol mull, on a different instrument (Perkin-Elmer 221), with the preparation of potassium tantalate used in the Raman and ultracentrifugation work, and again found no indication of an  $822 \text{ cm}^{-1}$  line. We therefore believe the attribution of  $O_h$  point symmetry is correct, but in any case, our main conclusion, that the  $Ta_6O_{19}^{8-}$  ion is present both in the solid and solution, is unaffected.

(10) J. Aveston, E. W. Anacker, and J. S. Johnson, *Inorg. Chem.*, **3**, 735 (1964).

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CONTRIBUTION NO. 324 FROM THE DEPARTMENT OF CHEMISTRY,  
TUFTS UNIVERSITY, MEDFORD, MASSACHUSETTS

## Isomerism in Some Boron and Boron-Carbon Frameworks

By T. E. HAAS

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The recent reports of an extensive derivative chemistry of some of the boron hydride anions<sup>1</sup> and the carboranes<sup>2</sup> have shown the desirability of a study of substitution isomers to be derived from the basic boron and boron-carbon frameworks of these compounds. The study of isomerism by group-theoretical methods is the most powerful and elegant method of attacking such a problem. Kennedy, McQuarrie, and Brubaker<sup>3</sup> have recently given a new, point-group formulation and extensive discussion of the technique. Their paper should be consulted for details.

**Calculations.**—The determination of the number of geometrical isomers and enantiomeric pairs was carried out by the method of Brubaker, *et al.*, for substitution by one kind of substituent. The structures considered are  $B_{10}H_{10}^{2-}$ ,  $B_{12}H_{12}^{2-}$ , and the three possible icosahedral dicarbaclododecaborane(12) isomers. For the carboranes, calculations were carried out for substitution on all atoms and substitution on borons only. Cycle indices for each of these cases are given in Table I for both the point group of the molecule and its rotation subgroup. The total number of isomers and the number of geometric isomers for each of the structures are given in Table II. Note that as both 1,2- and 1,7-carborane<sup>4</sup> have the same symmetry ( $C_{2v}$ ) and are of the same degree (12, or 10 for borons only), the cycle indices and number of isomers are the same for both structures, although the isomers are completely different.

## Discussion

The first communication on the susceptibility of the boron frameworks in  $B_{10}H_{10}^{2-}$  and  $B_{12}H_{12}^{2-}$  to electrophilic substitution<sup>1</sup> suggested that all isomers would not be formed in these reactions. For example, apical substitution in  $B_{10}H_{10}^{2-}$  seemed to occur first, and this

(1) W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, and E. L. Muetterties, *J. Am. Chem. Soc.*, **84**, 1056 (1962).

(2) See *e.g.*, H. Schroeder, T. L. Heying, and J. R. Reiner, *Inorg. Chem.*, **2**, 1092 (1963).

(3) B. A. Kennedy, D. A. McQuarrie, and C. H. Brubaker, Jr., *ibid.*, **3**, 265 (1964).

(4) These names will be used for brevity's sake to denote 1,2- and 1,7-dicarbaclododecaborane(12), and the 1,12 isomer will be named similarly.



least for halogenation reactions, the rates are comparable to collision rates, and random substitution seems to result. Hence a knowledge of the isomer possibilities seems even more important than would be the case if clear-cut directive influences were acting.

In Tables III and IV are shown all the possible isomers for  $B_{10}H_{10-n}X_n^{2-}$  and  $B_{12}H_{12-n}X_n^{2-}$ . The numbering system is that employed by Muetterties, *et al.*<sup>7</sup> Table IV gives, in effect, all of the possible permutations of two kinds of objects at the vertices of an icosahedron. All of the possible geometries of carborane derivatives are thus also included, although because of the nonequivalence of all vertices in those structures, each  $B_{12}H_{12-n}X_n^{2-}$  isomer corresponds to several isomers of  $B_{10}C_2H_{12-n}X_n$ .

No explicit consideration has been given to isomerism among products containing more than one kind of substituent. The number of isomers is, of course, enormous. The number of isomers of  $B_{12}H_{10-m}X_mY_2^{2-}$  is implicit in the total of the isomers for the three carboranes, using boron substitution only. Thus there are 11 isomers for  $m = 1$ , 57 for  $m = 2$ , 132 for  $m = 3$ , 246 for  $m = 4$ , and 278 for  $m = 5$ .

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF MARYLAND, COLLEGE PARK, MARYLAND

## Observations on the Complex between Uranyl and Chlorite Ions

BY GILBERT GORDON AND DAVID M. H. KERN

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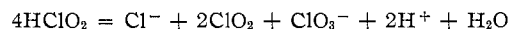
Chlorite is known to be a good oxidizing agent in aqueous solution,<sup>1</sup> but very little is known about its ability to form complexes with metal ions. During the course of some experiments in which aqueous solutions of uranium(IV) were being oxidized by  $ClO_2^-$ , a transient yellow color was observed. This color has been interpreted in terms of a complex between  $UO_2^{2+}$  and  $ClO_2^-$ . The purpose of this report is to indicate the progress which has been made in studying the properties of this complex.

### Experimental

In all of the measurements the quantity of interest was  $\Delta A$ , the enhancement of absorbancy per cm. of cell length in the mixed acidic solutions of  $UO_2^{2+}$  and  $ClO_2^-$  compared to that on the basis of no interaction. Both  $UO_2^{2+}$  and  $ClO_2^-$ , the decomposition product of  $ClO_2^-$  in acid solution, are yellow and absorb light in the same spectral region as the observed uranium chlorite complex. Therefore, in this region, where all three species are

absorbing, a blank solution containing each of these separately was run in the reference compartment *vs.* a cell containing the  $UO_2^{2+}$ - $ClO_2^-$  mixture. The hydrogen ion concentration and the ionic strength ( $I = 1.00 M$ ) were carefully matched in an attempt to minimize variation in activities. To effect changes in  $[H^+]$  and  $[UO_2^{2+}]$ , sodium perchlorate was substituted for these species. The reference cell with  $ClO_2^-$  contained  $Mg^{2+}$  in place of  $UO_2^{2+}$  to maintain similar ionic media in the two cells.

Although  $HClO_2$  disproportionates fairly rapidly to form  $ClO_2$ , this reaction is much slower than the formation of the  $ClO_2^-$  complex. The rate law for the disproportionation reaction<sup>2</sup>



reported by Barnett is<sup>2,3</sup>

$$-d(HClO_2)/dt = k(HClO_2)^2$$

and the value of  $k$  at 25° is 1.4 l. mole<sup>-1</sup> min.<sup>-1</sup>.

To minimize the effect of  $ClO_2$ , the  $ClO_2^-$  solutions of the appropriate ionic strength were injected simultaneously into the acidic solution of  $UO_2^{2+}$  in the sample compartment and the solution of identical ionic strength and acidity containing  $Mg^{2+}$  substituted for  $UO_2^{2+}$  in the reference compartment. This rapid injection and mixing was achieved by the use of matched spring-loaded syringes. The tandem firing of these syringes was within 10 msec. and the mixing time is less than 30 msec.<sup>4</sup> In this way the kinetic reaction of  $ClO_2^-$  to form  $ClO_2$ , a species absorbing in the region of interest, was automatically subtracted from the observed spectra. By use of a reference cell containing  $UO_2^{2+}$ , simultaneous corrections were made for the uncomplexed  $UO_2^{2+}$ . The effect of  $Cl^-$  and  $ClO_3^-$  on the  $UO_2^{2+}$  spectrum was shown to be negligible. It was also shown that the slit width required to make this type of measurement was not large enough to introduce any errors.

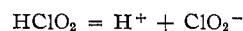
Differences in zero time mixing were carefully checked by comparing blank solutions of perchloric acid into which  $ClO_2^-$  was injected in both sample and reference compartments. Perfect mixing and timing should result in no change of absorbance as a function of time in the region of absorption of  $ClO_2$ . The blank experiments showed that the solutions could be matched to within 1% by this method. The spectra of the chlorite complex showed only very small changes with time, presumably due to errors in volume and zero time mixing, and none of the characteristics of the  $UO_2^{2+}$  or  $ClO_2$  spectra was evident. Changes as small as 5% in the  $ClO_2^-$  concentration would have been detected as differences in rate of  $ClO_2$  formation. Since differences of this type were not observed, it has been concluded that less than 5% of the  $ClO_2^-$  has been used in complex ion formation.

The analytical procedures used to determine the concentration of  $UO_2^{2+}$ ,  $ClO_2^-$ , and  $HClO_4$  are the same as those described previously.<sup>1a</sup> All measurements were made at 25° using a Cary Model 14M spectrophotometer with a thermostated cell compartment using 2-cm. quartz cells.

### Results and Discussion

Due to the absorption of light by  $UO_2^{2+}$  and  $ClO_2$  in the region of interest, the most meaningful data have been collected at 370  $m\mu$ , where these interferences could be minimized. These data are summarized in Table I.

The concentration of  $[UO_2^{2+}]$  and  $\Sigma ClO_2^-$  given in Table I are the stoichiometric quantities of these species. The actual concentration of free  $ClO_2^-$  and  $H^+$  have been calculated from the equilibrium



(1) (a) D. M. H. Kern and G. Gordon, "Theory and Structure of Complex Compounds," B. Jezowska-Trzebiatowska, Ed., Pergamon Press, 1964, p. 655; (b) B. J. Fontana and W. M. Latimer, *J. Am. Chem. Soc.*, **69**, 2598 (1947).

(2) H. Taube and H. Dodgen, *ibid.*, **71**, 330 (1949).

(3) B. Barnett, Thesis, University of California, 1935.

(4) R. Thompson and G. Gordon, *J. Sci. Instr.*, submitted for publication.