be noted that the ring signals appear to be doubled. This is consistent with the choice of isomers. Further, since high and low field signals are equally intense, the diastereoisomers are about equally abundant.

The failure of the protons of 1-phenylethylphenylphosphinic acid to exhibit doubled resonances, as with 2-propylphenylphosphinic acid, may be ascribed to near equivalence of the oxygen atom and OH group. Another possible explanation, of course, is that there are no preferred rotational isomers in these compounds. This possibility cannot be excluded on the basis of the present data. It seems unlikely, however, if the phosphinic esters and phosphinyl halides do have a preferred rotational isomer that the corresponding phosphinic acids would not have such an isomer.

Aside from implications as to rotational isomerism, some of these compounds show spectral peculiarities that are of interest in themselves. Since the alpha and beta protons have only a small chemical shift between them, the spectra are not entirely first order but have considerable second-order character. However, the protons on the beta carbon atoms are coupled quite strongly to the phosphorus atom. The high field halves of the spectra for the beta protons are much cleaner, and more similar to first-order spectra, than those of the low field half. Further, both the apparent coupling constant (J) between alpha and beta protons and the additional resonance doubling described above are different in the two halves of the spectra. Data for these coupling constants for a number of these compounds are compiled in Table I. The values for the coupling constant are based on only a first-order analysis of the spectrum, hence these values are only approximate.

It is plausible that this difference in the spectra is basically the same type of phenomenon as that seen as a result of C^{13} coupling to protons.[10] The combination of phosphorus to proton coupling and ordinary chemical shift may tend to cancel or to add in producing an over-all chemical shift. In the low field half of the spectra, the effective over-all shift is very small and the spectra are strongly second order. In the high field half, the over-all shift is larger and the spectra have approximate first-order character.

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[10] A. D. Cohen, N. S. Sheppard and J. J. Turner, *Proc. Chem. Soc.* (London), 118 (1958).

[CONTRIBUTION NO. 727 FROM THE CENTRAL RESEARCH DEPARTMENT, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE]

Chemistry of Boranes. III.[1] The Infrared and Raman Spectra of $B_{12}H_{12}^{=}$ and Related Anions

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The infrared and Raman spectra of the borohydride anion, $B_{12}H_{12}^{=}$, have been determined and found to be in complete agreement with predictions for a regular icosahedral structure, I_h, with equivalence of the boron and hydrogen sets and no B–H–B bridge bonds. The infrared and Raman fundamentals have been assigned with the aid of exchange deuteration. The Raman spectra of halogenated borohydride anions consist of single strong lines because of accidental cancellation of all but the out-of-phase breathing vibration.

Introduction

Molecular aggregates with regular icosahedral (I_h) symmetry amenable to vibrational analysis are rare. The regular icosahedral structure has been assigned to the anion $B_{12}H_{12}^{=}$ by the X-ray investigations of Wunderlich and Lipscomb.[2] Hence, we have determined the infrared and Raman spectra of this anion, $B_{12}H_{12}^{=}$, for comparison with group theoretical predictions of the number and depolarization of Raman lines and the number and Raman coincidence of infrared fundamental absorption bands.

Discussion

The tables of Jahn and Teller[3] indicate that the anion, $B_{12}H_{12}^{=}$, in point group, I_h, should give two strongly polarized Raman lines of symmetry species, A_g, one line from the set of symmetrically equivalent boron atoms and the other from the hydrogen set; four depolarized Raman lines of species H_g; and three infrared absorption fundamentals of species F_{1u}. The character table describing the molecular vibrations of the regular icosahedron is given in reference texts.[4]

The infrared and Raman data for the $B_{12}H_{12}^{=}$ anion (Fig. 1) are in good agreement with the above predictions of group theory for a regular icosahedral structure. For discussion purposes, the observed frequencies (ν_n in cm.$^{-1}$) for $B_{12}H_{12}^{=}$ are presented below in the form of the Teller–Redlich product ratios[5] of the three active symmetry species for approximately 90% conversion to $B_{12}D_{12}^{=}$, as:

Species A_g (Raman active)

$$\left(\frac{2518}{1912}\right)_1^2 \times \left(\frac{743}{716}\right)_{\nu_2}^{\nu^2} = \left(\frac{M_D}{M_H}\right)\left(\frac{M_B}{M_B}\right)$$

$$1.73 \quad \times \quad 1.08 \quad = \quad 1.87 \quad (vs.\ 2)$$

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[1] Paper II, W. H. Knoth and E. L. Muetterties, *J. Inorg. Nuclear Chem.*, **20**, 66 (1961).

[2] J. A. Wunderlich and W. N. Lipscomb, *J. Am. Chem. Soc.*, **82**, 4427 (1960).

[3] H. A. Jahn and E. Teller, *Proc. Roy. Soc.* (London), **161A**, 228 (1937).

[4] *Cf.* E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955, p. 330. (An error is noted in the character for C_2 in species H, which should be +1 instead of 0.)

[5] *Cf.*, G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., 1945, p. 232.

Species F_{1u} (infrared active)

$$\left(\frac{2480}{1882}\right)^2_{\nu_3} \times \left(\frac{1070}{932}\right)^2_{\nu_4} \times \left(\frac{720}{596}\right)^2_{\nu_5} \times \left(\frac{M_{BD}}{M_{BH}}\right) =$$

$$1.74 \times 1.32 \times 1.46 \times 1.085 =$$

$$\underset{3.6}{\left(\frac{M_D}{M_H}\right)^2} \quad \underset{(vs.\ 4)}{\left(\frac{M_B}{M_B}\right)}$$

Species H_g (Raman active)

$$\left(\frac{2475}{1867}\right)^2_{\nu_6} \times \left(\frac{949}{888}\right)^2_{\nu_7} \times \left(\frac{770}{736}\right)^2_{\nu_8} \times \left(\frac{584}{620}\right)^2_{\nu_9} =$$

$$1.76 \times 1.14 \times 1.09 \times 0.89 =$$

$$\underset{1.95}{\left(\frac{M_D}{M_H}\right)} \quad \underset{(vs.\ 2)}{\left(\frac{M_B}{M_B}\right)^3}$$

Vibrations ν_1, ν_3 and ν_6, having isotopic ratio squares near 1.75, may be assigned to largely hydrogen atom movements; those near unity to largely boron atom movements; and those with intermediate values, such as ν_4 and ν_5, to vibrations involving movements of both hydrogen and boron atoms against the valence stretching and bending force constants. Vibrations ν_1 and ν_2 may be assigned respectively to out-of-phase and in-phase breathing modes of the boron and hydrogen shells on the basis that the measured depolarization ratios are less than 0.15. The close agreement of the product ratio square for ν_2 (1.08) with the BD to BH mass ratio (1.085) suggests that in ν_2 the BH group vibrates as a single mass unit with little or no stress on the BH stretch force constant. Conversely, ν_1 should not involve the B–B stretch force constant. Thus, two important force constants, B–H stretch and B–B stretch, can be approximated directly from ν_1 and ν_2 by the well-known relation, $K = 4\pi c^2\nu^2\mu$.

The triply degenerate vibration, largely controlled by the BH angle bending force constant in which the hydrogen shell rotates against the boron shell, is in the inactive species, F_{1g}, so that the determination of the B–H and B–B angle bending force constants awaits complete solution of the secular equation.

The boron cage structures of the $B_{12}H_{12}^{=}$ and $B_{12}D_{12}^{=}$ anions used in this work are not strictly icosahedral because of the statistical distribution of B^{10} and B^{11} isotopes present in natural abundance. However, the infrared and Raman fundamentals apparently are observed as a qualitative average for a $B^{10.82}$ cage because of the as yet experimentally unresolved effects on frequency (location) and intensity (selection rules) of isotopic substitution in the highly spherical (*i.e.*, more isotopically intensity invariant[4]) molecular species present.

The Raman spectrum of $B_{10}H_{10}^{=}$ has six polarized lines—two in the BH stretching region—in agreement with the D_{4d} structure assigned by Lipscomb, Pitocheli and Hawthorne[6] but the thirteen depolarized Raman lines and twelve infrared fundamentals have not been completely located and assigned. The general non-coincidence of the observed infrared and Raman lines for $B_{10}H_{10}^{=}$ is also in agreement with a D_{4d} structure. No Raman or infrared lines were observed in the region[7,8] characteristic of BH stretch in a B–H–B bridge system. Boron isotope effects were unresolved because of the broad distribution of boron isotopic species present.

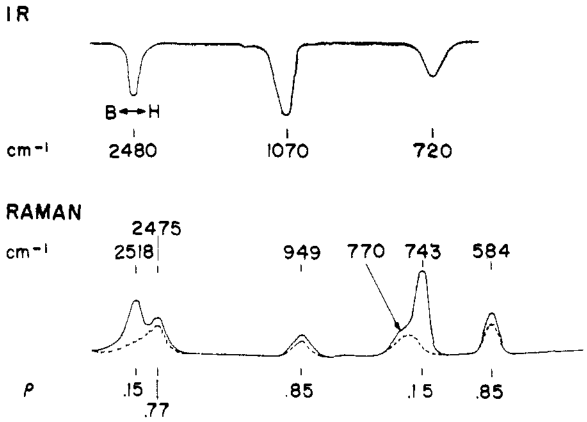

Fig. 1.—Infrared and Raman spectra of $B_{12}H_{12}^{=}$. (These are composites from several spectra and should not be dimensioned. The relative intensities are qualitatively consistent except that γ_3 is more intense than γ_4.)

The Raman spectra of $B_{12}Cl_{12}^{=}$, $B_{10}Cl_{10}^{=}$ and $B_{10}Br_{10}^{=}$ were unusual in that only a single strong line was observed for each anion, near 300 cm.$^{-1}$ for $B_{12}Cl_{12}^{=}$ (ρ = 0.38) and $B_{10}Cl_{10}^{=}$ (ρ = 0.27) and 199 cm.$^{-1}$ for $B_{10}Br_{10}$ (ρ = 0.27). Each of these lines may be assigned primarily to the symmetric out-of-phase breathing modes of the anions involving largely the boron–halogen stretching force constant (like ν_1 in $B_{12}H_{12}^{=}$). The depolarization ratios seem too high for spherical molecules and may indicate coincidence with depolarizing vibrations involving boron–halogen stretching. Values of the boron–halogen force constants approximated from the observed Raman frequencies depend upon selection of the appropriate reduced mass and assumptions concerning the involvement of other force constants than B–X stretching in the vibrations. R. C. Lord[9] has suggested that the failure to observe other strong Raman lines may be a consequence of accidental cancellation of polarizability changes of oppositely charged boron and halogen atoms in vibrations such as the totally symmetric in-phase breathing mode, which is too weak to be observed under the conditions of the present experiment. The infrared spectrum of the halogenated borohydride anions did not show any intensity cancellation but did show slight frequency shifts due to the varying masses of the halogens.

Experimental

The borohydride anions were in the form of sodium or cesium salts[10] prepared and carefully purified to meet the severe optical requirements of Raman spectroscopy. The Raman sample for the $B_{12}H_{12}$ = anion was an H_2O solution of approximately 20 grams of hydrated sodium salt in 40 ml.

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(6) W. N. Lipscomb, A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.*, **81**, 5833 (1959).

(7) W. J. Lehman, C. O. Wilson and I. Shapiro, *J. Chem. Phys.*, **34**, 1248 (1961).

(8) R. C. Lord and E. Nielsen, *ibid.*, **19**, 1 (1951).

(9) R. C. Lord, private communication.

(10) The substituted $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ anions are described by W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, J. C. Sauer and E. L. Muetterties, *J. Am. Chem. Soc.*, **84**, 1056 (1962).

total solution, treated with activated charcoal. A similar Raman sample for the anion, $B_{12}D_{12}^{=}$, in D_2O solution was prepared by successive exchange with D_2O. Since the exchange was at least 90% complete, the concentration distribution of $B_{12}D_nH_{12-n}^{=}$ anion species is in accord with the binomial expansion, *e.g.*, ~30% $B_{12}D_{12}^{=}$. While this incomplete deuteration is not ideal, it does not appear to introduce serious complications in interpretation, perhaps because of the relative insensitivity of the boron cage vibrations to the degenerate deuterium substitution. Raman samples for the other anions listed were limited to about 4 grams of salt in 10 ml. of total solution.

The Raman spectra were taken using blue line excitation (4358 Å.) using an instrument designed by Rank and similar to that described by Rank and Wiegand.[11] The instrument is equipped with a helical Toronto mercury arc source and a straight mercury arc source for depolarization measurements, both with water-cooled electrodes. The Raman frequencies presented here are from direct electron multiplier photocell recordings and are accurate to an estimated ±3 cm.$^{-1}$. Qualitative features of the Raman spectra were checked by photography. The infrared measurements of the F_{1u} species were on water or deuterium oxide solutions, using a Perkin–Elmer model 21 infrared spectrometer and NaCl prism, except for 596 cm.$^{-1}$, which was taken using a KBr wafer on a Perkin–Elmer "Infracord"® with KBr prism. KBr wafers were found to cause infrared band shifts and splittings when compared to data on "Nujol"® mulls or water solutions.

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[11] E. H. Rank and R. V. Wiegand, *J. Opt. Soc. Am.*, **36**, 325 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, NEW YORK]

Kinetics of Anionic Polymerization of Styrene in Tetrahydrofuran

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A flow technique suitable for studying the kinetics of fast polymerizations is described. The time of polymerization may be as short as 0.08 sec. The anionic polymerization of styrene in THF was investigated and was shown to be first order with respect to the monomer concentration, but the apparent first order rate constant seems to increase with decreasing concentration of "living" ends. No satisfactory explanation was found for this phenomenon. The activation energy of the polymerization was found to be 1.0 kcal./mole, and the entropy of activation was by ~14 e.u. more negative than the respective $\Delta S^{\ddagger}$ of propagation in a radical polymerization. This decrease in $\Delta S^{\ddagger}$ is attributed to the immobilization of the counter-ion in the transition state. In this respect the reaction resembles the anionic polymerization of α-methyl styrene in THF which proceeds with even a lower entropy of activation. On the other hand, the anionic polymerization of styrene in dioxane seems to require a much higher activation energy and its entropy of activation seems to be "normal."

Anionic polymerization may be carried out under conditions preventing the occurrence of any termination, and the polymer produced in this manner is referred to as a "living" polymer.[1] Addition of monomer to a "living" polymer is kinetically a pseudo-unimolecular reaction since the process involves the propagation step only, and the concentration of "living" ends remains constant during the whole course of the reaction. Hence

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_{\mathrm{p}}\cdot[\text{``living'' ends}]\cdot[\mathrm{M}]$$

where [M] denotes the monomer concentration and k_{p} is the rate constant of the propagation step. The plot of $\ln[\mathrm{M}_0]/[\mathrm{M}]$ as a function of time should therefore result in a straight line passing through the origin, its slope giving $k_{\mathrm{p}}\cdot[\text{``living'' ends}]$. Since the concentration of the "living" ends may be determined by a direct titration or by a photometric technique—the method gives the absolute value of k_{p}.

The growth of "living" polymers is often very rapid. This is not surprising since the concentration of the growing species in this polymerization is about 10^{-2}–10^{-3} *M*, whereas in a conventional radical polymerization the stationary concentration of growing radicals is 10^{-7}–10^{-8} *M*. Thus, the anionic polymerization of styrene in tetrahydrofuran solution is virtually completed in a second or two. Studies of such fast reactions require therefore special techniques, and in this investigation the capillary flow method[2] was adopted for this purpose.

Experimental

Although the capillary flow technique is well known, its application to the investigation of anionic polymerization poses a few problems. A description of details of our apparatus and its operation are therefore desirable.

The apparatus used in this study is shown in Fig. 1. Two cylindrical reservoirs contained the solution of the "living" polymer and of the monomer respectively. Each reservoir was calibrated and the level of the liquid could be measured with a cathetometer to 0.1 mm. accuracy. A narrow tube linked the bottom of each reservoir to 1 mm. wide capillaries forming arms of a T-shaped, three-way stopcock. The third vertical arm of the stopcock was immersed in a beaker containing wet tetrahydrofuran or methyl iodide dissolved in dry tetrahydrofuran. The stopcock contained a Teflon barrel with specially drilled 1 mm. holes which served as a mixing chamber. No greasing of the stopcock was required.

The liquid from each reservoir was pressed into the stopcock by dry and rigorously purified nitrogen introduced through special tubes which reached almost to the bottom of each vessel. This device ensured a constant rate of flow of each liquid, in spite of the fact that their levels, *i.e.* the hydrostatic pressures, varied in the course of the experiment. Of course, the pressure of nitrogen had to be kept constant during each experiment, and its possible fluctuations were minimized by inserting in the nitrogen line a 3 l. flask which acted as a barostat.

The reservoirs were immersed in larger vessels through which water, maintained at constant temperature by a

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[1] M. Szwarc, *Nature*, **178**, 5557 (1956); *Makromolek. Chem.*, **53**, 132 (1960).

[2] H. Hartridge and F. J. W. Roughton, *Proc. Roy. Soc.* (London), **B104**, 376 (1923); see also for a review, F. J. W. Roughton in "Techniques of Organic Chemistry," Vol. VIII, Interscience Publishing Co., New York, N. Y., 1953, p. 674.