

by a marked and abrupt drop in the equivalent conductivity and by an abnormal increase in the cationic transference number in the case of the cationic colloidal electrolytes. It is well known that both of these effects are observed in aqueous solutions of colloidal electrolytes. The essential difference between ionic and lamellar micelles is that the latter has solubilized the undissociated colloidal electrolyte.

Transference data on the effect of non-electrolytes upon solutions of colloidal electrolytes would be extremely helpful in explaining the mechanism of micelle formation and studies are now underway to determine the effect of various non-electrolytes upon the transference numbers of solutions of dodecylammonium chloride.

Summary

The effect of the presence of benzene, cyclo-

hexane, hexane, octane, dodecane, heptadecane, octadecane, hexanol, octanol, dodecanol, octadecanol, undecyl chloride, stearonitrile and stearamide upon the equivalent conductivity of aqueous solutions of dodecylammonium chloride has been determined. The influence of the presence of dodecane and lauronitrile upon the equivalent conductivity of aqueous solutions of dodecyltrimethylammonium chloride has also been investigated.

With the exception of heptadecane and octadecane all the compounds investigated lowered the equivalent conductivity and the critical concentration for micelle formation in the amine salt solutions.

The results have been discussed in relation to the micelle theory and it has been proposed that solubilization and micelle formation are allied phenomena.

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The Dissociation of Diborane by Electron Impact

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Introduction

The theory of the structures of some electron-deficient molecules, the hydroborons in particular, have recently received considerable attention. In 1942 the most fully developed valence theory of the hydroborons, as reviewed by Bauer,¹ assumed hydrocarbon-like structures. Because of inconsistencies between the hydrocarbon analogy and chemical and physical properties, Pitzer² and others further developed the four-membered-bridge bond originally proposed by Dilthey³ to a "protonated double bond" theory in which two protons are placed symmetrically between the boron atoms, one above and one below an ethylene-like double bond. More recently, Burg,⁴ in order to account for the lack of proton-deuteron exchange between ammonia and ammoniated diborane, proposed a "pseudoethane" structure in the form of a trigonal antiprism in which two sp^2 planar BH_3 groups are held together by resonating cross linkages between the B-B and B-H atoms. Another structure which he considers possible is a four-proton-bridge model in which the two boron atoms and four of the hydrogen atoms form the corners of a cube. The remaining two hydrogens extend outward along the diagonal of the cube connecting the two boron atoms.

Rundle⁵ accepts Pitzer's developed theory in the case of the hydroborons with an interpretation of the protonated double bond as two hydrogen

bridges consisting of "half-bonds." Each hydrogen bonds two boron atoms using its $1s$ -orbital and one electron pair. Thus, the bridge contains two pairs of electrons and should have the properties of the ethylene-like double bond.

Hipple⁶ has published a note on the mass spectrum of diborane. An analysis of this mass spectrum made by the authors differs significantly from the results reported by Hipple. As the results have a direct bearing on the structure of the diborane molecule we report in detail the analysis of this spectrum as compared with the mass spectra of ethane and ethylene.

Experimental

The Consolidated mass spectrometer used to obtain the mass spectra has been described elsewhere in detail.⁷ The gas to be studied is admitted to the ionization chamber at about 10^{-4} mm. pressure and ionized by a beam of electrons at 50 or 70 electron volts energy. The positive ions formed in the electron beam are accelerated by an electric field and sorted into 180° arcs by a constant magnetic field used as a velocity analyser. By varying the electric field the ions are separately collected and recorded. The ionizing current is automatically maintained constant and the ionization chamber is thermostated to maintain a temperature of about 245° . Two samples of diborane were obtained. Sample 1 was prepared at the U. S. Naval Research Laboratory and supplied by Roman R. Miller. About 25 ml. of gas (S.T.P.) were removed from the liquid phase and transferred from the stainless steel cylinder into a glass bulb. The glass bulb was stored at -78° to minimize decomposition to hydrogen and heavy hydroborons. A mass spectrometric analysis of the original sample showed a purity of about 99.4% with small amounts of tetraborane, ethane and diethyl ether. Sam-

(1) S. H. Bauer, *Chem. Rev.*, **31**, 43 (1942).

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

(3) W. Dilthey, *Z. angew. Chem.*, **34**, 596 (1921).

(4) A. B. Burg, *THIS JOURNAL*, **66**, 747 (1947).

(5) R. E. Rundle, *ibid.*, **69**, 1327 (1947).

(6) J. A. Hipple, Jr., *Phys. Rev.*, **67**, 350 (1940), abstract.

(7) H. W. Washburn, H. F. Wiley, S. M. Rock and C. E. Berry, *Ind. Eng. Chem., Anal. Ed.*, **16**, 54 (1943).

ple 2 was prepared at the University of Southern California by Anton B. Burg. The sample of about 70 ml. at slightly above atmospheric pressure was shipped by air-express in a glass tube with an inner break-off seal. Upon arrival it was stored under the same conditions as Sample 1. Except for a small amount of hydrogen, Sample 2 showed no impurities volatile at -78° . An additional precaution was taken by cooling both samples to -183° and pumping off accumulated hydrogen before each run.

The ethylene and ethane were Phillips Petroleum Company "Research Grade" hydrocarbons.

Results

The mass spectrum of diborane permits a determination both of the isotope abundance ratio of boron and the monoisotopic spectrum of diborane. By trial approximations on Sample 1 it was found that an abundance ratio $B^{10}/B^{11} = 0.251$ gives the best fit with the observed spectrum. In the same manner, Sample 2 showed a ratio $B^{10}/B^{11} = 0.256$. The former value is in good agreement with a value of 0.250 obtained in this Laboratory from the boron trifluoride spectrum. It is not in agreement, however, with a value of 0.232 found by Inghram.⁸ It seems probable that there are real differences in the isotope ratio depending on the previous history of the sample used in the experiments. For Sample 1, using the ratio $B^{10}/B^{11} = 0.251$, one derives the abundance ratios $B^{10}B^{11}/B_2^{11} = 2 \times 0.251 = 0.502$, and $B_2^{10}/B_2^{11} = 0.063$. To separate the mixture spectrum into monoisotopic spectra (Table I), one can start at the heavy mass end and use these ratios to compute the contribution of each B_2 and B_1 ion to each value of m/e . The peak at $m/e = 28$ is due entirely to the $B_2^{11}H_6^+$ ion; hence, the $B^{10}B^{11}H_6^+$ ion ($m/e = 27$) is $0.65 \times 0.502 = 0.33$ and the $B_2^{10}H_6^+$ ion ($m/e = 26$) is $0.65 \times 0.063 = 0.04$. The $B_2^{11}H_5^+$ ion ($m/e = 27$) is then $97.28 - 0.33 = 96.95$. From this in turn, the $B^{10}B^{11}H_5^+$ ion ($m/e = 26$) and the $B_2^{10}H_5^+$ ion ($m/e = 25$) are

TABLE I

SUMMARY OF THE MONOISOTOPIC SPECTRUM CALCULATIONS OF THE SAMPLE 1 MASS SPECTRUM FOR 50-VOLT ELECTRONS

| m/e | Mixture spectrum | Monoisotopic spectrum ^a | | | | |
|-------|------------------|------------------------------------|-------------|---------------|-------------------|---------------|
| | | $B^{10}H_2$ | $B^{11}H_2$ | $B_2^{10}H_2$ | $B^{10}B^{11}H_2$ | $B_2^{11}H_2$ |
| 10 | 6.48 | 6.47 | 0 | .. | ... | ... |
| 11 | 23.86 | 3.12 | 25.74 | .. | ... | ... |
| 12 | 18.50 | 6.07 | 12.43 | .. | ... | ... |
| 13 | 24.34 | 0.17 | 24.17 | .. | ... | ... |
| 14 | 0.68 | 0 | 0.68 | .. | ... | ... |
| 20 | 0.18 | .. | .. | 0.18 | 0 | 0 |
| 21 | 2.02 | .. | .. | 0.48 | 1.46 | 0 |
| 22 | 11.52 | .. | .. | 4.79 | 3.81 | 2.92 |
| 23 | 47.32 | .. | .. | 1.65 | 38.05 | 7.62 |
| 24 | 92.41 | .. | .. | 3.24 | 13.10 | 76.07 |
| 25 | 58.04 | .. | .. | 6.11 | 25.75 | 26.18 |
| 26 | 100 | .. | .. | 0.04 | 48.49 | 51.47 |
| 27 | 97.28 | .. | .. | 0 | 0.33 | 96.95 |
| 28 | 0.65 | .. | .. | 0 | 0 | 0.65 |

^a "x" assumes integral values from zero to six.

(8) M. Inghram, *Phys. Rev.*, **70**, 653 (1946).

similarly computed. Again, the $B_2^{11}H_4^+$ ion is calculated by difference and the cycle is repeated until all contributions to each peak are computed. There are three checks on the computations. The mass 21 peak is calculated to be 1.94 compared with 2.02 observed. The mass 20 peak agrees exactly with the calculations while the mass 10 peak is computed as 6.47 compared with 6.48 observed. A small change in the B^{10}/B^{11} ratio, *e. g.*, 0.251 to 0.253, materially increases the residuals. A similar calculation for sample 2 using $B^{10}/B^{11} = 0.256$ shows equally good agreement between computed and observed peaks.

The polyisotopic diborane dissociation pattern is now obtained by summing the contributions of all ions with the same number of hydrogen atoms regardless of isotopic species. The most abundant ion ($m/e = 27$) is given the value of 100. Other ion abundance values are relative to $m/e = 27$. Table II gives these patterns for 50 and 70-volt energies of the ionizing electrons.

TABLE II

DISSOCIATION PATTERNS OF DIBORANE, ETHYLENE AND ETHANE AT IONIZING VOLTAGES OF 50 AND 70 VOLTS

| Ion | Diborane | | Ion | Ethylene | | Ethane | |
|------------|----------|-------|------------|----------|-------|--------|-------|
| | 50 v. | 70 v. | | 50 v. | 70 v. | 50 v. | 70 v. |
| H^+ | 3.91 | 3.98 | H^+ | 3.85 | 4.11 | 2.14 | 2.58 |
| H_2^+ | 2.72 | 2.71 | H_2^+ | 0.52 | 0.51 | 0.22 | 0.30 |
| B^+ | 21.2 | 21.0 | C^+ | 1.73 | 2.14 | 0.42 | 0.56 |
| BH^+ | 10.2 | 10.6 | CH^+ | 3.19 | 3.48 | 0.96 | 1.19 |
| BH_2^+ | 19.9 | 19.5 | CH_2^+ | 6.16 | 6.24 | 3.00 | 3.41 |
| BH_3^+ | 0.55 | 0.62 | CH_3^+ | 0.56 | 0.54 | 4.48 | 4.62 |
| B_2^+ | 3.05 | 3.43 | C_2^+ | 3.01 | 3.71 | 0.49 | 0.75 |
| B_2H^+ | 7.74 | 7.00 | C_2H^+ | 11.5 | 11.7 | 3.47 | 4.13 |
| $B_2H_2^+$ | 78.4 | 76.8 | $C_2H_2^+$ | 61.1 | 61.9 | 23.1 | 23.7 |
| $B_2H_3^+$ | 27.0 | 26.2 | $C_2H_3^+$ | 62.1 | 64.7 | 33.1 | 33.5 |
| $B_2H_4^+$ | 52.9 | 52.6 | $C_2H_4^+$ | 100 | 100 | 100 | 100 |
| $B_2H_5^+$ | 100 | 100 | $C_2H_5^+$ | | | 21.6 | 21.7 |
| $B_2H_6^+$ | 0.67 | 0.64 | $C_2H_6^+$ | | | 24.9 | 24.7 |

The dissociation patterns obtained for both samples were very similar. Except for the $B_2H_6^+$ ion, the maximum deviation was about 3% ($B_2H_6^+$ ion). The disagreement of the $B_2H_6^+$ ion (0.49 compared to 0.67) may be due to a small amount of impurity in the latter sample.

The results differ from the published data of Hipple in several respects. The peaks at masses 11, 12, and 13 are unambiguously interpreted in terms of BH^+ and BH_2^+ polyisotopic ions of abundance 10.6% and 19.5% at 70 volts while Hipple reported BH^+ as zero and BH_2^+ as uncertain. We find a small $B_2H_6^+$ peak of about 0.5% while he reported it as 0 or less than 0.1%. The B_2H^+ ion abundance is 7% here as compared with 2.9%. We have measured the mass pattern at 100 volts and find only minor changes as compared with 50 and 70 volts. Hipple's measurements were at 90 volts. A more important difference in the experiments is that Hipple used an ionization chamber at about room temperature while ours operated at 245° . Relative intensities of mass spectra always depend on the temperature and in diborane there may be some thermal dissociation in the ioniza-

tion chamber. It is known that above 100° at pressures of the order of an atmosphere boron and solid boron hydrides of higher molecular weight begin to form (Gmelin's "Handbook"). The mass spectra show that there is no production of heavier boron hydrides within the ionization chamber.

For comparison with ethane and ethylene, the dissociation patterns of these molecules taken under similar conditions are also given in Table II.

Omitted from Table II for the sake of brevity, is a small peak in diborane at $m/e = 11.5$ amounting to 0.39% of the maximum peak at 50 volts and 0.43% at 70 volts. This is a doubly charged ion of mass 23 and can be either $B_2^{11}H^{++}$ or $B^{10}B^{11}H_2^{++}$ or both. These ions give other peaks coincident with the large peaks at $m/e = 11$ and $m/e = 12$. The $B_2^{10}H^{++}$ ion, expected at $m/e = 10.5$ is too small to observe so there is no basis for a unique interpretation of the peak at $m/e = 11.5$. The contribution of these doubly charged ions to peaks 11 and 12 is too small to introduce any serious uncertainty in the computation of monoisotopic spectra. Ethylene shows a small peak at $m/e = 13.5$ due to the $C_2H_3^{++}$ ion which is 0.41% of the maximum peak at 70 volts. Ethane shows two peaks at $m/e = 13.5$ and $m/e = 14.5$ due to the $C_2H_3^{++}$ ion and the $C_2H_5^{++}$ ion. The abundances are 0.07 and 0.72%, respectively, of the maximum. Also omitted from the table are two metastable-ion transition⁹ peaks near 21.1 and 22.1. These can be ascribed to the transition $B_2H_4^+ \rightarrow B_2H_2^+ + 2H$, which occurs after the B_2H_4 ion has traversed the electric field. The apparent mass, m_a , is given by the relation $m_a = m_f^2/m_i$, where m_f and m_i are the final and initial masses. For $B_2^{11}H_4$, $m_a = 22.2$; for $B^{10}B^{11}H_4$, $m_a = 21.2$. The observed peak at 22.2 is the larger peak in agreement with the isotope abundance although the peaks are too small for a quantitative check. A corresponding metastable transition $C_2H_4^+ \rightarrow C_2H_2^+ + 2H$ ($m_a = 24.1$) is found in both ethane and ethylene.

Discussion

No certain theoretical basis has yet been proposed for interpreting mass spectra in terms of molecular structure. The general rule is that ionization of a polyatomic molecule by electrons of 50 volts or more energy produces the molecular ion and ions of every possible dissociation process. Were it not for a large number of exceptions to this rule, mass spectra would give very specific information as to the structure of the polyatomic

molecules. The mass spectra of ethane and ethylene (Table II) illustrate this fact. The spectrum of ethane clearly suggests that C_2H_6 consists of two distinct methyl groups. In the spectrum of ethylene the structure of two methylene groups is also indicated. However, there is a small CH_3^+ ion, not expected from the ethylene structure. There are plausible explanations for this small peak but its presence is a warning that we cannot uncritically infer structure solely on the basis of mass spectra.

In the diborane mass spectrum the relatively intense BH_2^+ ion and the very small BH_3^+ ion are quite like the ethylene pattern and not at all like ethane. This strongly suggests that the diborane consists of an ethylene-like structure which as a whole binds two additional hydrogen atoms. The very small $B_2H_6^+$ ion is unexpected and unusual. One can only conclude that the $B_2H_6^+$ ion is quite unstable. This, of course, weakens the argument for the ethylene structure for it could likewise be argued that the BH_3^+ ion is unstable and its absence gives no positive evidence that BH_3 radicals do not exist. There is little theoretical basis for predicting which ion configurations are stable and which are not. However, as a matter of experiment, there seem to be relatively few configurations which cannot exist as single-charged ions. Thus, it is probable but not certain that BH_3 is not the unit structure.

The existence of a metastable transition $B_2H_4^+ \rightarrow B_2H_2^+ + 2H$ gives no further evidence as to the structure. The corresponding transition $C_2H_4^+ \rightarrow C_2H_2^+ + 2H$ is observed in both ethylene and ethane.

The fact that the H_2^+/H^+ ratio is much larger in diborane than the hydrocarbons may not be significant since there is some doubt as to whether all of the H_2^+ is from the ionization of diborane. It has been noted in the experimental section that diborane slowly decomposes at room temperature to give hydrogen, and in spite of the precaution of pumping off hydrogen immediately before measuring the spectrum, some hydrogen may accumulate in the inlet system during the run

Summary

The mass spectrum of diborane at ionizing voltages of 50 and 70 volts resembles ethylene more than ethane. This suggests that BH_2 is a unit structure in diborane rather than BH_3 and that two of the hydrogen atoms are not bound directly to the boron. The $B_2H_6^+$ ion is apparently quite unstable as evidenced by the low abundance of this ion in the mass spectrum.

(9) J. A. Hipple, R. E. Fox and E. U. Condon, *Phys. Rev.*, **69**, 347 (1946).