kcal/mol) (7), it is unlikely that the rate-determining step in the reaction of DM = $N_2^{\cdot-}$ involves hydrogen-atom abstraction. Furthermore, the addition of tenfold or greater excesses of diphenylmethane ($D^0(Ph_2CH\text{-}H)$ = 81.4 kcal/mol) (8) and aniline ($D^0(C_6H_5NH\text{-}H)$ = 80 kcal/mol) (9) had no apparent effect on the rate of DM = $N_2^{\cdot-}$ reaction (entries 3 and 4, Table I).

It is plausible that the rate-determining step in the reaction of DM = $N_2^{\cdot-}$ in the absence of an added proton involves protonation by either trace amounts of adventitious water ($pK_a^{Me_2SO}$ (H_2O) = 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 = N_2 were effected in the presence of a large excess of $(EtO_2C)_2CH_2$, an electroinactive carbon acid ($pK_a^{Me_2SO}$ ($(EtO_2C)_2CH_2$) = 16.4) (3). As determined by rapid-scan cyclic voltammetry, the addition of $(EtO_2C)_2CH_2$ caused no discernible change in the lifetime of DM = $N_2^{\cdot-}$ at −84°C. This means that $(EtO_2C)_2CH_2$ does not protonate DM = $N_2^{\cdot-}$. Furthermore, since $(EtO_2C)_2CH_2$ is a considerably stronger proton donor than either water or BN-0.1*M* $(n\text{-}Bu)_4NClO_4$, DM = $N_2^{\cdot-}$ cannot be undergoing rate-determining proton abstraction in aprotic media.

The controlled-potential electrolytic reduction of DM = N_2 in the presence of excess $(EtO_2C)_2CH_2$ affords DMH^- in 78% yield. However, in contrast to the n value of 1 that is obtained for the reduction of DM = N_2 in aprotic media, an n value of 2 is obtained when excess $(EtO_2C)_2CH_2$ is present. This change in n value is expected if DM = $N_2^{\cdot-}$ undergoes rate-determining loss of N_2 to give the carbene anion radical, $DM^{\cdot-}$ (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 presence of $(EtO_2C)_2CH_2$ (Eq. [4]). Since DM = $N_2^{\cdot-}$ is quite long-lived under these reaction conditions, it must decompose in bulk solution. The consumption of the second electron occurs, then, when $DM^{\cdot-}$ is protonated by $(EtO_2C)_2CH_2$ to give DMH· and DMH· is subsequently reduced by unreacted DM = $N_2^{\cdot-}$ (Eq. [5]). Because the cathodic peak potential for the reduction of DM = N_2 ($E_{p,c}$ = −1.8V at room temperature) is considerably more negative than the anodic peak potential for the oxidation of DMH^- ($E_{p,a}$ = 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 = N_2

$$DM = N_2 + e^- \underset{k_{b,h}}{\overset{k_{f,h}}{\rightleftharpoons}} DM = N_2^{\cdot-} \quad [1]$$

$$DM = N_2^{\cdot-} \xrightarrow{k} DM^{\cdot-} + N_2 \quad [2]$$

$$DM^{\cdot-} + SH \rightarrow DMH^- + S\cdot \quad [3]$$

$$DM^{\cdot-} + HA \rightarrow DMH\cdot + A^- \quad [4]$$

$$DMH\cdot + DM = N_2^{\cdot-} \rightarrow DMH^- + DM = N_2 \quad [5]$$

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

In order to test for possible competition between proton and hydrogen-atom abstraction by $DM^{\cdot-}$, the coulometric reduction of DM = N_2 was carried out in the presence of both $(EtO_2C)_2CH_2$ and 1,4-cyclohexadiene. Since these species have been demonstrated to have no apparent effect on the lifetime of DM = $N_2^{\cdot-}$, 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 $DM^{\cdot-}$. Accordingly, the coulometric n value is predicted to vary from the lower limit of 1 if reaction of $DM^{\cdot-}$ occurs exclusively by hydrogen-atom abstraction from 1,4-cyclohexadiene (Eq. [1]-[3]) to an upper limit of 2 if $DM^{\cdot-}$ is captured completely by $(EtO_2C)_2CH_2$ (Eq. [1], [2], [4], and [5]). With both 1,4-cyclohexadiene and $(EtO_2C)_2CH_2$ present, an n value of 1.61 is experimentally observed which demonstrates that hydrogen-atom abstraction is competitive with proton transfer under the specified reaction conditions.

In summary, evidence consistent with the formation of the carbene anion radical, $DM^{\cdot-}$, in the electroreduction of DM = N_2 has been obtained. 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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The Joseph W. Richards Summer Fellowship Report

Probing Polymer-Induced Reactivity Effects in Modified Electrode/Catalyst Systems

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The application of polymer-modified electrodes to electrocatalysis is currently an active area of chemical research (1). A number of reported studies have focused on elucidating the mechanisms of charge propagation through these modified electrodes, and, for outersphere systems, a fairly detailed picture of the factors controlling charge transport is now in hand (2-5). There are, however, few reported studies that address the question of whether or not the polymer environment can be utilized to change the intrinsic reactivity of an electrocatalytic system (6), despite the fact that one of the initial goals in the field of chemically modified electrodes was to determine whether unique reactivity could be observed for these immobilized systems (7).

In the related field of polymer-supported catalysis, it is well documented (8) that the activity of a supported catalyst may be considerably different than that observed for the same catalyst in homogeneous solution. Changes in the experimentally measured activity may be due to factors (9) such as reactant partition coefficients, reaction site homogeneity, and reactant and product diffusion, as well as changes in the intrinsic activation parameters.

The approach we are pursuing to elucidate reactivity effects in modified electrode systems involves using a well-defined (in solution) model catalyst system to probe the polymer environment, *i.e.*, the substitution kinetics of $Ru(NH_3)_5(H_2O)^{2+}$ with substituted pyridines, Eq. [1]

$$Ru(NH_3)_5(H_2O)^{2+} + R\text{-}Py \rightarrow Ru(NH_3)_5(R\text{-}Py)^{2+} + H_2O \quad [1]$$

In our system, the ruthenium(II) complex is electrostatically bound into Nafion films that have been recast on pyrolytic graphite electrodes. The substitution reaction has been well studied in aqueous solution (10-11) providing a point of reference with which to compare the results for the Nafion-phase reaction. Notably, in an earlier communication (12), we reported that the substitution kinetics for the reactions of isonicotinamide, pyridine, and 4-pyridyl-

carbinol at $Ru(NH_3)_5(H_2O)^{2+}$, electrostatically bound into Nafion-modified electrodes, showed substantial differences in reaction rates compared with aqueous solution. 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 Nafion was diluted with n-propanol to prepare stock Nafion solutions. The pyridine ligands used in this study were obtained from Aldrich and used without further purification. $Ru(NH_3)_5Cl_3$ was synthesized from $Ru(NH_3)_6Cl_3$ using the procedure of Voght *et al.* (13) and recrystallized from 0.1*M* aqueous HCl. 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 (0.05*M*) were prepared *in situ* by neutralization of the acid.

Electrode preparation.—Polymer-modified pyrolytic graphite electrodes (14) were prepared by the evaporation of 0.005 g/ml Nafion solutions. The polymer film thickness was estimated from the reported swollen density of the 1100 equivalent weight recast Nafion (15). Most kinetic experiments were conducted using a film thickness of approximately 0.4 μm. Each kinetic experiment was carried out with a freshly prepared electrode surface. Nafion/graphite electrodes containing $Ru(NH_3)_5(H_2O)^{3+}$ were prepared by dipping the Nafion-modified electrode into a 0.05-0.10 m*M* solution of $Ru(NH_3)_5Cl_3$. Prior to a kinetic experiment, the Nafion/Ru(III) electrode was cycled several times between +0.2 and −0.6V (*vs.* SCE) in a 0.05*M* 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 $Ru(NH_3)_5(H_2O)$ in the film was typically 0.01-0.02*M*.

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*, 0.05*M* 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 −0.6V. 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 cell half by evaporation of 0.0125 or 0.025 g/ml Nafion 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 film can be calculated by taking the difference in the absorbance recorded with and without Nafion 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 Nafion, 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 dialkylated analogue of isonicotinamide, 0.20 $M^{-1}s^{-1}$, is five times faster than isonicotinamide, while that for 3-chloropyridine (0.10 $M^{-1}s^{-1}$) is about the same as found for pyridine. The activation parameters for 3-chloropyridine and N,N-diethylisonicotinamide were derived from Eyring plots (5°-45°C). These activation values, as well as the data for isonicotinamide and pyridine, are listed in Table I along with the bimolecular rate constants at 298 K. Examination of the activation terms for N,N-diethylisonicotinamide and isonicotinamide demonstrates that, despite the greater activation enthalpy found for the N-alkylated ligand (17.8 *vs.* 14.8 kcal/mol), this ligand reacts faster due to a much more favorable activation entropy, −2.1 *vs.* −15.2 cal/(K · mol). 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 [−4.7 *vs.* −12.3 cal/(K · mol)].

Two reasonable explanations may be invoked to explain the observed entropic control of the substitution reactions in Nafion. The ligand structure may either effect the "solvent" properties of the Nafion 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 Nafion 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 Nafion (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 (10-11). A rate-determining step that involves breaking 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 outersphere complex formation between $Ru(NH_3)_5(H_2O)^{2+}$ 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, K_{eq}, are increased. Larger values of K_{eq} for the more hydrophobic ligands are also consistent with our mea-

Table I. Comparison of rates and activation parameters in Nafion for ligands of varying hydrophobicity at 25°C.

Reactant	k_{bi} ($M^{-1}s^{-1}$)	ΔH^* (kcal/mol)	ΔS^* [cal/(K-mol)]
N,N-diethylisonicotinamide	0.20	17.8 ± 0.4	−2.1 ± 2.2
Isonicotinamide	0.041	14.8 ± 0.1	−15.2 ± 0.5
3-Chloropyridine	0.10	17.4 ± 0.5	−4.7 ± 2.3
Pyridine	0.11	15.1 ± 0.2	−12.3 ± 1.4

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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Table II. Summary of rates and activation parameters; 25°C

Ligand	k_{bi} ($M^{-1}s^{-1}$)	ΔH^* (kcal/mol)	ΔS^* [cal/(K-mol)]
2-Chloropyridine	0.27		
N,N-diethylisonicotinamide	0.20	17.8	−2.1
2-Propylpyridine	0.16		
2-Methylpyridine	0.11	15.9	−9.6
Pyridine	0.11	15.1	−12.3
3-Chloropyridine	0.10	17.4	−4.7
4-Pyridylcarbinol	0.070	14.2	−16.4
Isonicotinamide	0.041	14.8	−15.2

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