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Investigation of the Ultraviolet Spectra of Pentaborane(9) Derivatives

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Received February 9, 1970

The uv spectra of pentaborane(9) and its derivatives have received little attention. On the basis of a simple molecular orbital model, Eberhardt¹ suggested that for B₅H₉, the first allowed electronic transition of the molecule would be (a₁)²(e)⁴(¹A₁) → (a₁)²(e)³(b₁)¹(E) at an energy of $-\sqrt{2}\beta$. With reasonable values of β , it was suggested that a transition would appear in the region of 4400–2900 Å. Platt² reported a structureless absorption of B₅H₉ in *n*-heptane commencing at about 2100 Å and increasing in intensity with decreasing wavelength. It is the object of this research to investigate the uv spectra of pentaborane derivatives and to relate these with the results of prior molecular orbital calculations.

Experimental Section

Source of Samples.—Methyl chloride, boron trichloride, dimethyl ether, ethylene, 2,6-lutidine, and propylene were obtained from the Matheson Co., Inc., and used without further purification. Aluminum chloride, mercurous chloride, and bromine were obtained from Allied Chemical Co., aluminum was from J. T. Baker Chemical Co., and pentaborane(9) was from Callery Chemical Co., Inc. 1-Methyl-,^{3–6} 2-methyl-,^{5,7} 1-iodo-,^{4,6} 2-iodo-,⁸ 1-bromo-,^{9–11} 2-bromo-,¹² and 2-chloropentaborane¹³ were prepared using previously reported procedures. All reactions and chemicals were handled in a standard high vacuum system. A sample of 1-chloropentaborane was obtained from Gaines¹³ at the University of Wisconsin.

Spectroscopy.—The uv investigation of the 1 and 2 isomers of B₅H₉X was carried out in the vapor phase at room temperature. This involved the preparation of the sample in a standard high-vacuum apparatus and then sublimation into a gas uv cell having a path length of 10 cm. The samples were allowed to warm to room temperature. The equilibrium vapor pressure was sufficient to obtain good gas-phase spectra. The spectra were obtained using a Perkin-Elmer 202 and a Cary Model 14. The experimental results are given in Table I. The values of λ_{\max} are probably accurate to ± 1 m μ .

Results and Discussion

The results shown in Table I show that there is a definite hypsochromic (blue) shift in going from the 2 to the 1 isomer of each of the pentaborane(9) derivatives. A hypsochromic shift also exists for each of the

TABLE I
EXPERIMENTALLY DETERMINED VALUES OF λ_{\max}

Compound	λ_{\max} , m μ	Diff in λ_{\max} between isomers, m μ	Compound	λ_{\max} , m μ	Diff in λ_{\max} between isomers, m μ
1-ClB ₅ H ₉	197	10	1-IB ₅ H ₉	199	2
2-ClB ₅ H ₉	207		2-IB ₅ H ₉	201	
1-BrB ₅ H ₉	208	8	1-CH ₃ B ₅ H ₉	205	5
2-BrB ₅ H ₉	216		2-CH ₃ B ₅ H ₉	210	
			B ₅ H ₉	213	

1 derivatives relative to the 213-m μ pentaborane absorption.

In terms of the simple spectroscopic convention of Kasha¹⁴ the transition in question is probably $\pi \rightarrow \pi^*$ with some σ mixing, as the molecule is nonplanar, and the assumption of straight σ or π categorization is impossible. It is recognized¹⁵ that $\pi \rightarrow \pi^*$ transitions are usually of high intensity and subject to hypsochromic shifts upon the introduction of electron-acceptor groups. In contrast, $n \rightarrow \pi^*$ transitions undergo bathochromic (red) shifts upon introduction of electron-acceptor groups.

Table II shows the results of extended Hückel cal-

TABLE II
RESULTS OF EXTENDED HÜCKEL CALCULATIONS

Compound	Δ (HFMO-LUFMO), eV	Absorption predicted, m μ	Diff between isomers, m μ
1-ClB ₅ H ₉	4.264	251.6	63.2
2-ClB ₅ H ₉	3.596	315.4	
1-BrB ₅ H ₉	5.550	166.4	35.5
2-BrB ₅ H ₉	5.310	201.9	
1-IB ₅ H ₉	5.530	188.4	23.9
2-IB ₅ H ₉	5.269	212.3	
1-CH ₃ B ₅ H ₉	4.972	209.4	240.9
2-CH ₃ B ₅ H ₉	2.460	450.3	
B ₅ H ₉	5.116	205.9	

culations performed on the compounds in question.¹⁶ The calculations involved essentially the same procedure as outlined by Hoffmann.¹⁷ There appears to be good qualitative agreement between Δ (energy gap between the highest filled molecular orbital and the lowest unfilled molecular orbital) values and the experimentally determined transition energies, the one exception being that of CH₃B₅H₉. It is believed that this can be accounted for in the fact that extended Hückel calculations tend to overestimate the extent of steric interactions.

The agreement between theory and experiment is quite encouraging, as attempts to explain absorption spectra from calculations which do not incorporate electronic interactions generally leave much to be desired. Higher state mixing and spin-orbit coupling, which are important contributions to transition energies, have been neglected. The investigated transitions involve complex excited states which make any more involved interpretation difficult.

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The hypsochromic shifts reflect the same trends as found in B-X bond dissociation energies.¹⁶ The conclusion that may be drawn is that the extent of the shifts may be proportional to the thermodynamic stability of the compounds investigated.

Acknowledgment.—C. B. M. is indebted to NASA for a research fellowship for the period during which this work has done.

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Kinetics and Equilibria in Substitution of Nitro by Iodide and Thiourea in Nitrodiethylenetriamineplatinum(II) Nitrate

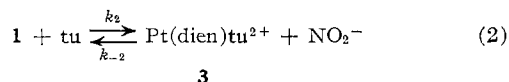
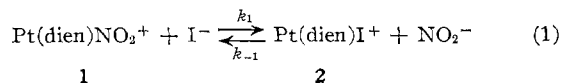
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Received August 7, 1969

In displacement at platinum(II), there is little direct evidence for the associative mechanism²⁻⁴ which seems most reasonable and is supported by considerable data.⁴ We have therefore investigated the kinetics of displacement in a complex in which the leaving group is difficult to displace, since this is a likely case in which kinetic evidence for association² might be found. The rates of reaction of nitrodiethylenetriamineplatinum(II) cation (1) with two displacing agents have been measured.⁵ Although kinetic evidence for association has not been found, the results are of concern in interpretation of published kinetic data and in the design of future kinetic experiments.

Results

We studied the reactions (eq 1 and 2)⁶ of 1 with I⁻ (eq 1) and thiourea (eq 2). With iodide present in ex-



cess, apparent first-order rate constants were obtained for reaction 1 in the usual way.⁷ Although k_1 (ap-

parent) was linear in [I⁻] at high [I⁻], k_1 (apparent) was higher than predicted by linear dependence on [I⁻] at low [I⁻] (Table I). The reactions were followed spectrophotometrically by product absorption at 310 m μ . Examination of the A_∞ values (Table I) for 0.02 and 0.04 M I⁻ indicated an equilibrium for reaction 1 and incomplete formation of 2. This explains the nonlinear dependence of k_1 (apparent) at low [I⁻].

TABLE I
RATE AND EQUILIBRIUM CONSTANTS FOR
REACTION OF 1 WITH I⁻ (EQ 1) AT 74.4^oa

[I ⁻], M	10 ⁴ k_1 (apparent), ^b sec ⁻¹	A_∞ ^c	10 ⁴ k_1 , ^d sec ⁻¹	k_{-1} , ^d M ⁻¹ sec ⁻¹
0.02	1.59	0.514	0.59	0.059
0.04	2.07	0.570	1.25	0.051
0.06	2.75	0.601	1.77	0.047
0.08	3.57	0.615	2.47	0.053
0.10	4.38	0.618	3.23	0.065

^a Aqueous solution; [1] = 0.00174 M; ionic strength maintained at 0.10 M by addition of NaNO₃. ^b k_1 (apparent) = the apparent first-order rate constant obtained by treatment of the data by the rate equation for a nonreversible, first-order reaction. ^c Optical density at 310 m μ at the end of the reaction. ^d From treatment of eq 1 as reversible.

Therefore, reaction 1 was treated as a reversible reaction⁸ with k_1 first order and k_{-1} second order. This gave the values for k_1 and k_{-1} in Table I. The resulting k_1 values are now linear in [I⁻] and give a nearly zero intercept using the rate law (3) usually found for displacements at platinum(II).⁴ Therefore we cannot evaluate k_s , but $k_{I^-} = 3.25 \times 10^{-8} \text{ M}^{-1} \text{ sec}^{-1}$.

$$k = k_s + k_{I^-} [\text{I}^-] \quad (3)$$

When thiourea is used as a displacing agent (eq 2), spectrophotometric data indicate that at equilibrium products predominate and k_{-2} can be neglected. When eq 3 is applied to the data (Table II), a straight

TABLE II
PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE THIOUREA
SUBSTITUTION OF NITRODIETHYLENETRIAMINEPLATINUM(II)
NITRATE IN AQUEOUS SOLUTIONS AT 48.6^oa

[Thiourea], M	10 ⁴ k_2 , ^b sec ⁻¹	[Thiourea], M	10 ⁴ k_2 , ^b sec ⁻¹
0.02	0.44	0.08	1.56
0.04	0.80	0.09	1.62
0.06	1.05	0.11	1.98
0.07	1.30		

^a [Complex] = 0.00174 M. ^b Determined by least-squares treatment of first-order rate equation with spectrophotometric data at 320 m μ .

line is obtained with $k_s = 1.2 \times 10^{-5} \text{ sec}^{-1}$ and $k_{\text{tu}} = 1.73 \times 10^{-8} \text{ M}^{-1} \text{ sec}^{-1}$.⁹ The value of k_s is so small that considering the standard deviations there can be considerable uncertainty in the exact value of k_s . The complete reaction in this case is consistent with (1) the greater displacing power of thiourea than of iodide ion noted previously¹⁰ and also here (at the same tempera-

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(9) This is in reasonable agreement with an extrapolated value based on an energy of activation reported for this reaction.^{5d}

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(6) Abbreviations: dien, diethylenetriamine; tu, thiourea, (H₂N)₂CS.

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