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Kinetic Studies of Ligand Substitution Rates for the $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ Ion in Nafion Films

Charles M. Lieber, Michael H. Schmidt, and Nathan S. Lewis*

Contribution from the Department of Chemistry, Stanford University,
Stanford, California 94305. Received January 21, 1986

Abstract: Substitution rates have been measured for reaction of a number of pyridines with the Nafion-bound $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ complex. Reaction activities have been determined by electrochemical techniques, which also allow for determination of site thermodynamics and heterogeneity during the course of the reaction. Diffusion-coefficient effects are investigated by variation in polymer film thickness, and partition coefficients have been determined under equilibrium conditions by optical absorbance techniques. The partition-coefficient corrected rate law is found to be first order in Nafion-bound $[\text{Ru}^{\text{II}}]$ and first order in ligand concentration in the polymer phase. The partition-coefficient corrected bimolecular rate constants for a variety of pyridine ligands are found to vary by a factor of 5, which contrasts with the relatively constant substitution rates observed in aqueous solution. Also, sterically hindered ligands, such as 2-propylpyridine, exhibit surprisingly high substitution rate constants on the Nafion-bound Ru^{II} ion. These rate data indicate that pronounced molecular reactivity changes can occur upon electrode modification and have implications with respect to the design of chemically modified electrodes for use in electrocatalysis.

Modified electrode systems have received considerable attention for their possible applications in electrocatalysis.¹⁻¹⁰ Most studies to date have concentrated upon the kinetics and thermodynamics of electron propagation through electrode films, and detailed information is now available for charge transport involving outer-sphere electron-transfer processes.¹⁻⁵ However, for many electrocatalytic systems, *binding* of the substrate to the immobilized redox species is required. In this work, we present a kinetic study of such binding between a solution reagent and a supported molecule in a modified electrode system.¹¹ We demonstrate that the polymer-coated electrode system possesses several unique features which allow identification of the kinetic processes in a supported catalyst system. We also present quantitative comparisons of the polymer-bound substitution reactions to the substitution kinetics which occur between these same metal/ligand pairs in aqueous solution.

An underlying assumption in most previous studies comparing homogeneous and modified electrode catalysis is that the intrinsic reactivity of an immobilized catalyst will be the same as its catalytic rate in homogeneous solution. In some cases, however, the literature suggests that polymer-modified electrodes can exhibit different reaction kinetics than are found in homogeneous solution. For example, Anson et al. have found that the oxidation of Fe^{2+} by IrCl_6^{3-} supported in protonated poly-L-lysine/poly(vinylpyridine) was apparently faster than in aqueous solution.^{3e,f} In contrast, Murray and co-workers have found that the Marcus electron-transfer theory satisfactorily predicts rate differences at poly[M(vinylbipyridine)₃]^{3+/2+} (M = Ru, Os) coated electrodes for several outer-sphere electron-transfer reactions.^{4e-g} It is expected that the solvent reorganization energies, substrate partition coefficients, and polymer-induced environmental effects will be important in determining the detailed kinetic behavior of such

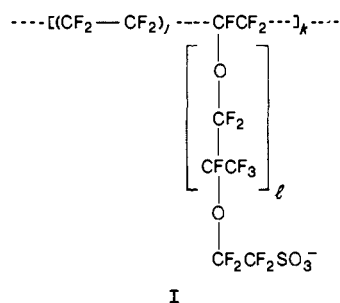
systems, but little quantitative information on these properties is available for most systems studied to date.

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* Author to whom correspondence should be addressed.

Similar problems have been recognized in the study of polymer-bound transition-metal catalysts.¹² A number of studies have reported supported catalyst *activities* that are considerably different than those observed when the same catalyst is dissolved in solution.¹³⁻¹⁵ However, a measure of the *intrinsic reactivity* of the polymer-bound species has been elusive, since no quantitative information on the effects of reactant partitioning and diffusion coefficients has been available. These experimental shortcomings were recognized in a 1976 critical review of this area,¹² yet little progress has been achieved to date on a quantitative kinetic comparison of polymer-bound catalyst vs. solution catalyst reactivity.

We have chosen a particularly simple, well-defined system for study: the substitution of the aquo ligand in the $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ ion by a variety of pyridine ligands. The kinetics of this system in aqueous solution have been studied; the effects of ligand variation and the reaction mechanism are well established.^{16,17} In our study, the Ru complex has been immobilized by electrostatic binding¹⁸ of the metal ion into recast films of a perfluorosulfonated polymer, I (Nafion).



The reaction rate with entering ligands has been conveniently monitored by electrochemical techniques on these chemically modified electrode surfaces. Variation in the film thickness has provided an assessment of the effects of reactant diffusion. Optical absorption measurements have been used to quantify equilibrium partition coefficients of the pyridine ligands. Also, activation parameters have been obtained from the measured temperature dependence of the bimolecular substitution rate of this polymer-confined metal ion complex.

A preliminary account of this work¹¹ demonstrated substantial differences between polymer-confined Ru(II) and solution Ru(II) substitution activity and demonstrated that such differences occurred through both partition coefficient effects and changes in the intrinsic reaction rate. In this report, we describe kinetic

studies which provide additional insight into the factors responsible for changes in the kinetic properties of this model immobilized-catalyst/substrate system.

Experimental Section

1. Chemicals. All aqueous solutions were prepared from distilled water that was further purified by passage through a Barnstead Nanopure (17 Mohm-cm) water purification system. Trifluoromethanesulfonic acid (HTFMS) solutions were prepared by diluting the neat acid (Aldrich), and NaTFMS solutions were prepared by neutralization with NaOH. Most of the substituted pyridines were obtained commercially (Aldrich, highest purity available) and were used without further purification. 2-Methylpyridine, distilled from KOH, was a gift from D. Ware. *N,N*-Dimethylbenzamide was donated by S. Singh. Buffer and simple electrolytes were obtained from commercial sources in the highest purity available.

2. Electrode Preparation. Polymer-modified pyrolytic graphite electrodes (edge plane exposed, Union Carbide, Inc.) were prepared by the evaporation of 0.005 g/mL of Nafion (1100 g equiv weight, Aldrich Co.) solutions in *n*-propyl alcohol. Typically two to four 3- μL aliquots of Nafion solution were applied to an electrode surface; each aliquot was spread over the electrode surface and allowed to evaporate almost completely before another portion was added. The swollen polymer film thickness, typically 0.4 μm , was estimated from the reported swollen Nafion density of 1.6 g/cm³.¹⁹

Nafion-modified electrodes impregnated with $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$ were prepared by immersion (5–10 s) into 0.05–0.10 mM solutions of $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$, which was synthesized and purified according to literature procedures.^{20,21} The ruthenium loading was varied by changing the concentration and/or time of equilibration with the Ru solutions. Each kinetic experiment was carried out with a freshly coated electrode surface.

Prior to a kinetic experiment, the Nafion/Ru(III) electrode was rinsed thoroughly with deionized water and was transferred to an electrochemical cell containing an argon-purged 0.5 M aqueous NaTFMS solution at pH 7. The electrode was cycled repetitively at a rate of 50 mV/s between +0.2 and -0.6 V (vs. SCE) to convert the chloride complex to the aquo complex and to facilitate equilibration of the Ru within the film. The peak current was observed to be linearly proportional to scan rate (≤ 200 mV/s). Typical coverages of electroactive Ru were in the range of $4\text{--}8 \times 10^{-10}$ mol/cm² (corresponding to concentrations of 0.01–0.02 M). The voltammetric peak-to-peak separation was < 10 mV, and the full-width at half-maximum was 90–100 mV, indicating that counterion motion and/or slow electrochemical rate constants will not interfere with a quantitative analysis of the Ru sites by rapid sweep voltammetric techniques. Satisfactory procedures yielded electrodes which showed stable peak currents for the Ru(III/II) couple and displayed no additional peaks due to electroactive impurities.

3. Kinetic Measurements. All kinetic experiments were run under an argon atmosphere. The electrochemical cell was a conventional two-compartment "H-cell", and the working (graphite/Nafion-Ru) and counter (Pt foil) electrodes were placed in a common thermostated compartment. The reference compartment (aqueous SCE reference electrode) was filled with 3.5 M KCl, and this side of the cell was maintained at room temperature. Prior to transferring the modified electrode to the cell, the appropriate ligand solution (typically 0.02–0.2 M ligand, L; 0.05 M NaTFMS; buffered at pH 6–8 with phosphate or at pH 2.5–5.5 with phthalate) was purged with argon, and the solution was allowed to equilibrate with a constant temperature bath (VWR Model 1140).

A kinetic experiment was initiated by reducing the Ru(III) to Ru(II) with a potential step to -0.6 V vs. SCE. At regular intervals, the reaction progress was monitored with either coulometry or linear sweep voltammetry (LSV). For LSV analysis, the potential was scanned from -0.6 to +0.2 V vs. SCE at 200 mV/s. The potential of the electrode was then stepped back to -0.6 V to reinitiate the substitution reaction. This procedure was typically repeated until the substitution reaction was $> 90\%$ complete. A minimum of five data points was collected for each kinetic experiment. The coulometric method was similar, except that the potential sweep was replaced by potential steps to -0.22 and +0.2 V vs. SCE. The total anodic charge was recorded during each of these steps, and the amount of electroactive Ru reactant and product was obtained after subtraction of the background charge for a graphite/Nafion electrode that had no Ru incorporated. The LSV peak currents were pro-

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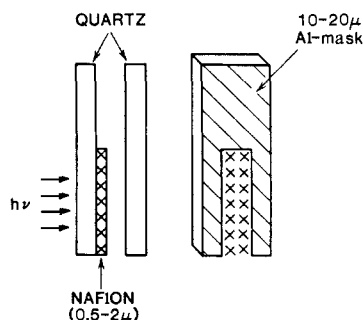
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Scheme I



portional to the integrated charge obtained by the coulometric analysis, indicating agreement between the LSV and coulometric methods for kinetic analysis.

Rate constants, k_{obsd} , were obtained by standard kinetic analysis for pseudo-first-order conditions.²² Excellent linearity in plots of $\ln [\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}]$ vs. t and in $\ln [\text{Ru}(\text{NH}_3)_5(\text{L})^{2+}]$ vs. t was obtained for greater than three $[\text{Ru}^{2+}]$ half-lives. The rate of product appearance was found to be in agreement with the rate of reactant disappearance. Data analysis was performed by linear least-squares fits of the semilog plots. Plots of k_{obsd} vs. the partition-coefficient-corrected ligand concentration yielded the bimolecular rate constant k_{bi} . For all ligands, kinetic data were obtained at solution pH values at least 2 units greater than the $\text{p}K_{\text{a}}$ of the ligand, and the k_{obsd} values were verified to be constant in response to further pH increases.

The rate for substitution of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ with 4-pyridylcarbinol in aqueous solution was measured with cyclic voltammetry. A 1 mM aqueous solution of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ (obtained from Zn amalgam reduction of $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$) was injected into the electrochemical cell along with a solution of ligand and electrolyte. The time dependence of the reactant and product peak currents was monitored with cyclic voltammetry; these currents are directly proportional to the reactant and product concentrations. In order to avoid any depletion of reactant or product near the electrode surface, the solution was stirred intermittently between voltammetric analyses.

4. Partition Coefficients. A demountable, two-piece, thin-layer optical cell with quartz windows was used for all partition-coefficient measurements. The cell was constructed by attaching a stainless steel (Shopaid, 0.0005 in. shim stock) or aluminum foil mask (10–20 μm thick) to one of the quartz windows with GC-Bond adhesive (GC Electronics) which had been diluted (70% (v/v)) with benzene. The dimensions and placement of this mask on the quartz window are shown in Scheme I. The mask served both to set the cell path length and to define the area for Nafion film deposition.

Polymer films (0.5–2.0 μm swollen thickness) were deposited on this cell window by evaporation of 0.0125 or 0.025 g/mL of Nafion solutions. Films in the 0.5–1.0- μm range were prepared with the 0.0125 g/mL solution, while those in the 1.0–2.0- μm range were deposited with the 0.025-g/mL solution. After preparation of the quartz/Nafion window, the cell was assembled and was then filled with the ligand solution by capillary action. The bottom end of the cell was kept in contact with the ligand solution (total volume 2–3 mL) during the optical absorption measurements. Absorption data were obtained with a Cary-17 spectrometer.

The uniformity of the deposited film was checked by varying the spectrophotometer slit height. If the difference between the sample absorbance at the highest and lowest beam heights (approximately 40% height variation) was greater than 5%, the results were discarded and a new film was cast.

The absorbance measurement for a cell containing a Nafion film was recorded when there was no change in absorbance with time. Equilibration was generally achieved within the time necessary to fill the cell and record the UV spectra (<60 s). Identical equilibrium absorbance values were obtained when the cell was initially filled with the desired concentration of ligand or when the desired $[\text{L}]_{\text{sol}}$ value was obtained by injecting known quantities of ligand into the filled bathing solution/cell assembly. When the partition coefficient for a thick (>1.4 μm) film was obtained in a dilute (<0.02 M) solution of a ligand with a high partition coefficient, an increase in absorbance was observed before reaching the steady state. The films were not stable indefinitely, as evidenced by a

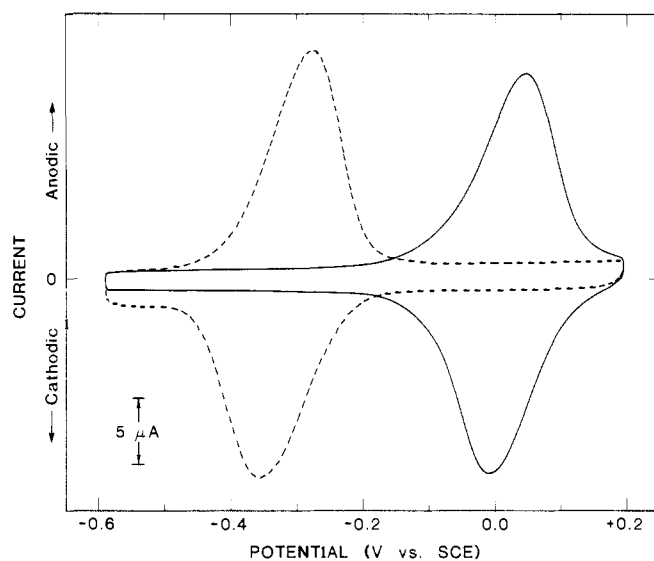


Figure 1. Cyclic voltammetry of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+/2+}$ incorporated onto a Nafion-coated pyrolytic graphite electrode. The scan rate is 200 mV/s, and the electrolyte is pH 7.0, 0.05 M NaTFMS. (---) With no ligand in solution. (—) After completion of reaction upon addition of 0.15 M isonicotinamide to the solution.

decrease in absorbance at long times (>1 h). Because a stable absorbance reading for the pyridinium ion was not obtained within 1 h, only a lower limit on this partition coefficient could be determined.

Partition coefficients were determined by difference between absorbance determinations with and without Nafion films in the cell. Partition-coefficient data were verified for consistency at several different Nafion film thicknesses. When this procedure is used, the concentration of ligand within the polymer is based on the swollen film volume and is not corrected to the polymer void volume. Partition coefficient values determined for the Ru-free Nafion films were taken to be good approximations to values at low loadings of Ru(II) (0.01–0.02 M). A valuable check on the procedure is the observation that plots of k_{obsd} vs. $[\text{L}]_{\text{sol}}$ were not linear, but plots of k_{obsd} vs. $[\text{L}]_{\text{pol}}$ (with $[\text{L}]_{\text{pol}}$ deduced from the partition coefficient data) yielded straight lines.

Results

1. Reaction Activity Data. Kinetic data for the substitution rates of the Nafion-bound $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ ion with a variety of entering pyridine ligands have been conveniently obtained by voltammetric techniques. Electrostatic binding of Ru^{3+} ions into Nafion films yields cyclic voltammetry in accord with the ideal model for a surface-confined, electroactive species (Figure 1). Under these conditions, the peak current is proportional to the coverage of electroactive Ru ions in the film. Introduction of a substituted pyridine into the electrolyte solution of Figure 1 yields irreversible changes in the voltammograms with time. Because the electrochemical potential of $\text{Ru}(\text{NH}_3)_5(\text{L})^{3+/2+}$ (where L is a substituted pyridine) is typically 250–300 mV more positive than for the $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+/2+}$ complex,²⁴ the growth of a second peak in the voltammograms allows a quantitative analysis of the progress of the substitution reaction. As expected, we observe that reaction occurs only when the electrode potential is sufficiently negative to produce the labile Ru(II) oxidation state. The results of a typical kinetic experiment are represented in Figure 2, which displays the substitution of pyridine on the Nafion-bound $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ ion.

The linearity of semilog plots of electroactive $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ vs. reaction time (i.e., the elapsed time the electrode was maintained potentiostatically at -0.6 V vs. SCE, Figure 3) indicates that the reaction is kinetically first order in $[\text{Ru}(\text{II})]$. The conservation of faradaic charge in the voltammograms indicates that over 95% of the initial electroactive reactant is still bound in the Nafion phase after the ligand-substitution reaction has proceeded for at least 3 half-lives. Similar plots to Figures 2 and 3 were obtained for all of the reactions studied in this work.

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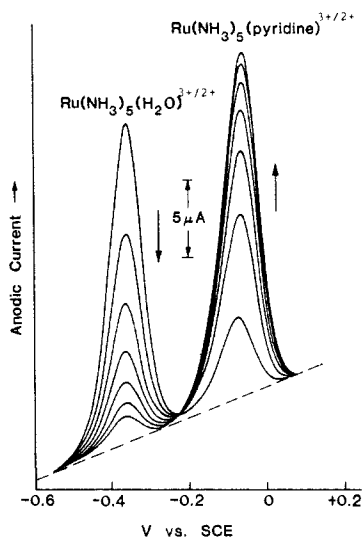


Figure 2. Linear sweep voltammetric kinetic determination of the substitution rate of Nafion-bound $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ by pyridine. The solution is water at pH 7.5, with 0.1 M NaTFMS and 0.020 M pyridine. Each scan consisted of a pulse to -0.6 V vs. SCE, followed by a 10-s interval (under potentiostatic control) at this potential, followed by a positive voltage sweep at 200 mV/s to monitor the progress of the reaction. The dashed line is the background voltammetric current determined in the same electrolyte on a Nafion-coated electrode which contained no $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+/2+}$.

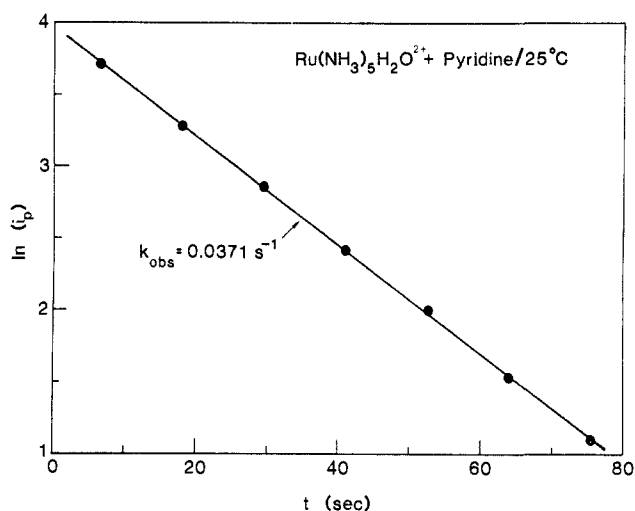


Figure 3. Plot of the natural logarithm of the voltammetric peak current for $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ oxidation vs. reaction time. The data are from the LSV experiment depicted in Figure 2. Similar data were obtained by coulometric steps (see text) from -0.6 to -0.2 V vs. SCE. Also, the rate of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ decay was in excellent agreement with the rate of $\text{Ru}(\text{NH}_3)_5(\text{pyridine})^{2+}$ appearance.

Reaction activity data for all of the ligands investigated are compiled in Table I. In this study, we define a reaction activity as the bimolecular rate constant obtained by assuming identical concentrations of ligand in the aqueous and polymer phases. The general trend for uncharged pyridine ligands is that the more hydrophobic ligands have high k_{act} values compared to those of pyridine. Also, the sterically demanding, although hydrophobic, 2-propylpyridine and 2-methylpyridine ligands have surprisingly high reaction activities in Nafion. Anionic species have low k_{act} values, while positively charged ligands exhibit similar reaction activities to those observed for the neutral ligands.

The ability to electrochemically monitor the polymer-bound Ru sites during the reaction provides a direct thermodynamic measure of site homogeneity and reactivity. Such data are not available for most polymer-supported systems, because the reaction is typically monitored only by measurement of the product appearance. We have not observed any detectable change in the

Table I. Substitution Activity of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ in Nafion

ligand (pyr = pyridyl)	soln concn, M	electrolyte pH; (pK_a , lig)	k_{act} ^a $\text{M}^{-1} \text{s}^{-1}$	$k_{\text{soln}}(\text{H}_2\text{O})$ ^b $\text{M}^{-1} \text{s}^{-1}$
2-propyl-pyr	0.020	8.0 (6.0)	3.2	
<i>N,N</i> -diethyl- isonicotinamide	0.10	7.0 (3.6)	1.7	
pyridinium	0.0040	3.0 (5.2)	1.4	0.004
3-Cl-pyr	0.10	7.0 (2.8)	1.1	0.065
2-CH ₃ -pyr	0.10	8.0 (6.0)	0.88	0.003
pyr-H	0.10	7.5 (5.2)	0.77	0.093
4-CH ₂ (OH)-pyr	0.10	7.6 (5.2)	0.48	0.082 ^c
isonicotinamide	0.10	7.0 (3.6)	0.20	0.105
4-pyr-CO ₂ ⁻	0.10	8.0 (3.6)	0.029	0.88
cianoacetate	0.10	7.0 (2.5)	0.053	1.1
azide	0.10	7.0	0.018	8.2

^a k_{act} is the bimolecular substitution rate calculated assuming equal ligand concentrations in the electrolyte and in the Nafion film. All electrolytes were aqueous 0.1–0.2 M trifluoromethane sulfonate salts (Na^+ and/or H^+). ^bData taken from ref 16 and from R. Shepherd, Ph.D. Thesis, Stanford University. ^cFrom ref 11.

Table II. Dependence of Isonicotinamide Substitution Rate on Polymer Film Thickness

swollen Nafion thickness, μm	k_{obsd} ^a s^{-1}
0.30	0.0205
0.40	0.0210
0.60	0.0218
0.80	0.0199

^aRate of Nafion-bound $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ decay; [isonicotinamide]_{soln} = 0.1 M. Solution is pH 7.0, 0.1 M NaTFMS.

Table III. Partition Coefficient Data for the Nafion/Water System

ligand	pH	partition coefficient for $[\text{L}]_{\text{sol}} =$			
		0.020 M	0.050 M	0.10 M	0.20 M
$[\text{Na}^+][4\text{-CO}_2\text{-pyr}^-]$	8.0			0.5	
isonicotinamide	7.0		5.2	5.0	3.9
4-CH ₂ (OH)-pyr	7.6		8.0	6.9	4.2
pyr-H	7.5	14.0	10.0	7.0	
<i>N,N</i> -diethyl- isonicotinamide	7.0	16.5	12.9	8.6	
2-CH ₃ -pyr	8.0	19.1	12.0	8.1	
2-Pr-pyr	8.0	19.8	14.0		
3-Cl-pyr	7.0			10.9	
pyridinium(1+)	3.0	$[\text{L}]_{\text{sol}} = 0.0040$; $P > 140$			

voltammetric full-width at half-maximum for either the reactant $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+/2+}$ or product $\text{Ru}(\text{NH}_3)_5(\text{L})^{3+/2+}$ peaks during the course of all ligand substitutions studied to date and have not observed any detectable shift in $E_{1/2}$ for either species. These observations imply that the monitored sites are kinetically equivalent and/or that rapid equilibration occurs between the various detectable Ru sites on the time scale of these reactions.

Reaction activities for several representative ligand substitutions were also investigated as a function of polymer thickness and as a function of Ru ion loading. At a given loading, the reaction activity for isonicotinamide substitution was found to be independent of polymer thickness (Table II), indicating that mass transport of material into the polymer film is not rate limiting. The reaction activity was also found to be independent of Ru(II) loading over a range of 0.01–0.02 M for the reactions with isonicotinamide and pyridine.

2. Partition Coefficient Data. In order to properly analyze the rate constants obtained in the Nafion media, partition coefficient data are required for all entering ligands. Partition coefficients were determined to be independent of polymer thickness but were a function of the solution concentration of ligand, $[\text{L}]_{\text{sol}}$ (Table III). An interesting feature of the data in Table III is that the partition coefficients for neutral pyridines are typically on the order of 10, indicating that Nafion is a better solvent for these ligands than is water. For the positively charged species, partition coefficient data vs. $[\text{L}]_{\text{sol}}$ were more difficult to obtain than for the neutral pyridines. The favorable electrostatic interactions obviously will lead to large P values for these species,

Table IV. Partition-Corrected Rate Data and Activation Parameters

ligand	k_{bi} , M ⁻¹ s ⁻¹	k_{soln} , ^a M ⁻¹ s ⁻¹	ΔH^\ddagger , ^b kcal/mol	ΔS^\ddagger , ^b eu
<i>N,N</i> -diethyl-isonicotinamide	0.20		17.8	-2.1
2-propyl-pyr	0.16			
2-CH ₃ -pyr	0.11	0.0030	15.9	-9.6
		0.0036 ^c		
pyr-H	0.11	0.093	15.1 (16.9)	-12.3 (-6.6)
3-Cl-pyr	0.10	0.065	17.4	-4.7
4-CH ₂ (OH)-pyr	0.070	0.082 ^d	14.2 (17.3) ^d	-16.4 (-5.6)
isonicotinamide	0.040	0.105	14.8	-15.2

^a Rate constants in aqueous solution taken from ref 16 except where indicated otherwise. ^b Obtained from Eyring plots of substitution data for Nafion-bound Ru(NH₃)₅(H₂O)²⁺. Errors are typically ± 0.3 kcal/mol in ΔH^\ddagger and ± 2.0 eu for ΔS^\ddagger . ^c This work; aqueous 1.8 M NaTFMS. ^d This work; aqueous 0.1 M NaTFMS.

and we have only been able to determine a lower limit of *P* for the pyridinium ion. Electrostatic repulsions are expected to produce low *P* values for negatively charged ions, and this is consistent with the measured value for the pyr-CO₂⁻ anion.

3. Intrinsic Rate Data. Plots of the partition-coefficient-corrected concentration of ligand in the Nafion film, [L]_{pol}, vs. the observed pseudo-first-order rate constant (obtained from the rate of disappearance of Ru(II), Figures 2 and 3 and Table I) indicate that the Nafion-bound reaction obeys the simple rate law represented in eq 1. This is the same rate law found for ligand

$$\text{rate} = \frac{-d[\text{Ru(II)}]}{dt} = k_{bi}[\text{Ru(II)}][\text{L}]_{pol} \quad (1)$$

substitution reactions at the Ru(NH₃)₅(H₂O)²⁺ ion in aqueous solution.^{16,17} Values of the intrinsic bimolecular rate constant (k_{bi}) calculated from the rate law in eq 1 and values for the corresponding rate constants in aqueous solution (k_{sol}) are reported in Table IV.

The general trend in intrinsic rates is that the more hydrophobic ligands exhibit larger k_{bi} values. The data in Table IV clearly indicate that the large reaction activity differences observed in Table I cannot simply be ascribed to partition coefficient effects but also reflect intrinsic reactivity differences of the various ligands in the Nafion environment.

4. Activation Parameters. Activation entropies and enthalpies were obtained by analysis of the temperature dependence of k_{bi} . Substitution rates were measured between 5 and 45 °C (at 10 °C intervals), which is similar to the temperature range used in aqueous solution kinetic studies of the Ru(II) ion. The activation parameters were determined from a weighted linear least-squares analysis of plots of $\ln(k_{bi}/T)$ vs. $1/T$. Activation parameters are provided in Table IV, along with the relevant activation parameters for the aqueous solution reactions of the Ru(II) ion. In Nafion, the activation enthalpies are relatively constant; however, the entropic terms vary considerably, with the more hydrophobic ligands exhibiting more favorable values of ΔS^\ddagger .

Discussion

1. Partition Coefficients. The elucidation of changes in the intrinsic reactivity of the polymer-confined metal ion system was possible in this study because equilibrium measurements of partition coefficients provided information about ligand concentration in the polymer phase. Such data have not been available for polymer-supported systems in the past. The data presented in Table III indicate that the partition coefficients for uncharged pyridines in Nafion vary by a factor of 5, with the more hydrophobic ligands generally having larger values of *P*. The data are consistent with trends identified by Martin and co-workers, who found that the magnitude of the Nafion partition coefficients is dominated by electrostatic interactions with the anionic sulfonate sites and by hydrophobic interactions with the polymer backbone.²⁵

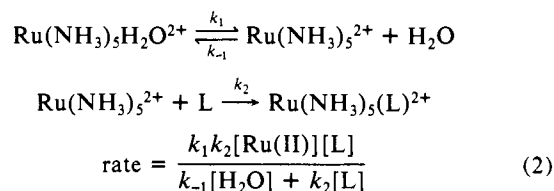
An implicit assumption in the optical determination of *P* is that the extinction coefficients for the ligands in Nafion are the same

as those in aqueous solution. Turro has presented evidence for a change in extinction coefficient for several organic fluorescent probes in sulfonated polystyrene.²⁶ However, we find no evidence for a change in extinction coefficient in our system; addition of a 4.5 mol excess of soluble Nafion to an aqueous solution of isonicotinamide resulted in no change in absorbance in the 270-nm region after correction for dilution. Furthermore, this observation is in accord with extinction-coefficient data reported by others for transition-metal complexes bound in Nafion.^{3,25}

2. Reaction Activity Data and Partition-Corrected Rate Data. The reaction activity data (Table I) for the ligands studied span a factor of greater than 10². For the charged ligands in our system, partition coefficient effects clearly produce large changes in k_{act} compared to k_{soln} . For example, relative to pyridine, the electrostatic attractions in aqueous solution between the positively charged Ru(NH₃)₅(H₂O)²⁺ ion and the isonicotinate ion produce a 10-fold increase in reaction rate, while we observe a 20-fold decrease in activity for the isonicotinate ligand in the Nafion-supported Ru(II) system. For the neutral substituted pyridine ligands, the reaction activities in Nafion are 2–300 times larger than the substitution rates in aqueous solution. Although some of this range is due to the variation in partition coefficients, a comparison of the bimolecular rate constants in Nafion (Table IV) with rate constants in aqueous solution signals substantial intrinsic rate differences between the two media. Particularly striking is the observation that the sterically demanding 2-methylpyridine and 2-propylpyridine ligands have the same or larger specific rate constants in Nafion than does pyridine, while in solution, much lower reactivity is observed for the ortho-substituted ligands.^{16,17} Furthermore, hydrophobic substitution even on relatively remote positions leads to larger specific rate constants in Nafion (e.g., k_{bi} for *N,N*-diethylisonicotinamide = 0.20 M⁻¹ s⁻¹; k_{bi} for isonicotinamide = 0.04 M⁻¹ s⁻¹). These data clearly contrast with the essentially constant specific rate values for substitution of unhindered pyridines on the Ru(II) ion in aqueous solution.^{16,17} The effect is not simply due to the higher effective ionic strength in the polymer phase, as evidenced by the low substitution rates for 2-methylpyridine in aqueous solution at high electrolyte concentrations (Table IV).

The activation parameters indicate that most of the reactivity difference is attributable to a change in the activation entropy. In fact, for the ligands with the highest k_{bi} values, the activation enthalpy values are slightly more positive than for the other ligands, but these increases in ΔH^\ddagger are more than compensated by increases in the corresponding ΔS^\ddagger values. We also note that the ΔH^\ddagger values for the entire series of ligands are comparable to the values determined in aqueous-phase measurements for pyridine ligands and for a variety of other entering ligands of different basicity, including N₂O, N₂, and organonitriles.^{16,17}

3. Mechanistic Considerations. The aqueous solution Ru(NH₃)₅(H₂O)²⁺ substitution data have been interpreted in terms of a mechanism that involves reversible dissociation of the aquo ligand, followed by a rapid capture of the five-coordinated intermediate by the entering ligand.^{16,17} A steady-state treatment of the pentacoordinate intermediate yields eq 2 as the rate law.



In aqueous media, where $k_{-1}[\text{H}_2\text{O}] \gg k_2[\text{L}]$, the rate law for the dissociative mechanism predicts similar values of the activation parameters for a series of ligands with a range of equilibrium binding constants, which is in accord with the solution kinetic data.^{16,17}

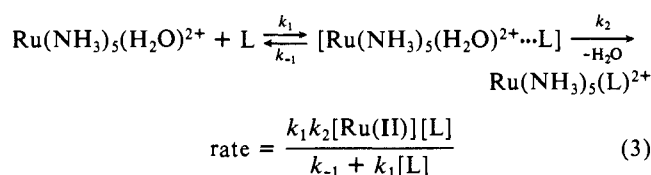
The variation in k_{bi} and ΔS^\ddagger for the pyridine ligands in Nafion, combined with the 30-fold rate increase for 2-methylpyridine in

Table V. Isonicotinamide Substitution Activity in the Presence of *N,N*-Dimethylbenzamide

k_{obsd}^a , s ⁻¹	[dimethylbenzamide] ^b , M	k_{obsd}^a , s ⁻¹	[dimethylbenzamide] ^b , M
0.020	0.00	0.012	0.020
0.016	0.0050	0.010	0.050
0.014	0.010	0.0091	0.10

^aRate of Nafion-bound Ru(NH₃)₅(H₂O)²⁺ decay; [isonicotinamide]_{soln} = 0.10 M. Solution is 0.1 M NaTFMS, pH 7.0.
^bConcentration of amide in the aqueous solution.

Nafion as compared to H₂O, suggests that the substitution reactions in Nafion proceed with a degree of associative character. Additionally, the large $k_{\text{bi}}/k_{\text{soln}}$ ratios for the hydrophobic pyridines and small $k_{\text{bi}}/k_{\text{soln}}$ values for polar pyridines are difficult to rationalize with the dissociative mechanism. A particularly attractive mechanistic interpretation of the data involves a preequilibrium binding step between the Ru(NH₃)₅(H₂O)²⁺ ion and the entering ligand, followed by rate-determining dissociation of water and rapid collapse to the Ru(NH₃)₅(L)²⁺ product species.



This rate law has been proposed to explain the observed saturation kinetics in the substitution of *N*-methylpyrazinium on the Ru(NH₃)₅(H₂O)²⁺ ion in aqueous solution by Malin and Toma.²⁷ Additionally, preequilibria of the "outer-sphere" type followed by rate-determining ligand dissociation are well preceded in substitution reactions of Co(NH₃)₅(H₂O)³⁺ and other metal ions in aqueous media (the "I_d" mechanism).^{28,29} In the present case, the preequilibrium may reflect actual outer-sphere binding of the ligand or might result from a high local concentration of the ligand and complex in a favored domain of the Nafion, and the exact nature of this process cannot be ascertained from the available kinetic data.

The rate law for this preequilibrium situation (eq 3), although similar to that of eq 2, contains important differences with regard to rate variation among entering ligands. Within this framework, changes in the specific rate are predominantly caused by a variation in the equilibrium binding constant, K_{eq} . The variations in specific substitution rates in Nafion are thus taken to indicate an increased importance of complex formation in this medium relative to that found in aqueous solution. With regard to the activation parameters, formation of a weakly bound preequilibrium complex would also lead to a relatively constant activation enthalpy (because the bond-breaking step involved in k_2 will dominate the activation enthalpy) and would produce increases in ΔS^\ddagger (in the bimolecular rate regime) as K_{eq} increases. All of these predictions are found to be in accord with the data of Tables I and IV for the Nafion-bound Ru(II) substitution reactions.

A possible cause of the apparent rate acceleration for the more hydrophobic ligands might be due to a change in the Nafion void volume or in hydrogen-bonding interactions upon introduction of hydrophobic groups into the film, both of which could effect a reduction in the $k_{-1}[\text{H}_2\text{O}]$ term in the denominator of eq 2. However, we find that introduction of *N,N*-dimethylbenzamide as a hydrophobic spectator species produces slight *decreases* in the activity of isonicotinamide substitution (Table V). Additionally, variation of the water content in response to the nature

of L is unlikely to yield the observed linear behavior of k_{obsd} on $[\text{L}]_{\text{pol}}$. We thus rule out solvent-induced swelling changes of the film or ion pairing effects induced by a more hydrophobic mixed solvent system in the membrane as the cause of the rate increase for the hydrophobic ligands. Also, internal partitioning of the pyridine ligands between hydrophobic and hydrophilic portions of the Nafion film would lead to ambiguities in the calculated values of k_{bi} . However, such partition effects alone are not sufficient to explain the trends in Table IV, because this would produce *underestimates* in the rates for the hydrophobic ligands, and would therefore increase the range of k_{bi} values in Nafion relative to the aqueous k_{soln} rate constants.

Diffusional variations of the ligands in the two media might be invoked to explain the data within the dissociative framework, as this effect could lead to changes in the relative ratio of $k_{-1}[\text{H}_2\text{O}]/k_2[\text{L}]$. However, this would not seem to account for the following observations in Table IV: the increased k_{bi} values for *N,N*-diethylisonicotinamide relative to isonicotinamide; the substantial rate differences between 2-propylpyridine and pyridine; and the 30-fold rate *increase* in k_{bi} for 2-methylpyridine relative to k_{soln} . Furthermore, encounter-limited rates are ruled out from the observations that the Ru decays are independent of film thickness and from estimates of the equilibration time of pyridines in the Nafion film as determined by the optical partition coefficient measurements. Also, using literature data for the diffusion coefficient of methylviologen^{2+/+} ($D = 2 \times 10^{-10}$ cm²/s^{19,30}) as a lower limit to D for the neutral, smaller pyridine ligands in Nafion films, the Smoluchowski equation³¹ yields encounter-limited rate values which are greater than 10^5 M⁻¹ s⁻¹.

In general, the range of substitution rates in Nafion, combined with the intrinsic rate differences from Nafion to aqueous media, indicates that substantial reactivity variation can be effected by interactions with the environment in the polymer phase. The rate effects detailed in this work indicate that product selectivity can be obtained by variation in ligand-binding properties in conjunction with partition coefficient effects. Further confirmation of the pronounced interaction between the Nafion environment and the Ru(II) ion is provided by ground-state reaction entropy measurements which are detailed in a separate paper.³² These data, in conjunction with our kinetic data, suggest that proper design of environmental effects can lead to novel reactivity patterns at polymer-coated electrodes and in other polymer-supported catalytic applications.

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Registry No. NaTFMS, 2926-30-9; 2-pr-pyr, 622-39-9; 3-Cl-pyr, 626-60-8; 2-CH₃-pyr, 109-06-8; pyr-H, 110-86-1; 4-CH₂(OH)-pyr, 586-95-8; 4-pyr-CO₂⁻, 3198-31-0; Ru(NH₃)₅Cl²⁺, 21560-19-0; Ru(NH₃)₅(H₂O)²⁺, 21393-88-4; Ru(NH₃)₅(H₂O)³⁺, 25590-52-7; Ru(NH₃)₅(pyr-H)³⁺, 33291-25-7; Ru(NH₃)₅(pyr-H)²⁺, 21360-09-8; Nafion, 39464-59-0; graphite, 7782-42-5; *N,N*-dimethylbenzamide, 611-74-5; *N,N*-diethylisonicotinamide, 530-40-5; pyridinium, 16969-45-2; isonicotinamide, 1453-82-3; cyanoacetate, 23297-32-7; azide, 14343-69-2.

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