cycloöctatetraenes. Such copolymerizations apparently have not been described. It has been reported that phenylacetylene fails to polymerize, and that vinylacetylene yields a gel-like polymer,[3] although ref. 2a (p. 37) states that homologs of acetylene would lead to corresponding substituted cycloöctatetraenes.

In the copolymerizations, the substituted acetylene (20–50 g.) was included with the tetrahydrofuran solvent, nickel acetylacetonate and calcium carbide in a 1-l. stirred autoclave, which was pressured to 250–300 p.s.i. with acetylene and stirred and heated at 70–90° with periodic repressuring in the manner previously described[2b] for a reaction period of 7 to 12 hours. The product was steam distilled, and the substituted cycloöctatetraene was isolated from the steam distillate, or from the residue. The steam distillates contained benzene, cycloöctatetraene, an alkyl benzene (from copolymerization of the substituted acetylene with acetylene in a 1:2 ratio) and the substituted cyclooctatetraene (if volatile with steam). The less volatile substituted cycloöctatetraenes were isolated from the water-insoluble residue (largely cuprene) from the steam distillation by extraction with benzene in a Soxhlet apparatus. The substituted cycloöctatetraenes were isolated by fractional distillation, or through silver nitrate adducts, in yields of 16–25%. Phenylcycloöctatetraene and *n*-butylcycloöctatetraene were identified by direct comparison with authentic samples.[4] Methylcycloöctatetraene was isolated as a yellow liquid, b. p. 84.5° (67 mm.), $n^{25}{}_{\mathrm{D}}$ 1.5249, $d^{25}{}_4$ 0.8978. (*Anal.* Calcd. for C_9H_{10}: C, 91.47; H, 8.53. Found: C, 91.17; H, 8.35). Quantitative reduction of methylcycloöctatetraene in the presence of platinum in acetic acid required 97% of four molar equivalents of hydrogen and yielded methylcycloöctane.

1,2-Dimethylcycloöctatetraene was isolated as a yellow liquid, b.p. 107° (96 mm.), $n^{25}{}_{\mathrm{D}}$ 1.5218 (*Anal.* Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 91.01; H, 9.21). Hydrogenation in the presence of 1% palladium on calcium carbonate in methanol resulted in the absorption of three molar equivalents of hydrogen and the formation of 1,2-dimethylcycloöctene, which was characterized by ozonization. Hydrogenation of the ozonide yielded 39% of decane-2,9-dione, which after recrystallization melted at 56–57°, and formed a dioxime (m.p. 131.5–132.5°). Both the diketone and dioxime were identical with authentic samples in melting point and mixed melting point.

Investigation of the preparation of substituted cycloöctatetraenes by the copolymerization of acetylene with substituted acetylenes, including derivatives containing various functional groups is being continued.

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RECEIVED JUNE 12, 1951

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(3) K. Kammermeyer, "Polymerization of Acetylene to Cycloöctatetraene," Hobart Publishing Co., Washington, D. C., 1947, p. 2 (based upon work of the group headed by Reppe).

(4) A. C. Cope and M. R. Kinter, THIS JOURNAL, **72**, 630 (1950); **73**, 3424 (1951); A. C. Cope and H. O. Van Orden, to be published.

ION-PAIR FORMATION IN ION EXCHANGE SYSTEMS

Sir:

When a movable, exchange ion forms an associated ion-pair with a fixed exchange group in an ion exchange resin, the formulation of the thermodynamic equilibrium constant must consider the unique conditions which exist in these systems. For example, consider the process, $A^- + R^+ = RA$, where A^- is a movable anion, R^+ the fixed exchange group, and RA the ion-pair. Since R^+ and RA are both fixed to the resin matrix, and are at finite distances of separation (7–10 Å.), they do not possess translational degrees of freedom and should be regarded as separate, solid phases. The exchanger system has four phases, the external solution (o), the internal solution phase (i), and the two solid phases R^+ and RA. Under these conditions, the dissociation constant $K_m = (m_{A^-})(\gamma_\pm)$, where m_{A^-} is the molality of the A^- ion in the solution phase,[1] and $\gamma_\pm$ the mean activity coefficient of R^+A^-; m_{R^+} and m_{RA} are set equal to unity.

Dissociation constants for this process have been written in the conventional manner as for solutions, $K'_m = (m_{A^-})(m_{R^+})/m_{RA}$.[2] A critical test of these equations is a comparison of calculated and experimental values for the variation in the selectivity coefficient, K_D, as a function of the fraction of the exchange capacity (X^i) taken up by an exchanging ion. Where ion-pair formation exists, the selectivity (which favors the ion-pair forming ion) should decrease as X^i_A increases according to K_m, but should increase according to K'_m.

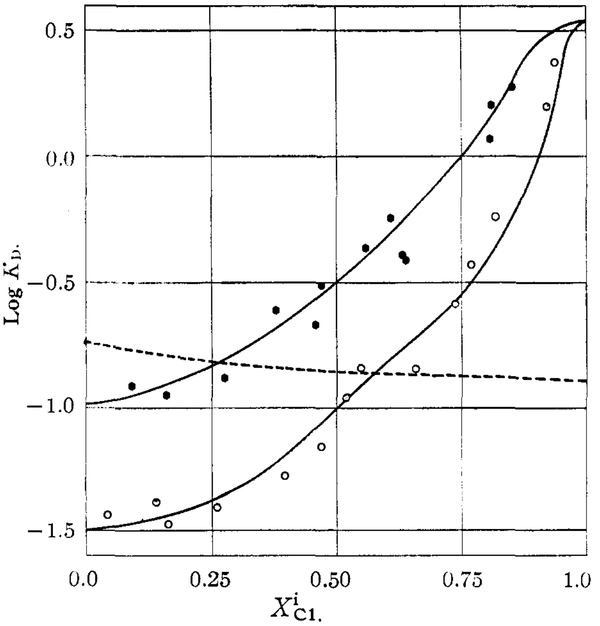

Fig. 1.—Variation in logarithm of K_D with fraction of exchange capacity in chloride state: experimental points for perchlorate–chloride exchange, O; for trichloroacetate–chloride exchange, ●; calculated curves by new theory (K_m) are thus ——; by old theory (K'_m) is - - -.

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(1) H. P. Gregor, F. Gutoff and J. I. Bregman, *J. Colloid Sci.*, in press.

(2) D. K. Hale and D. Reichenberg, *Faraday Soc. Discussion*, **7**, 79 (1949).

A critical, experimental test of these equations has been made, by measuring $K_D = (\mathrm{Cl/A})_i \cdot (\mathrm{A^-/Cl^-})_o$ as a function of X^i_{Cl} for perchlorate-chloride and trichloroacetate-chloride exchange using Dowex-2, a quaternary base anion exchanger. (The quaternary ammonium perchlorates are somewhat insoluble; the trichloroacetate forms ion-pairs to a marked extent, while the chloride appears to form ion-pairs to a smaller extent). The curves shown in Fig. 1 were calculated assuming $K_m = 0.12$ for perchlorate, $K_m = 0.4$ for trichloroacetate, $K_m = 1.2$ for chloride. According to the theory the value of K_D at $X^i_A - \rightarrow 1$, is the same as K_m for that ion. Values taken for K_m' are 0.04 for perchlorate and trichloroacetate, and 0.4 for chloride. The resin phase contains about 250 g. of water per mole of exchange capacity. Pressure-volume effects were neglected in these calculations, since they are small for these systems.

The experimental points fit the calculated curve based upon K_m well; the K_m' curves obviously do not apply. For loosely cross-linked gels where translational degrees of freedom may exist, a trend from K_m to K_m' may be anticipated. A series of papers dealing with ion-pair phenomena is in preparation.

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ON THE STRUCTURE OF STABLE PENTABORANE

Sir:

We have found several arrangements of the boron atoms which appear to be capable, with appropriate disposition of the hydrogen atoms, of giving complete agreement with the electron diffraction pattern of gaseous B_5H_9, whereas neither the model reported by Bauer and Pauling[1] nor the planar five-membered ring proposed by Pitzer[2] is satisfactory. Of the satisfactory arrangements, however, only the tetragonal pyramid, originally proposed and later discarded in the original electron diffraction study[1] but recently further advocated by Pauling,[3] has the high symmetry suggested by the spectrum[4] and entropy.[5] For this arrangement, which we at first thought unsatisfactory,[6] the position and shape of the radial distribution peak at about 2.57 Å. (Fig. 1), as well as intensive analysis of the pattern by trial and error, eventually led us to the structure shown in Fig. 2, which is of the type that had been suggested to us by King and Lipscomb[7] on the attractive grounds outlined in the following communication by Dulmage and Lipscomb. The parameter values

B_1–B_2 = 1.70 Å.
B_2–B_2 = 1.80
B_2–H_2 = 1.23
B_2–H_3 = 1.36
∠ B_1–B_2–H_2 = 120°
external dihedral ∠ $B_1B_2B_2$–$B_2B_2H_3$ = 185°,

which are surely close to the final values to be obtained from our data, give excellent agreement, qualitative and quantitative (12-feature average deviation for q/q_0, 0.008, with $\overline{q/q_0}$ adjusted to 1.000). Limits of error, not yet completely determined, are large for the two angle values and about ±0.03 Å. and ±0.05 Å. for the B–B and B–H distances, respectively.

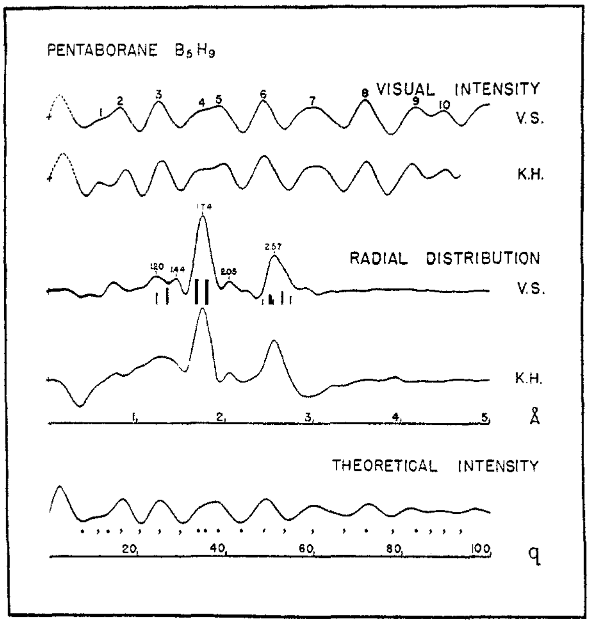

Fig. 1.—Visual, radial distribution and theoretical intensity curves. Theoretical intensity curve for the following model B–H_{av}/B–B_{av} = 1.275/1.74, B_1–B_2/B_2–B_2 = 1.69/1.79, B_2–H_1/B_2–H_3 = 1.20/1.35, ∠ B_1–B_2–H_1 = 125°, external ∠ plane B_1–B_2–B_2, plane B_2–B_2–H_3 = 190°.

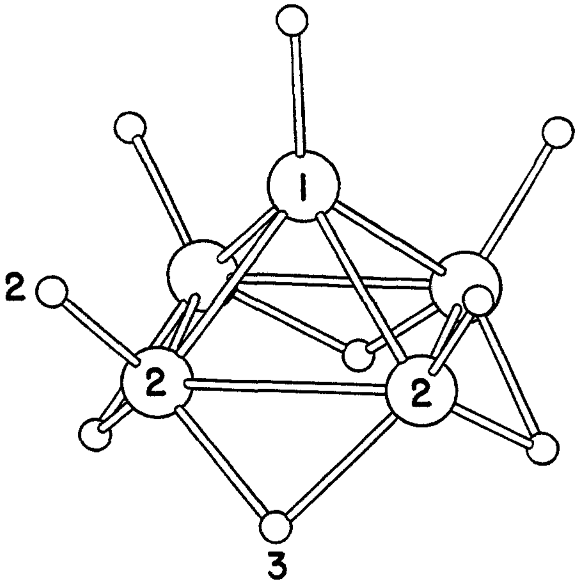

Fig. 2.—B_5H_9, diagram of the structure.

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(1) S. H. Bauer and L. Pauling, THIS JOURNAL, **58**, 2403 (1936).

(2) K. S. Pitzer, *ibid.*, **67**, 1126 (1945).

(3) Private communication.

(4) Private communications from Professor K. S. Pitzer and from Dr. G. C. Pimentel.

(5) W. J. Taylor, C. W. Beckett, J. Y. Tung, R. B. Holden, and H. L. Johnston, *Phys. Rev.*, **79**, 234 (1950).

(6)(a) V. Schomaker, *J. chim. phys.*, **46**, 252 (1949); (b) K. Hedberg, V. Schomaker, M. E. Jones, *Abstracts*, Chicago Meeting, A. C. S., September 1950. Substantially the present result was given at the meeting, however.

(7) M. V. King and W. N. Lipscomb, private communication.