kcal/mol) (7), it is unlikely that the rate-determining step in the reaction of DM = N₂~ involves hydrogen-atom abstraction. Furthermore, the addition of tenfold or greater excess of diphenylmethane (D₇H₇CH₂H - 81.4 kcal/mol) (8) and aniline (D₇CH₂NH₃H₂ - 80 kcal/mol) (9) had no apparent effect on the rate of reaction of DM = N₂~ reaction (entries 3 and 4, Table I).

It is plausible that the rate-determining step in the reaction of DM = N₂~ in the absence of an added proton involves protonation by either trace amounts of adventitious water (pKₐ(H₂O) = 31.4) (10) or a component of the solvent-electrolyte system. In order to test this possibility, the cyclic voltammetric and coulometric reductions of DM = N₂~ were performed in the presence of (EtO₂C)₂CH₂, an electroactive carbon acid (pKₐ(EtO₂C)₂CH₂ = 16.4) (8). As determined by rapid-scan cyclic voltammetry, the addition of (EtO₂C)₂CH₂ caused no discernible change in the lifetime of DM = N₂~ at -84°C. This means that (EtO₂C)₂CH₂ does not protonate DM = N₂~.

Furthermore, since (EtO₂C)₂CH₂ is a considerably stronger proton donor than either water or BN⁻(n-Bu)₄NCIο₄, DM = N₂~ cannot be undergoing rate-determining proton abstraction in aprotic media.

The controlled-potential electrolytic reduction of DM = N₂~ in the presence of excess (EtO₂C)₂CH₂ affords DMH⁻ in 78% yield. However, in contrast to the n value of 1 that is obtained for the reduction of DM = N₂~ in aprotic media, an n value of 2 is obtained when excess (EtO₂C)₂CH₂ is present. This change in n value is expected if DM = N₂~ undergoes rate-determining loss of N₂ to give the carbene anion radical, DM~ (Eq. [2]). This species would then either hydrogen-atom abstract from a component of the solvent-electrolyte system in aprotic media (Eq. [3]) or be protonated to give the electroactive radical DMH⁻ in the electrolyte system in aprotic media (Eq. [4]). Since DM = N₂~ is quite long-lived under these reaction conditions, it must decompose in bulk solution. The consumption of the second electron occurs, then, when DM~ is protonated by (EtO₂C)₂CH₂ to give DMH⁻ and DMH⁻ is subsequently reduced by unreacted DM = N₂~ (Eq. [5]). Because the cathodic peak potential for the reduction of DM = N₂~ (E₈/₉ = -1.8V at room temperature) is considerably more negative than the anodic peak potential for the oxidation of DMH⁻ (E₈/₉ = 0.8V), this homogeneous electron-transfer reaction is thermodynamically favorable and should proceed rapidly.

The following is a proposed scheme for the electroreduction of DM = N₂~.

\[
\begin{align*}
DM = N₂~ & \rightarrow DM = N₂^- + e^- + \frac{k_a}{k_b} \rightarrow DM = N₂~ + e^- \\
DM = N₂^- & \rightarrow \text{DM} + N₂ \\
\text{DM} + SH & \rightarrow \text{DMH}^- + S \tag{3}
\]

\[
\text{DMH}^- + HA \rightarrow \text{DMH}^- + A^- \tag{4}
\]

\[
\text{DMH}^- + DM = N₂^- \rightarrow \text{DMH}^- + DM = N₂ \tag{5}
\]

where SH = hydrogen atom donor and HA = proton donor.

In order to test for possible competition between proton and hydrogen-atom abstraction by DM~ in the coulometric reduction of DM = N₂~, it was carried out in the presence of both (EtO₂C)₂CH₂ and 1,4-cyclohexadiene. Since these species have been demonstrated to have no apparent effect on the lifetime of DM = N₂~, any change in the coulometric n value that occurs when either one or both of these species are present must be the result of their reaction with DM~. Accordingly, the coulometric n value is predicted to vary with the ratio of the carbene anion radical, DM~, in the electroreduction of DM = N₂~. Whether or not carbene anion radical reactions of synthetic importance can compete with hydrogen-atom and proton abstraction pathways will be examined in future studies in this laboratory.

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**REFERENCES**

binol are considerably slower than pyridine in Nation, and, in addition, this initial study indicated that these reactivity changes were predominantly controlled by entropic effects. The work described in this report provides additional insight into the unique reactivity effects that can be observed in polymer-modified electrode systems.

**Experimental**

**Materials.** — A commercially available (Aldrich) 5.0 weight percent (w/o) solution of 1100 equivalent weight Nation was diluted with n-propanol to prepare stock Nation solutions. The pyridine ligands used in this study were obtained from Aldrich and used without further purification. Ru(NH₃)₅Cl₂ was synthesized from Ru(NH₃)₅Cl₃ using the procedure of McFarlane et al. (10). All aqueous solutions were prepared from distilled water that was further purified by passage through a Barnstead Nanopure water purification system. Sodium trifluoromethanesulfonate (NaTFMS) electrolyte solutions (0.05M) were prepared in situ by neutralization of the acid.

**Electrode preparation.** — Polymer-modified pyrolytic graphite electrodes (14) were prepared by the evaporation out with a freshly prepared electrode surface. Nation/graphite electrodes containing Ru(NH₃)₅(H₂O)³⁺ were prepared by dipping the Nation-modified electrode into a 0.05-0.10 M solution of Ru(NH₃)₅Cl₃. Prior to a kinetic experiment, the Nation/Ru(III) electrode was cycled several times between +0.2 and −0.6 V (vs. SCE) at a 0.25M NaTFMS solution to convert the chloride complex to the aquo form. The cyclic voltammograms recorded over this range were linearly dependent on scan rate (to at least 200 mV/s); the concentration of Ru(NH₃)₅(H₂O) in the film was typically 0.01-0.02M.

**Kinetic measurements.** — All kinetic experiments were run under an argon atmosphere in a conventional two-compartment "H-cell." The working compartment, filled with the ligand solution (0.02-0.2 M, 0.05M NaTFMS), was purged with argon and equilibrated with a constant temperature bath, before the modified electrode was placed in the cell. Kinetic experiments were initiated by reducing the Ru(III) to Ru(II) at −0.6 V. The reaction progress was monitored at 10-20s intervals by recording the voltammogram that resulted from rapidly sweeping (200 mV/s) the potential of the reduced electrode to +0.2V. The potential of the electrode was then stepped back to −0.6V to "turn on" the substitution reaction again. This procedure was repeated until the substitution reaction was at least 90% complete. Pseudo-first-order rate constants were obtained from an analysis of the peak current vs. time data (16).

**Partition coefficients.** — A demountable two-piece thin layer optical cell with quartz windows was used for all partition coefficient measurements (14). Polymer films (0.5-2.0 µm) were deposited on one celling by recrystallization from 0.0125 or 0.025 g/ml Nation solutions. The quartz window/Nafion film assembly was clamped together with an unmodified one, and the cell was filled by capillary action from an excess of ligand solution placed at the bottom of the cell. Absorbance measurements were made using a Cary-17 spectrometer. The concentration of ligand within the polymer void volume was calculated by subtracting the absorbance recorded with and without Nation film in the cell. The ligand concentrations were not corrected for polymer void volume.

**Results and Discussion**

**Kinetics.** — We previously reported (12) that the substitution rates (Eq. [1]) for isonicotinamide and 4-pyridylcarbinol are considerably slower than pyridine in Nation, and that these rate differences could be attributed to less favorable activation entropies for the more polar ligands. These data indicate that a decrease in the ligand polarity should result in an enhanced substitution rate due to a more favorable activation entropy. To test this supposition, the substitution behavior of the more hydrophobic (than pyridine) ligands 3-chloropyridine and N,N-diethylisonicotinamide were investigated.

The partition coefficient corrected substitution rate for N,N-diethylisonicotinamide, the hydrophobic dialkylamine analogue of isonicotinamide, 0.20 M⁻¹s⁻¹, is five times faster than isonicotinamide, while that for 3-chloropyridine (0.10 M⁻¹s⁻¹) is about the same as found for pyridine. The activation parameters for 3-chloropyridine and N,N-diethylisonicotinamide were derived from cyclic voltammograms recorded over this range were linearly dependent on scan rate (to at least 200 mV/s); the concentration of Ru(NH₃)₅(H₂O) in the film was typically 0.01-0.02M. Although the corrected bimolecular rate constants for 3-chloropyridine and pyridine are approximately equal, the activation parameters are quite different. Notably, 3-chloropyridine has a higher activation enthalpy (17.4 vs. 15.1 kcal/mol), which is, however, compensated by the more positive entropy of activation (14 vs. 12.3 cal/K·mol).

Two reasonable explanations may be invoked to explain the observed entropic control of the substitution reactions in Nation. The ligand structure may either effect the "solvent" properties of the Nation environment (e.g., polymer swelling, ion pairing) or influence some step in the substitution mechanism. We have demonstrated that the first possibility is unlikely, because addition of N,N-dimethylbenzamide, a hydrophobic spectator species, does not increase the substitution rate for isonicotinamide, whereas decreasing isonicotinamide's polarity through N,N-dialkylation does cause a factor of five increase in the rate. It is likely, therefore, that the ligand polarity influences one of the elementary steps in the overall reaction.

The rate constants and activation parameters presented in Table I suggest the very interesting possibility that one can also enhance the substitution rates of sterically hindered, 2-substituted pyridines in Nation relative to aqueous solution (2-methylpyridine is 30 times slower than pyridine in aqueous solution). In fact, we find that the substitution rates for the hydrophobic ligands 2-chloropyridine and 2-propylpyridine are faster than that found for pyridine substitution (Table II), a clear contrast to the aqueous solution results.

**Mechanistic implications.** — The substitution rates and activation parameters measured for a number of pyridines in Nation (Table II) vary substantially, whereas in aqueous solution these kinetic parameters have been reported to be nearly constant. The accepted mechanistic interpretation of the aqueous solution results is that substitution involves an initial unimolecular dissociation of water followed by irreversible attack of the entering ligand (10). The rate-determining step that involves the ruthenium-water bond is then consistent with the relatively constant rates and activation parameters found in solution.

Our data, which show substantial variations in both the substitution rates and activation parameters, are difficult to rationalize in the framework of the above dissociative mechanism. They are consistent, however, with an associative mechanism involving pre-equilibrium outer sphere complex formation between Ru(NH₃)₅(H₂O)²⁺ and the entering ligand, followed by a rate-determining decomposition of this complex to the final products. Within this mechanistic framework, the enhanced substitution rates found for the hydrophobically substituted pyridine ligands results from the formation of more stable intermediate complexes, i.e., the preequilibrium binding constants, Kₘ, are increased. Larger values of Kₘ for the more hydrophobic ligands are also consistent with our mea-
sured activation entropies; the ligands that can shield the Ru(II) center from interactions with the ordered Nafion environment, in the intermediate complex, will cause the association constant to be favored on entropic grounds. In conclusion, the unique reactivity trends that we have observed in Nafion suggest that polymer-modified electrodes may be utilized to effect chemical transformations that are considerably different than those found in homogeneous solution.

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