## Discussion

The data of Table I clearly show that the average absorption intensity differences between the cyclotrisiloxanes, cyclotetrasiloxanes, and higher cyclics are much larger than the standard deviations for each group of cyclics. The differences between the cyclopentasiloxanes and the cyclohexasiloxanes do not appear to be significant.

If we consider the geometric configurations of these cyclics in order of increasing ring size, we find that the average angle between the substituents on successive silicon atoms and consequently the average distance between these substituents will decrease as the ring size increases. These changes in intergroup distance as the ring size changes from cyclotetrasiloxane to cyclopentasiloxane to cyclohexasiloxane could be less important as opportunity for ring puckering increases in the larger rings. Cases of rigidly enforced proximity and orientation of phenylene groups are found in the paracyclophanes and 1,4-polymethylenebenzene cyclics studied by Cram<sup>3</sup> and in the siloxane analog of the paracyclophanes studied by MacKay.<sup>4</sup> MacKay's compound is



In these compounds the benzene rings of the smaller cyclics are distorted from planarity and bathochromic and hypochromic effects are observed in the ultraviolet. In our compounds the distortion would be smaller, and we do not detect a bathochromic shift but do observe a hypochromic effect, weaker than Cram's, upon going from the cycloterisiloxane to the cyclotetrasiloxane. A still weaker hypochromic effect is observed upon going from cyclotetrasiloxane to groups of cyclopentasiloxanes and cyclohexasiloxanes, which are undifferentiated. It would appear that methyl, ethyl, vinyl, and propyl groups on adjacent silicons have as large an effect on the transition probability as does the phenyl group.

Brown and Prescott<sup>1</sup> stress calculation of oscillator strengths and analyze them into vibrational and substituent components following the method of Petruska.<sup>5</sup> However, in the case of our compounds, the substituents on silicon are similar so that intensity maxima are sufficient. The spectra of all the compounds are superposable with vertical shifts.

Lastly, the development of Tinoco<sup>6</sup> used by Brown and Prescott<sup>1</sup> to estimate hypochromism in monophenylsiloxane structures cannot explain the results presented here as these authors have themselves observed. Induced dipole-dipole interaction between

phenyl groups has nothing to do with the virtual identity of  $\epsilon_{max}$  for, say, compounds I and III of Table I among the trisiloxanes and for compounds VII and XII among the tetrasiloxanes.

(5) J. Petruska, J. Chem. Phys., 34, 1111, 1120 (1961).

(6) I. Tinoco, J. Am. Chem. Soc., 82, 4785 (1960).

# Electrooxidation of the Tetraphenylborate Ion in Aqueous Solution at the Platinum

## Disk Electrode

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The tetraphenylborate ion will undergo electrochemical oxidation at the wax-impregnated graphite electrode in aqueous solution,<sup>1,2</sup> although Geske<sup>3</sup> has reported being unable to obtain voltammetric waves for this ion in aqueous solution at the rotating platinum wire electrode. He was able to obtain a single wave in acetonitrile which was ascribed to the reactions

$$B(C_6H_5)_4 \xrightarrow{-} B(C_6H_5)_2 \xrightarrow{+} (C_6H_5)_2 + 2e \qquad (1)$$

$$B(C_6H_5)_2^+ + H_2O \longrightarrow B(C_6H_5)_2OH + H^+ \qquad (2)$$

During the course of an investigation of the electrooxidation of tetraphenylborate in aqueous solution at the pyrolytic graphite electrode,<sup>4</sup> the oxidation at a platinum disk electrode was attempted. Waves were obtained at both the stationary and rotated platinum disk electrodes which were comparable to those obtained at the pyrolytic graphite electrode (Figure 1A). In addition to the wave observed by Geske, a second wave has been characterized at the pyrolytic graphite electrode<sup>4</sup>

$$\begin{array}{rcl} B(C_{6}H_{5})_{2}OH \,+\, 2H_{2}O \longrightarrow \\ & & & \\ B(OH)_{3} \,+\, (C_{6}H_{5})_{2} \,+\, 2H^{\,+} \,+\, 2e^{-} \quad (3) \end{array}$$

(1) P. J. Elving and D. L. Smith, Anal. Chem., 32, 1849 (1960).

<sup>(3)</sup> D. J. Cram, N. L. Allinger, and H. Steinberg, J. Am. Chem. Soc., 76, 6132 (1954).

<sup>(4)</sup> F. P. MacKay, Thesis, The Pennsylvania State University Graduate School, 1956.

<sup>(2)</sup> D. L. Smith, D. R. Jamieson, and P. J. Elving, *ibid.*, 32, 1253 (1960).

<sup>(3)</sup> D. H. Geske, J. Phys. Chem. 63, 1062 (1959).

<sup>(4)</sup> W. R. Turner and P. J. Elving, Anal. Chem., 37, 207 (1965).

Two waves were obtained at the stationary platinum disk electrode in acid solution (pH 2.0 and 4.6); however, half-peak potentials  $(E_{p/2})$  and peak currents  $(i_p)$  were not too reproducible due to the lack of an adequate method for renewing the surface of the platinum electrode. It has been amply demonstrated that the previous use of platinum electrodes can profoundly affect the results<sup>5</sup> obtained with them and that there is no satisfactory method of guaranteeing a reproducible behavior for this electrode. The following procedure was adopted in the present study. Prior to running the voltammogram, the electrode was maintained at 0.0 v. vs. s.c.e. until the current was negligible; i.e., less than 0.2 µa. However, larger background currents were frequently observed at higher potentials. The electrode was wiped clean between runs with a clean tissue wetted with acetone to remove any organic films which may have formed. When not in use, the electrode was stored in 0.1 Mperchloric acid. Care was taken that the electrode was not held at positive potentials. At no time was the electrode used beyond +1.0 v. and, when the background electrolyte discharge occurred at less positive potentials than +1.0 v., the circuit was broken when the current reached about 30  $\mu$ a.

A typical voltammogram at pH 4.6 had a wellformed wave with an  $E_{\rm p/2}$  of 0.34 v. and an  $i_{\rm p}$  of 9.9  $\mu$ a., and a second less well-formed wave with an  $E_{\rm p}$  of 0.83 v. When the electrode was rotated at 200 r.p.m., a single large rounded wave resulted (Figure 1B). At pH 2,  $E_{\rm p/2}$  for the first wave was 0.33 v. and  $i_{\rm p}$  was 15  $\mu$ a.

An interesting phenomenon was observed at pH 12. In acid solution, the evolution of oxygen occurs at potentials beyond 1.0 v. However, at pH 12, the evolution is shifted to about 0.6 v. Figure 1C shows three successive voltammograms recorded at pH 12. A waxy film was observed on the electrode surface which was probably a mixture of biphenyl and diphenylborinic acid. This film was soluble in acetone; cleaning the electrode with an acetone-soaked tissue removed it and restored the bright platinum surface. Although the electrode was cleaned between runs in this manner, the wave was successively shifted into the region of background discharge. This would indicate that the electrolytic discharge of the background electrolyte in basic solution alters the surface of the platinum electrode to such an extent that the half-peak potential for the oxidation of tetraphenylborate ion is shifted to a potential greater than that required for the background discharge process. A similar effect has been observed by Lingane for the oxidation of oxalate ion at the platinum electrode.<sup>6</sup> Successive chrono-



Figure 1. Voltammograms of tetraphenylborate.
A: (1) At the stationary graphite electrode (area: 0.126 cm.<sup>2</sup>); (2) at the stationary platinum disk electrode (area: 0.283 cm.<sup>2</sup>). Solution composition: 1.0 mM sodium tetraphenylborate, 0.5 M acetate buffer (pH 4.6).
B: At the rotating platinum disk electrode (rate of rotation: 200 r.p.m.). Solution composition as in A.
C: Successive voltammograms of 1 mM tetraphenylborate in 0.01 M NaOH-0.5 M NaCl solution at the stationary platinum disk electrode. Numbers refer to the order in which the voltammograms were recorded.

potentiograms showed a marked decrease in the transition time and a shift to more positive potentials. This was shown to be due to the formation of platinum oxides which apparently decrease the rate of the electron-transfer process.

It should be noted that, in the present investigation, the potential scan was stopped at +1.0 v., which is insufficient to produce background discharge or oxygen evolution in acid or neutral solution. However, in basic solutions a discharge current was observed.

If the electrode used by Geske<sup>3</sup> had been inadvertently held at a sufficiently positive potential to produce a platinum oxide film on the electrode, then

<sup>(5)</sup> See, for example, F. C. Anson and J. J. Lingane, J. Am. Chem. Soc., 79, 1015 (1957).

<sup>(6)</sup> J. J. Lingane, J. Electroanal. Chem., 1, 379 (1960).

negative results would be expected; this seems to be a likely possibility.<sup>7</sup>

## Experimental

The platinum disk electrode was prepared by sealing a disk (6-mm. diameter) to the base of a piece of 6-mm. soft glass tubing using Epon 815 epoxy resin. Electrical contact was made by placing a small quantity of mercury in the tube and inserting a piece of copper wire into the mercury.

Voltammograms were recorded using a Sargent Model XV polarograph and a jacketed H-cell maintained at  $25.0 \pm 0.1^{\circ}$ . Potentials were measured vs. the saturated sodium chloride calomel electrode whose potential is within a few millivolts of that of the saturated potassium chloride calomel electrode. The polarization rate was 1.66 mv./sec.

A Holtzer-Cabot 300 r.p.m. synchronous motor was used to rotate the electrode. The rate of rotation was varied by means of belt-driven pulleys.

Sodium tetraphenylborate (Fisher Scientific) was used without further purification. All solutions were 1.0 mM in sodium tetraphenylborate and 0.5 M in total ionic strength.

Acknowledgment. The authors wish to thank the U. S. Atomic Energy Commission for partial support of this work. W. R. T. thanks the Institute of Science and Technology of The University of Michigan for a postdoctorate fellowship.

The Thermodynamic and Physical Properties of Beryllium Compounds. VII. Enthalpy and Entropy of Sublimation of Beryllium Fluoride

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The limited amount of data concerning the sublimation of  $BeF_2(c)$  which are available is of a controversial nature. Efimenko<sup>1</sup> has recently reported a value of  $55.35 \pm 0.53$  kcal./mole for the heat of sublimation of  $BeF_2(c)$  at  $755^{\circ}$ K. based upon data obtained by means of mass spectroscopy. A value of 63.0 kcal./mole at an average temperature of 794°K. and based upon data obtained by means of transpiration was reported by Novoselova, *et al.*<sup>2</sup>

In an effort to obtain a reliable value for the heat of sublimation of  $BeF_2(c)$ , it was decided to undertake an experimental program to determine a definitive value for this thermodynamic property which could then be combined with the value for the heat of vaporization previously reported from these laboratories<sup>3</sup> to yield a value for the heat of fusion. This was accomplished by direct measurement of the vapor pressure of crystalline  $BeF_2$ .

The vapor pressure data for  $BeF_2(c)$  were obtained in the temperature range of 713-795°K. by means of the torsion effusion technique. The present experimental technique differs from the one previously described<sup>3</sup> only in the following details. A radiation shield was placed around the graphite effusion cell and reference block within the vacuum chamber. With the furnace in a fixed position, it was found that the temperature difference between the positions occupied by the effusion cell and reference block was less than 1° at all temperatures within the experimental range.

Crystalline BeF<sub>2</sub> of 99.8% purity was obtained commercially (Brush Beryllium Co.). The loaded cell was outgassed at 500° and 10<sup>-6</sup> mm. pressure for 24 hr. before actual measurements were made. It was found that samples treated in this manner gave no further shift in measured equilibrium pressures when pressures were measured on successive days.

The possible presence of an accommodation coefficient of significant magnitude was investigated by duplicating the data in two cells having different orifice areas.

#### **Results and Discussion**

The experimental data obtained in this study are tabulated in Table I and are shown plotted in Figure 1 in the manner prescribed by the van't Hoff equation. The geometrical constants of the two cells are listed in Table II.

An examination of the data plotted in Figure 1 reveals that there is, within experimental error, no evidence that the accommodation coefficient differs significantly from unity. Owing to the small temperature range within which data could be taken, it was not possible to vary the total cross-sectional area of the orifices by more than a factor of 4.

<sup>(7)</sup> D. H. Geske, private communication.

<sup>(1)</sup> J. Efimenko, NBS Report 8033, July 1963.

 <sup>(2)</sup> A. V. Novoselova, F. Sh. Muratov, L. P. Reshetnikova, and I. V. Gordeev, Vestn. Mosk. Univ. Ser. Mat. Mekhan. Astron. Fiz. i Khim., 13, No. 6, 181 (1958).

<sup>(3)</sup> M. A. Greenbaum, J. N. Foster, M. L. Arin, and M. Farber; J. Phys. Chem., 67, 36 (1963).