the results are shown in Fig. 2. In agreement with theory, the total area under the curve is negligible, being less than 1% of the actual area without regard to sign. Measuring areas under the curve with a planimeter one finds

$$\int_{6.000}^{6.852} \frac{R}{N_0}\left(\frac{\partial N}{\partial t}\right) dR = 27.9 \times 10^{-6}$$

Using 0.62 for δ and this value, one finds 0.21×10^{-13} for the sedimentation constant and 1.0×10^{-6} for the diffusion constant. The values corrected to water at 20° are 0.41×10^{-13} and 2.5×10^{-6}, respectively. The results obtained with the synthetic boundary cell are shown in Table II. The diffusion constants were calculated from the half-widths at the inflection point of the centrifuge patterns.

TABLE II

Concn., g./100 ml.	Diffusion constant[a] $\times 10^6$	Sedimentation constant[a] $\times 10^{13}$
1.00	2.4	0.41
0.655	2.2	.38
0.353	2.4	.37

[a] Corrected to water at 20°.

Discussion

A value of 0.62 for δ corresponds to a molecular weight of 1310. There is a difference of 6.5% between this value and the formula weight of 1229. The fact that a repeat run gave a value of 1300 with equal values of δ at the two ends of the cell suggests that this difference is not entirely due to experimental error.[12] There is an indication that the sedimentation constants determined in the synthetic boundary cell and consequently the apparent molecular weight may depend on concentration. Precipitation of the digitonin at the bottom of the cell prevented an accurate analysis of a run made with 1% solution. However, δ appeared to be of the order of 0.7 at this concentration.

The agreement between the values of δ found at the two ends of the cell suggest that if there is any dependence of the apparent molecular weight upon concentration, it is not due to aggregation but to some other deviation from ideal behavior.[13] Dr. L. G. Longsworth of the Rockefeller Institute has measured the diffusion constant of a 0.4% digitonin solution in 63% ethanol at 24.92° by the Rayleigh interference fringe method.[14] Although the peak was definitely non-Gaussian it was reasonably symmetrical. One would infer from the lack of skewing that the diffusion constant did not vary markedly over the concentration interval of the boundary. The observed diffusion constant in the 63% ethanol solution was 1.10×10^{-6}. This corresponds to a value of 2.35×10^{-6} in water at 20°.

The diffusion constants obtained in the synthetic boundary cell are in reasonable agreement with the value obtained by interferometry. There is a larger error in the first value obtained by the Archibald procedure. The value (2.6×10^{-6}) obtained in the second experiment is in even poorer agreement.

The molecular weight (1310) obtained by Dr. Longsworth's diffusion constant and the velocity sedimentation constant measured at a concentration of 0.65% is in excellent agreement with those obtained by the Archibald procedure.

In general, one would expect the molecular weights determined by the Archibald procedure to be more precise than the diffusion and sedimentation constants. The latter measurements involve the calculation of a small difference between two large numbers which is subject to large experimental errors.

There are several advantages to the Archibald procedure. If one estimates the partial specific volume and refractive index increment, a determination of the molecular weight and heterogeneity of a low molecular weight material may be made in a 2° sector cell with only a 3-mg. sample.

A preliminary analysis of peptides may thus be obtained with very small quantities of material. Once the order of magnitude of the molecular weight of a peptide is known, a precise value may be calculated from the amino acid composition. The Archibald procedure should prove a valuable tool in peptide chemistry.

Acknowledgments.—We wish to thank Dr. Longsworth for making the diffusion measurements. The centrifuge work was done with the technical assistance of Mr. Gilbert Richmond and Miss Mary Englert.

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LEDERLE LABS. DIV.
AMERICAN CYANAMID CO.
PEARL RIVER, NEW YORK

(12) The experiments with digitonin and work with several peptides would indicate that the molecular weight values are reproducible to 2–3%.

(13) In a two-component solvent, there will be small differences in solvent density at the two ends of the cell. However, the resulting errors in δ are less than 1%.

(14) L. G. Longsworth, THIS JOURNAL, **74**, 4155 (1952).

Dimethylphosphinoborine Trimer. Mass Spectra and Thermal Decomposition[1]

BY R. E. FLORIN, L. A. WALL, F. L. MOHLER AND EDITH QUINN

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In connection with the recent description[2] of the dimethylphosphinoborine trimer

$$\overline{P(CH_3)_2BH_2P(CH_3)_2BH_2P(CH_3)_2BH_2}$$

it is of interest to report the results of some mass spectrometric and pyrolytic studies on this quite unusual compound. We wish to thank Dr. A. B. Burg for kindly supplying the sample used in this work.

1. Mass Spectra

Measurements were made with a model 21-103 Consolidated Mass Spectrometer using standard operating conditions except that some spectra were obtained with the ionizing voltage reduced to low values. Crystals of the phosphinoborine trimer were evaporated directly into the reservoir of the mass spectrometer. There was no evidence of any appreciable impurity in the compound.

(1) The research reported in this paper was performed in part under the sponsorship of the Ordnance Corps, Department of the Army.

(2) Anton B. Burg and R. I. Wagner, THIS JOURNAL, **75**, 3872 (1953).

Table I lists relative intensities of some of the larger peaks in the mass spectra obtained with ionizing voltages of 70, 20 and 12 v. The mass spectrum at 70 v. is extremely complicated, with peaks at almost every mass number from 24 to 222. At low voltage the spectrum becomes simpler and only the heavier fragment ions are observed. The relative intensity of the isotope peaks indicates the number of boron atoms in each fragment ion or, at least, sets an upper limit to the number. (B^{10} is 0.25 × B^{11}, $B^{10}B^{11}$ is 0.50 × $B_2{}^{11}$ and $B^{10}B_2{}^{11}$ is 0.75 × $B_3{}^{11}$.) Thus, it is found that the ion of mass 208 cannot contain three boron atoms and must be the fragment ion indicated in the last column. Table I gives in the last column the probable chemical formulas of some of the ions, but formulas enclosed in parentheses are open to some uncertainty as there are alternative possibilities.

TABLE I

PARTIAL MASS SPECTRUM OF $(P(CH_3)_2BH_2)_3$

Mass	Relative intensity 70 v.	20 v.	12 v.	Positive ion
27	65	0	0	$B^{11}CH_4$
41	100	0	0	$B^{11}(CH_3)_2$
75	23.6	0.5	0	$(P(CH_3)_2B^{11}H_3)$
89	27.1	2.0	0	$(P(CH_3)_3B^{11}H_2)$
131	14.6	3.2	0	
136	13.4	4.6	0	$P_2(CH_3)_4B^{11}H_3$
145	21.6	6.1	0	$(P_2(CH_3)_4B_2{}^{11}H)$
161	53.6	28.2	6.9	$(P_2(CH_3)_4B_3{}^{11}H_6)$
178	10.3	8.3	6.9	
205	19.8	11.4	6.5	
208	17.5	11.0	3.0	$P_3(CH_3)_6B_2{}^{11}H_3$
220	47.1	29.6	9.3	$P_3(CH_3)_6B_3{}^{11}H_4$
222	18.6	10.0	4.2	$P_3(CH_3)_6B_3{}^{11}H_6$

This is an unusual spectrum in several respects. The most abundant ion in the 70 v. spectrum, $B(CH_3)_2{}^+$, involves a very unusual type of rearrangement in the ionization process and it has a very high appearance potential of over 20 v. It is of interest that the fragment ions of mass 208 and mass 161 appear below 12 v. ionizing potential, for these fragment ions involve breaking the ring and breaking another P–B bond in the ionization process.

2. Pyrolysis Studies

A static technique was used in which samples of 2.0 mg. were sealed in evacuated 10-ml. ampules designed so that they could be broken and the products led into the mass spectrometer. These ampules containing the samples were heated in a muffle furnace for various times of from 1 to 5 hours at temperatures ranging from 251 to 510°. Products were then examined mass spectrometrically.

Very little decomposition if any occurred in 4 hours at 251°. At 360° hydrogen was gradually evolved, reaching 0.35 mole H_2 per mole of trimer in 5 hours, and was accompanied by very small amounts of methane. At 510° the identified products were hydrogen, methane, ethane and elemental phosphorus, found in the ratio of approximately 0.5 mole, 1 mole, 0.2 mole and 1 gram-atom per mole of trimer used, and liberated mainly during the first hour of pyrolysis. The amount of phosphorus present may have been much greater than observed because of incomplete vaporization into the mass spectrometer inlet reservoir. Peaks characteristic of the original trimer were observed in all cases but were very much diminished in intensity in the experiments at 510°. In the latter experiments the appearance of a $B^{11}(CH_3)_2{}^+$ peak also strongly suggests the formation of methyl derivatives of mixed boranes. This and the production of large amounts of phosphorus indicate a relocation of the methyl groups during pyrolysis.

The relative intensities in the spectrum of phosphorus vapor are as follows: $P_1{}^+$ 20, $P_2{}^+$ 26, $P_3{}^+$ 7.6, $P_4{}^+$ 100. The sensitivity to the $P_4{}^+$ ion is about 0.5 times the sensitivity of the mass 43 peak of *n*-butane. A spectrum obtained in a different type of mass spectrometer has been described by Dukelskii and Zandberg.[3]

The thermal decomposition data indicate that the dimethylphosphinoborine trimer does not depolymerize into its monomer but decomposes in a more complicated manner. The decomposition appears to occur in two stages: (1) at 360° liberation of hydrogen and small amounts of methane with possible ring condensation and (2) at 510° destruction of the ring and relocation of the methyl groups with the formation of elemental phosphorus and methyl derivatives of the boranes. This migration of methyl groups also occurs in the mass spectra as noted above.

For a coördination compound this material has an unusual degree of stability, as indicated by both the mass spectrometer and thermal results.

(3) V. M. Dukelskii and E. Ya. Zandberg, *Doklady Akad. Nauk. S.S.S.R.*, **86**, 263 (1952).

NATIONAL BUREAU OF STANDARDS
WASHINGTON 25, D. C.

Homogeneous Catalytic Hydrogenation. II. The Effect of Catalyst Environment on the Activation of Molecular Hydrogen

BY L. W. WRIGHT AND SOL WELLER

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A number of investigators have reported the homogeneous catalytic activation of hydrogen[1-3] by cuprous acetate in quinoline. We wish to report the effects obtained by altering the coördination sphere around the metal atom by chelation. Ethylenediamine (en) and ethylenediaminetetraacetic acid (enta) inhibit both the rate and extent of reduction of *p*-benzoquinone and cupric acetate monohydrate in quinoline solution at 100° (Table I). The magnitude of the inhibition increases with increasing concentration of the chelating agent (*e.g.*, runs 372, 293; 364, 352). The effect on the reduction of cupric acetate monohydrate is less, at a given level of chelating agent concentration, than on the reduction of quinone (runs 372, 409).

A quinoline solution of cuprous acetate alone is relatively stable toward hydrogenation (run 485). However, the reduction of cuprous acetate to metallic copper is catalyzed by reduced quinone (run 287), en (run 371), and cystine (run 466), but not by enta (runs 364, 352, 408).

When a mixture of cupric acetate monohydrate and *p*-benzoquinone was reduced in the absence of enta, the usual reduction of cuprous acetate to metallic copper after the break point (Table I, run 251) occurred (Fig. 1A). When enta was present (Fig. 1B), however, the reduction of cuprous acetate to copper metal was prevented.

(1) M. Calvin, *Trans. Faraday Soc.*, **34**, 1181 (1938)
(2) Sol Weller and G. A. Mills, THIS JOURNAL, **75**, 769 (1953).
(3) W. K. Wilmarth and Max K. Barth, *ibid.*, **75**, 2237 (1953)