

addition it has nine close water molecule neighbors, most of which are undoubtedly hydrogen-bonded. No hydrogen bonds link bases directly.

(6) The bond distances and angles do not differ significantly from the expected values; the standard errors average about 0.012 Å. and 0.7° for distances and angles not involving hydrogen atoms. The C₁' atom of each sugar is very nearly in the plane of the base to which it is attached (deviation 0.01 and 0.03 Å.), unlike the situation in adenosine phosphate² and 5-fluoro-2'-deoxy-β-uridine.⁵

(5) D. R. Harris and W. M. Macintyre, unpublished work.

CONTRIBUTION No. 1639
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Molecular Structure of a Carborane (1,2-Dicarboclovododecaborane) Derivative, B₁₀Cl₈H₂C₂H₂

Sir:

The carborane^{1,2} B₁₀C₂H₁₂ is usually assumed²⁻⁴ to have very nearly the icosahedral geometry of the B₁₂H₁₂²⁻ ion⁵ (Fig. 1a). However, an X-ray diffraction study⁶ of B₁₀H₁₀C₂(CH₂Br)₂ has supported an ethylene decaborane type of B₁₀C₂ unit (Fig. 1b.). We report here the results of a three-dimensional single crystal X-ray diffraction study of B₁₀Cl₈H₂C₂H₂ which indicates the nearly regular icosahedral arrangement for the B₁₀C₂ structural unit (Fig. 1a).

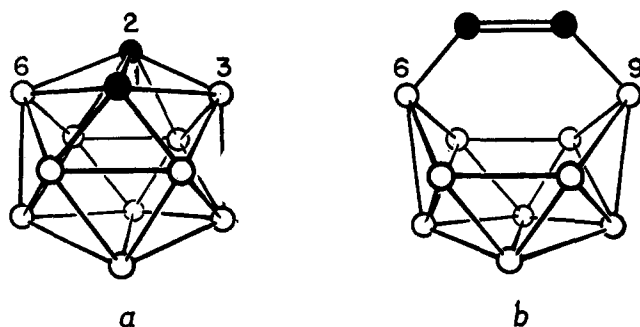


Fig. 1.—a represents the near icosahedral B₁₀C₂ framework in B₁₀Cl₈H₂C₂H₂. Open and black circles indicate, respectively, B atoms and C atoms. Substitution of Cl has taken place at all H atoms of the parent B₁₀C₂H₁₂ except those attached to B₃, B₆, C₁, and C₂. b represents the boron-carbon framework described⁶ for B₁₀H₁₀C₂(CH₂Br)₂.

The crystal symmetry is Pbn_a, and there are eight molecules in a unit cell of dimensions $a = 17.10$, $b = 13.46$, and $c = 13.65$ Å. All B and C atoms were located and distinguished from one another by their electron densities in three-dimensional Fourier series

(1) M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *Inorg. Chem.*, **2**, 1111 (1963).

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(3) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962); *Inorg. Chem.*, **2**, 231 (1963).

(4) W. N. Lipscomb, "Boron Hydrides," The W. A. Benjamin Co., New York, N. Y., 1963.

(5) J. Wunderlich and W. N. Lipscomb, *J. Am. Chem. Soc.*, **82**, 4427 (1960).

(6) L. I. Zakharkin, V. I. Stanko, V. A. Brattsev, Yu. A. Chapovsky, and Yu. T. Struchkov, *Izv. Akad. Sci. SSSR*, 2069 (1963).

from which the Cl atoms had been subtracted. The present value of $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ is 0.13 for the 1739 observed X-ray diffraction maxima.

Two other features of the structure are of interest here. The C-C distance of 1.68 ± 0.02 Å. is considerably larger than the distance⁷ of 1.43 Å. in B₄H₆C₂(CH₃)₂, which contains two adjacent C atoms in a slightly less strongly electron-deficient environment. Also, substitution of Cl has taken place at all B atoms (4,5,7,8,9,10,11,12) except for the two B atoms (3,6) which are indicated to be most positively charged by both molecular orbital and resonance theories³ of charge distribution.

A comparison⁸ of ¹¹B nuclear magnetic resonance in B₁₀C₂H₁₂ and in B₁₀Cl₁₀C₂H₂ indicates that direct chlorination produces essentially no change in the B₁₀C₂ framework. Also, the thermal stability of carborane up to a temperature of 470°, at which it transforms³ readily and without decomposition to neocarborane,^{8,9} is more easily understood on the basis of the icosahedral structure (Fig. 1a) rather than the ethylene decaborane type of structure (Fig. 1b). However, the possibility that the structure of Fig. 1b is an intermediate in the synthesis of carborane derivatives is not excluded. Further structural studies of carborane and neocarborane derivatives are in progress.

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(7) W. E. Streib, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 2231 (1963).

(8) H. Schroeder and G. D. Vickers, *Inorg. Chem.*, **2**, 1317 (1963).

(9) D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963).

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Decreasing Sorption Effect with Increasing Pressure

Sir:

In a recent article by Cimino, *et al.*,¹ the hypothesis was advanced that the surface of polycrystalline ZnO was very likely conditioned for further H₂ uptake by a rapid initial adsorption of H₂. This initial adsorption is frequently observed^{2,3} with other systems but much less frequently measured. A somewhat similar effect has been observed during the study of the uptake of oxygen by Pr₂O₃. This effect, in general, is a small loss of sorbed gas with an increase in gas pressure. The effect has been noted during "equilibrium" as well as kinetic measurements. Three separate pieces of evidence seem to indicate that the effect is real.

(1) During the course of a general study of the Pr-O system it was noted that in some cases the oxygen content on and/or in the solid PrO_x could be reduced slightly by increasing the oxygen pressure. The effect was observed specifically⁴ during the investigation of

(1) A. Cimino, E. Molinari, C. Borgianni, and E. Pepe, *J. Phys. Chem.*, **67**, 2238 (1963).

(2) J. R. Ligenza, *ibid.*, **64**, 1017 (1960).

(3) M. J. D. Low, *Chem. Rev.*, **60**, 267 (1960).

(4) P. A. Faeth and A. F. Clifford, *J. Phys. Chem.*, **67**, 1453 (1963).

the interior of the isothermal, composition-pressure hysteresis loops exhibited by this system. The effect was not always observed and depended somewhat on the region of the loop under investigation. The effect, when evident, was most noticeable near the center of the hysteresis envelopes.

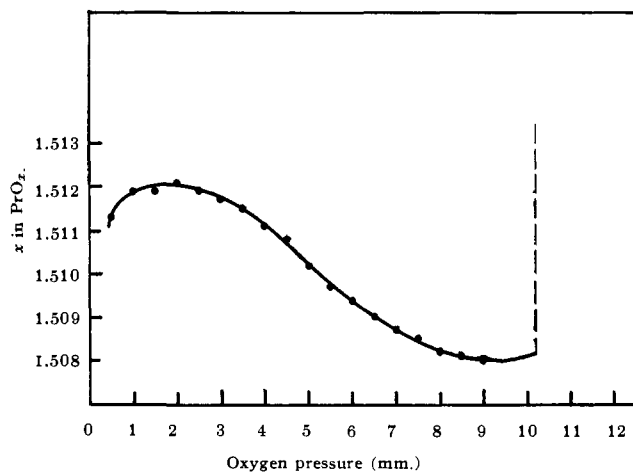


Fig. 1.—The variation of composition with oxygen pressure at 900°

(2) A related effect was also noted during the study of the phase diagram of the Pr-O system.⁵ A typical high temperature (>900°) isothermal uptake, from fairly low pressures up to a "break" pressure where rapid uptake occurred, is illustrated in Fig. 1. The effect was not observed below 900°. The data for the curve were taken over a period of 5 days. It can be seen from the figure that as the oxygen pressure was increased at constant temperature, the amount of gas taken up at first increased, then became relatively constant, and finally decreased slightly. Upon a further pressure increase the uptake again increased slightly until a critical pressure was attained, at which value the uptake cascaded. The cascade reaction is probably related to the surface reaction in an isotheric way. The region of interest here is the pressure region for pressures less than the cascade pressure.

(3) In addition to these two irregularities, another peculiar pressure effect has been observed during a study of the rate of uptake of oxygen by hexagonal Pr₂O₃.⁶ It was found that while the rate of bulk uptake increased rapidly with increasing pressure as expected, the amount initially taken up (rapid initial adsorption) prior to bulk uptake appeared to be inversely proportional to the ambient pressure. Slightly more gas was taken up initially by the surface at lower oxygen pressures than at higher pressures. The pressure range observed was between 9 and 23 torr oxygen and the gas had been admitted as rapidly as possible. The results of these latter studies are in preparation and will be reported shortly.

At high temperatures the temperature dependence of the PrO_x-O₂ system is such that the uptake increases with decreasing temperature. Some uptake could be accounted for by considering a lowering of the solid

temperature during the rapid admissions of oxygen. However, a pressure effect opposite to that observed would be expected. From the three observations of O₂ on PrO_x noted above, one might conclude that the initial rapid adsorption involves some kind of a reflex action at the surface. Additional work is planned to help elucidate these findings.

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The Initiation of Ionic Reactions in Liquid Hydrocarbons via Photoionization with Vacuum Ultraviolet Radiation. The Polymerization of Isobutylene

Sir:

We wish to report a novel method for studying ionic reactions in low dielectric liquids which does not depend upon the presence of a chemical initiator or a stabilizing surface to sustain the reaction.

A study of the ionic polymerization of isobutylene is a particularly good test case since the ionic nature of this reaction at low temperatures appears well established and there is little interference from free-radical processes. Such ionic polymerizations are usually chemically initiated by a catalyst-cocatalyst system interacting with reactants in an active solvent medium.¹ It is obviously quite difficult to assess the importance of the individual components in such a multicomponent system. Another method of approach was attempted by Davison, Pinner, and Worrall in the γ -ray polymerization of isobutene at low temperatures,² where there is strong evidence for an ionic mechanism. Several other γ -ray-induced polymerizations have also been claimed to go by an ionic process,³ though this has often been difficult to establish. It has, however, been found that the presence of various solids, including powdered glass, considerably enhances the polymerization yields of such reactions⁴ and, hence, makes it likely that the heterogeneous surface is necessary for the polymerization process. In the absence of an added solid, the vessel walls serve to provide the heterogeneous surface. Though the initial process is probably the ejection of an electron, this will recombine

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(4) (a) R. Worrall and S. H. Pinner, *J. Polymer Sci.*, **34**, 229 (1959); (b) R. Worrall and A. Charlesby, *Intern. J. Appl. Radiation Isotopes*, **4**, 84 (1958); (c) F. L. Dalton and K. Hayakawa, *Polymer*, **4**, 285 (1963); (d) A. Charlesby, S. H. Pinner, and R. Worrall, *Proc. Roy. Soc. (London)*, **A259**, 386 (1960).

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(6) P. A. Faeth and A. F. Clifford, "Rare Earth Research," K. Vorres, Ed., Gordon and Breach, New York, N. Y., in press.