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Improved Synthesis of *nido*-Dicarbaoctaborane (10)

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We wish to report a more efficient synthesis of the interesting nido carborane $C_2B_6H_{10}$. Although the records indicate our work to have been the first actual isolation of this unstable compound, it is clear that others accomplished the same reaction independently, after earlier mass spectral evidence had suggested its existence.[1] Also, we are glad to acknowledge their essential interpretations, without which the structural character of our product would have been more difficult to recognize.

Our work began with the 25° vapor-phase reaction of $C_2B_3H_5$ with twice as much B_2H_6, during 2 days in a sealed tube at 2 atm pressure. The $C_2B_3H_5$ was 85% consumed, with 6% conversion to $C_2B_6H_{10}$, accompanied by an equimolar amount of hydrogen. The mass spectrum directly indicated the formula $C_2B_6H_{10}$, with H-abstraction showing nido character. The ^{11}B nmr spectrum was identical with that which was obtained later on the same instrument, for a sample furnished by Gotcher, *et al.*[1] Our apparently pure sample had an equilibrium vapor pressure of 24 mm at 0° and decomposed at a rate comparable to that of tetraborane(10).

A better synthesis was accomplished by means of a 750-ml concentric-cylindrical hot-cold reactor having a diameter of 90 mm and an interwall distance of 11 mm. The internal cold finger was held at $-78°$ and the outer wall was heated to 165°. A 4-hr operation with 2.15 mmol of $C_2B_3H_5$ and 4.37 mmol of B_2H_6 led to 78% consumption of the $C_2B_3H_5$ and a 0.61-mmol yield (36.5%) of $C_2B_6H_{10}$. The accompanying less volatile mixture of other carboranes (0.40 mmol) was not resolved but showed a mass spectrum having the correct isotopic patterns for $C_2B_7H_9$ and $C_2B_8H_{10}$.

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Registry No. *nido*-$C_2B_6H_{10}$, 50442-30-3; $C_2B_3H_5$, 20693-66-7; B_2H_6, 19287-45-7.

(1) A. J. Gotcher, J. F. Ditter, and R. E. Williams, *J. Amer. Chem. Soc.*, **95**, 7514 (1973).

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Unusual Activation Parameters in the Oxidation of $Fe(H_2O)_6^{2+}$ by Polypyridine Complexes of Iron(III). Evidence for Multiple Paths for Outer-Sphere Electron Transfer

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We recently reported the kinetics of oxidation of $Fe(H_2O)_6^{2+}$ by a series of polypyridine complexes of ruthenium(III)[1]

$$Fe(H_2O)_6^{2+} + Ru(III) \rightarrow Fe(H_2O)_6^{3+} + Ru(II) \qquad (1)$$

($Ru(III)$ is $Ru(terpy)_2^{3+}$, $Ru(phen)_3^{3+}$, $Ru(bipy)_3^{3+}$, or $Ru(bipy)_2(py)_2^{3+}$[2]). The activation parameters for the reactions are remarkable in that the $\Delta H^{\ddagger}$ values are small or even slightly negative ($\Delta H^{\ddagger} = -2.80 \pm 0.50$ to $\Delta H^{\ddagger} = 0.30 \pm 0.05$ kcal/mol). It was suggested by us that the activation parameters are indicative of an activation process which differs in detail from the Marcus-Hush model for outer-sphere electron transfer.[3]

The rates of oxidation of $Fe(H_2O)_6^{2+}$ by a series of iron(III)-polypyridine complexes have been studied by Ford-Smith and Sutin[4] and Sutin and Gordon,[5] *e.g.*

$$Fe(H_2O)_6^{2+} + Fe(phen)_3^{3+} \rightarrow Fe(H_2O)_6^{3+} + Fe(phen)_3^{2+} \qquad (2)$$

Because of the similarity in activation parameters for reactions 1 and 2 it was also suggested by us that the Fe(III)- and Ru(III)-polypyridine reactions occur by the same "non-Marcus" path.

We report here the kinetics of oxidation of $Fe(H_2O)_6^{2+}$ by $Fe(terpy)_2^{3+}$ and $Fe(bipy)_3^{3+}$. The activation parameters for the two reactions provide further support for a similarity in mechanism for the Fe(III)- and Ru(III)-polypyridine reactions.

Experimental Section

Materials. Water used for the kinetic experiments was doubly distilled from alkaline permanganate. Perchloric acid (Reagent grade from MCB), ferrous sulfate (Reagent ACS from Allied Chemical), sodium perchlorate (G. F. Smith), 2,2′,2″-terpyridine (G. F. Smith), 2,2′-bipyridine (Aldrich Chemical Co.), lead dioxide (Alfa Inorganics), and tetra-*n*-butylammonium chloride (Eastman) were used without further purification. Ceric ammonium nitrate (G. F. Smith) was vacuum-dried at 84° for 4 hr. Ferrous perchlorate (G. F. Smith) was recrystallized from perchloric acid. Other solvents used were reagent grade.

Preparations. The complexes $Fe(bipy)_3(ClO_4)_2$ and $Fe(terpy)_2(ClO_4)_2$ were prepared using published procedures.[4,6] Conversions to the more water-soluble chloride salts were carried out by dissolving the perchlorates in acetone and adding a saturated solution of tetra-*n*-butylammonium chloride. The chloride salts, which precipitated, were collected on a frit and washed with acetone. The iron polypyridine content of the salts was determined spectrophotometrically using known extinction coefficients.[7] The salts are extensively hydrated, as has been found, for example, for $Os(phen)_3Cl_2 \cdot 8H_2O$[8] and can best be formulated as $Fe(bipy)_3Cl_2 \cdot nH_2O$ and $Fe(terpy)_2Cl_2 \cdot nH_2O$ ($n \approx 10$).

Solutions. Solutions of the iron(III) complexes $Fe(terpy)_2^{3+}$ and $Fe(bipy)_3^{3+}$ were prepared by oxidizing stock solutions of the appropriate iron(II) complex by ceric ammonium nitrate. The iron(III) solutions were 0.45 *M* in $HClO_4$. The use of lead dioxide as the oxidant gave erratic results. Stock solutions of $Fe(H_2O)_6^{2+}$ were prepared in 0.1 *M* $HClO_4$ and the concentration of iron(II) was deter-

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(2) Abbreviations used here include terpy for 2,2′,2″-terpyridine, phen for 1,10-phenanthroline, bipy for 2,2′-bipyridine, and py for pyridine.

(3) For pertinent reviews see (a) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1966); (b) J. E. Earley, *Progr. Inorg. Chem.*, 13, 243 (1970); (c) R. G. Linck, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One*, 9, 303 (1971); (d) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1966; (e) N. Sutin, *Chem. Brit.*, **8**, 148 (1972).

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(5) N. Sutin and B. M. Gordon, *J. Amer. Chem. Soc.*, **83**, 70 (1961).

(6) W. B. Fortune and M. B. Mellor, *Ind. Eng. Chem., Anal. Ed.*, **10**, 60 (1938).

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(8) J. C. Solenberger, Ph.D. Thesis, Washington University, St. Louis, Mo., June 1969.