electron-transfer characteristics of the film.

Slow electron transfer has also been noted for other electroactive agents in Nafion. While well-developed CV's are seen for cations like $Ru(bpy)_3^{2+}$, the peak widths and anodic–cathodic peak separations are far from showing the reversible characteristics of the solution species.[16] The kinetics of the electron transfer no doubt depends upon the structural details of the anionic pockets in the film. The electroactive agents must be free to diffuse to the electrode surface or else must be packed in an arrangement that allows for electron "hopping". In addition, counterions must migrate freely through the film. Evidently, one or more of these critical pathways are inhibited in the cobalt porphyrin-loaded films.

On the hypothesis that the highly charged (4+) Co^{II}TMAP may reduce film mobility in Nafion by strong Coulombic attraction to the polymer-bound sulfonate groups, we explored the use of CoTPyP, whose charge can be adjusted by varying the solution pH. At low pH, the cationic porphyrin was satisfactorily taken up by the Nafion and electron transfer was slow. At neutral pH, electron transfer remained slow and the absorption spectrum showed evidence that the neutral porphyrin was migrating to hydrophobic regions of the Nafion, as suggested for CoTPP by Buttry and Anson.[15] Thus, the attempt to improve electroactivity by loosening the charge interactions was thwarted by partitioning with the hydrophobic domains. The uniqueness of Nafion in this regard is emphasized by the behavior of sulfonated polystyrene in the same experiment. In this case, neutralization of the charged CoTPyP in the film led to coordination of Co by the pyridine groups of the adjacent porphyrins, producing a prominent blue shift in the optical Soret band, and a negative shift of the Co(III)/Co(II) redox potential. Unfortunately, this behavior is unhelpful with regard to H_2 generation, since the same intermolecular coordination shifts the Co(II)/Co(I) potential to more negative values, thereby reducing the effectiveness of this couple in water-reduction catalysis.

Thus, although the present experiments demonstrate the feasibility of H_2-evolution catalysis by electrode-bound cobalt porphyrins, the problem of finding a suitable substrate that affords favorable electron-transfer characteristics and resistance to inactivation during the H_2-generation reaction has yet to be solved.

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Registry No. CoTPP, 14172-90-8; $CoTPP^+$, 38414-01-6; CoTAPP, 96481-61-7; $CoTAPP^-$, 96481-62-8; $CoTMAP^{4+}$, 80137-20-8; $CoTMAP^{5+}$, 79619-73-1; CoTPyP, 14244-55-4; $CoTPyP^+$, 61136-56-9; (CoTPyP)–(*p*-xylyl α,α'-dibromide) (copolymer), 96481-64-0; $(CoTPyP^+)$–(*p*-xylyl α,α'-dibromide) (copolymer), 96481-63-9; H_2, 1333-74-0; C, 7440-44-0; H_2O, 7732-18-5; TFA, 76-05-1; SnO_2, 18282-10-5; poly(sodium *p*-styrenesulfonate), 25704-18-1; Nafion, 39464-59-0.

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Reactions of Diborane with Aromatic Heterocycles. 3.[1] Diborane-Catalyzed Polymerization of Imidazole–Borane

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Imidazole–borane eliminates hydrogen in ether solution over a period of 1–2 weeks to form an air-stable polymer. The polymerization is catalyzed by excess diborane. The rate law is first order in diborane and first order in NH protons with a rate constant of $9.6 \pm 0.5\ M^{-1}\ s^{-1}$. A possible mechanism for the reaction is discussed.

Introduction

Primary and secondary amine–boranes undergo oligomerization by hydrogen elimination (eq 1). Several authors have studied

$$n(\mathrm{RR'NH})\mathrm{BH_3} \rightarrow n\mathrm{H_2} + (\mathrm{RR'NBH_2})_n \qquad \mathrm{R'} = \mathrm{R\ or\ H} \tag{1}$$

the mechanisms of such reactions of group 13[7] hydrides and generally have found the condensations to be bimolecular.[2,3]

As part of our program to examine the action of diborane on aromatic heterocycles, we had occasion to prepare imidazole–borane, observe its thermal polymerization, and study its behavior in the presence of excess diborane. In the course of this research we discovered that diborane *catalyzed* the polymerization of imidazole–borane in ether media at room temperature. The purpose of this paper is to report the results of our studies on the properties of imidazole–borane and its condensation polymer and to describe the kinetics of the diborane-catalyzed polymerization.

Experimental Section

Reagents. Diborane was prepared by the reaction of sodium borohydride with warm polyphosphoric acid. Imidazole (Aldrich) was reagent grade and was used without further purification. The solvent 1,2-dimethoxyethane (monoglyme) was purchased from Aldrich Chemical Co., purified by distillation from lithium aluminum hydride, and stored over this material is evacuated bulbs. When needed, the monoglyme was vacuum transferred directly into reaction vessels.

Spectra. Boron-11 NMR spectra were obtained with a Varian HA-100 spectrometer operating at 32.1 MHz. Chemical shifts are relative to the ethtyl ether complex of boron trifluoride, and downfield shifts are positive. Proton NMR spectra were obtained with a Varian T-60 spectrometer. Chemical shifts are in ppm downfield tetramethylsilane. Infrared spectra were obtained with a Perkin-Elmer 337 spectrophotometer.

Synthesis and Characterization of Imidazole–Borane. In a typical reaction a 0.110-g (1.61-mmol) sample of imidazole dissolved in 8 mL of monoglyme was allowed to react with 3.30 mmol of diborane for 5 min at room temperature. Removal of volatile materials left a colorless crystalline solid. Recovery of unreacted diborane showed a borane:imidazole ratio of 0.981. The product could be recrystallized under dry nitrogen by dissolving in fresh monoglyme and adding hexane; mp 93–94 °C. ^{11}B NMR (monoglyme): δ −19.0 (quartet), $J = 91$ Hz. ^1H NMR: δ 7.1 (s, 1 H), 7.2 (s, 1 H), 8.0 (s, 1 H), 11.6 (br s, 1 H). IR (film on KCl disk, in cm^{-1}): NH 3820 s; BH 2370 s, 2260 s, 2140 sh, m. Methanolysis of the adduct gave unaltered imidazole.

Polymerization of Imidazole–Borane. A monoglyme solution of imidazole–borane at room temperature evolves 1 equiv of hydrogen over a 2-week period; hydrogen evolution is faster if diborane is present. In a typical experiment a solution of 3.04 mmol of the adduct was prepared by reaction of imidazole with a slight excess of diborane of 1 min followed by rapid removal of volatiles and addition of 10 mL of fresh monoglyme. After 4 days at room temperature, 0.25 mmol of hydrogen had formed. At this point 0.43 mmol of diborane was added to the mixture, and after 20 h, 1.97 mmol of hydrogen was collected.

Characterization of the Polymer. The colorless, glassy, ether- and chloroform-soluble product gave only 4–5% of the expected hydrogen open methanolysis. Although initial reaction was rapid, further exposure and even prolonged boiling in concentrated hydrochloric acid failed to degrade the substance. Treatment with alkaline hydrogen peroxide gave unaltered imidazole after workup. IR (freshly prepared film on KCl plate, in cm^{-1}): BH 2400 vs, 2340 s, sh, 2275 m; no NH. After the film was exposed to air for 2 h, the IR showed an additional weak band at 3200 cm^{-1}. No further change in band intensity was observed over an 8-day period. ^1H NMR (monoglyme): δ 7.1 (s, 2 H), 8.0 (s, 1 H). ^{11}B

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(1) Part 2: Keller, P. C.; Marks, R. L.; Rund, J. V. *Polyhedron* **1983**, *2*, 595–602.
(2) Ryschkewitsch, G. E.; Wiggins, J. W. *Inorg. Chem.* **1970**, *9*. 314–317.
(3) Beechley, O. T., Jr. *Inorg. chem.* **1981**, *20*, 2825–2828.

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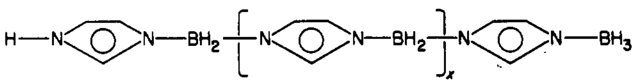
NMR (monoglyme): very broad singlet at −9 ppm.

Kinetic Studies. Kinetic runs were set up by vacuum transferring a weighed amount of monoglyme and a measured quantity of diborane into a vessel containing a magnetic stirrer and a known quantity of imidazole. The kinetics vessel was equipped with a manometer of negligible volume and has been described in a previous paper.[4] All runs were performed with the vessel immersed in a water bath maintained at 30.00 ± 0.01 °C. The progress of the reaction was followed by observing the change in hydrogen pressure. Some 39 runs were successfully completed in which initial imidazole concentrations ranged from 0.28 to 0.60 M and the borane:imidazole ratio varied from 0.47 to 3.10. The reactions were usually followed for 3 half-lives.

Results

The Polymer. Imidazole–borane is a colorless, air-stable, crystalline solid that eliminates hydrogen in ether solution over a period of weeks at 25 °C to form the condensation polymer



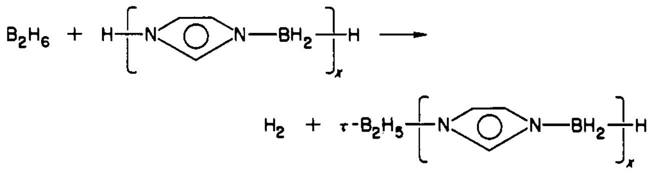
In the presence of diborane, hydrogen elimination is much faster. Since the product is the same material as that produced in the slow thermal reaction and no diborane is consumed, the process must involve catalysis by diborane. Experimentally, we have found that diborane can be separated rapidly and completely at any time from a reaction in progress.

The polymer is a colorless, glassy, air-stable solid that is largely unaffected by alcohol or water. With hot aqueous acid only 4–5% of the expected hydrolytic hydrogen is produced. Assuming this hydrogen results from hydrolysis of BH_3 end groups only, the average length of the polymer chains is 32–38 monomer units. In solution the chains are of sufficient length that the ${}^1H$ NMR signals of the 4,5-protons of the imidazole ring are equivalent. The polymer is degraded to imidazole by alkaline hydrogen peroxide. This high resistance toward hydrolysis is typical of compounds with BH_2 groups coordinated to two nitrogen donors, as in the diaminoboronium cation salts.[5] Similar *B*-alkyl-substituted imidazole polymers have been described by Trofimenko.[6]

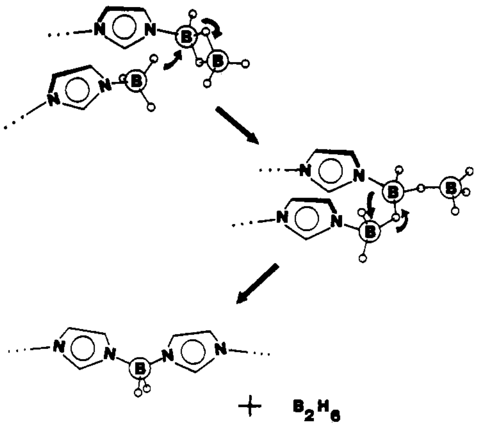
Polymerization Kinetics. The progress of the reaction was monitored by measuring the increase in hydrogen pressure in a closed system. Individual reactions were found to follow pseudo-first-order kinetics, and values of k_{obsd} were calculated by plotting ln $(1 - P_H^t/P_H^\infty)$ vs. time (P_H = hydrogen pressure). The kinetics follow a pseudo-first-order pattern because the concentration of diborane (catalyst) does not change in any one experiment. A graph of k_{obsd} *vs.* the diborane:imidazole ratio showed k_{obsd} values of essentially zero until the ratio reached 0.5. At this point the graph increased linearly with a slope of 9.6 ± 0.5 s^{-1}. This is the rate constant (with units of $M^{-1}\ s^{-1}$) for the second-order rate expression $-d[HIm]/dt = k_2[HIm][B_2H_6]$. In this equation [HIm] represents the concentration of NH protons remaining on imidazole rings in the system, the N–H of both the imidazole–borane itself and the imidazolyl end group of an oligomer in the polymerization reaction.

Discussion of the Mechanism

The formation of imidazole–borane is a fast reaction, so the rate-determining step must involve reaction of this or similar species with diborane. The following reaction fits the first-order dependence on both diborane and imidazole N–H proton concentrations. It is a simple hydrogen elimination between the hydridic reagent diborane and the imidazole proton donor. The attack by diborane on the NH proton must be relatively insensitive to chain length ($n = 1$ or $n > 1$), but this is not unreasonable since the differing structural features are several atoms removed from the point of reaction. This intermediate product is a terminally substituted diborane derivative.



The final steps illustrated in the following scheme show the growth of the polymer chain (B–N bond formation) by means of elimination of diborane. These steps must be fast relative to the reaction above to be consistent with the observed kinetics.



Registry No. Imidazole–borane, 54304-42-6; poly(imidazole–borane) (homopolymer), 96481-45-7; poly(imidazole–borane) (SRU), 96455-45-7; diborane, 19287-45-7.

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(6) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3903–3904.

(7) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise group 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)