

Table I. Solvent and Counterion Effect on Self-Exchange Electron-Transfer between **2** and **2**⁺X⁻

solvent	X	dielectric const, ϵ	temp, ^a °C	$10^{-4}k_{et}$, M ⁻¹ s ⁻¹	ΔG^\ddagger , kcal/mol
(CD ₃) ₂ SO	NO ₃	46.7	23.8	1.27	11.80
	PF ₆		22.4	1.11	11.82
	OTs		22.4	1.31	11.71
CD ₃ CN	NO ₃	37.5	23.5 ^b	1.30 ^b	11.77 ^b
(CD ₃) ₂ CO	NO ₃	20.7	24.2	2.91 ^c	11.18
CD ₂ Cl ₂	NO ₃	8.9	22.9	5.42	10.91
CDCl ₃	NO ₃	4.8	23.0 ^d	1.22 ^d	11.79 ^d
	OTs		24.8	0.55	12.33
CD ₃ OD	NO ₃	32.7	24.4	0.095	13.36

^a Temperature of NMR probe controlled to ± 0.1 °C. ^b $T = 20.8$ °C, $10^{-4}k_{et} = 1.20$ M⁻¹ s⁻¹, $\Delta G_{et}^\ddagger = 11.70$ kcal/mol; $T = 23.7$ °C, $10^{-4}k_{et} = 1.34$ M⁻¹ s⁻¹, $\Delta G_{et}^\ddagger = 11.75$ kcal/mol. ^c Methanol was used to dissolve **2**⁺NO₃⁻, the value quoted is calculated by extrapolation to 0% methanol from samples containing 0.49–5.50% methanol. ^d $T = 20.1$ °C, $10^{-4}k_{et} = 1.12$ M⁻¹ s⁻¹, $\Delta G_{et}^\ddagger = 11.72$ kcal/mol.

to **2**⁺NO₃⁻ in chloroform.^{7,8} A similarly small rate dependence upon dielectric constant was observed by Bard and co-workers⁹ for PhCN, PhCN⁻ electron exchange, although the fact that their solutions were 0.1 M in *n*-Bu₄NClO₄ and over 5 M in PhCN made the actual effective dielectric constant change somewhat uncertain. The effect of counterion is negligible in Me₂SO and rather small even in chloroform, which has a dielectric constant of only 4.8.

Activation parameters for electron transfer were measured in CD₂Cl₂. Exchange broadenings of 88.9, 33.1, 17.9, and 8.5 Hz were measured for a solution 5.04 mM in **2**⁺NO₃⁻ at 22.9, 3.5, -8.4, and -22.3 °C, respectively. The Eyring plot of the derived rate constants is a straight line ($r = 0.999$) and gives $\Delta H_{et}^\ddagger = 7.4$ kcal/mol and $\Delta S_{et}^\ddagger = -12.0$ cal/(mol deg). Two-thirds of the total barrier to electron transfer at room temperature is an enthalpy effect, which we attribute to the large geometry change between the equilibrium structures of **2**⁰ and **2**⁺ (a large internal reorganization energy in Marcus terms).

The stability of **2**⁺ in the presence of **2**, favorable NMR properties of **2**, and large enough k_{et} values to observe exchange broadening by NMR combine to make **2** a convenient compound for accurate electron-transfer rate studies. This work provides the first organic neutral, cation radical self-exchange ($\Delta G_{et}^\ddagger = 0$) rate constants that are less than 10^8 M⁻¹ s⁻¹, as well as the most detailed study of solvent and counterion effects on k_{et} .¹⁰ We hope that other Bredt's Rule protected adducts from the proton-driven Diels-Alder reaction will also give measurable k_{et} values so the effect of the size of the neutral, cation geometry change upon electron-transfer rate can be quantitatively studied.

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Registry No. **2**, 90046-42-7; **2**⁺NO₃⁻, 98920-52-6; **2**⁺PF₆⁻, 98920-53-7; **2**⁺OTs⁻, 98920-54-8.

Supplementary Material Available: Tables of concentration and observed broadenings for three sample kinetic runs (first, fourth, and eighth entry of Table I) (2 pages). Ordering information is given on any current masthead page.

(7) At 24.5 °C, $10^{-4}k_{et}$ (conc added *n*-Bu₄NClO₄, M): 1.26 (0), 1.10 (0.020), 0.93 (0.057), 0.82 (0.109), 0.79 (0.152) (corresponding to a 37% decrease in rate at 0.915 M).

(8) Nielson and Wherland (Neilson, R. M.; Wherland, S. *J. Am. Chem. Soc.* **1985**, *107*, 1505) report somewhat larger increases in rate for addition of *n*-Bu₄NBF₄ to manganese hexaisocyanate cation/dication systems.

(9) Kowert, B. A.; Marcoux, L.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 5538.

(10) Alder and co-workers have shown that organic electron transfers can be far slower than observed here for hydrazines. For example, the exothermic exchange between 1,6-diazatricyclo[4.4.4]tetradecane and its dication has a second-order rate constant of only 0.2 s⁻¹ in acetonitrile: Alder, R. W.; Sessions, R. B. *J. Am. Chem. Soc.* **1979**, *101*, 3651.

Probing Polymer Effects on Chemical Reactivity: Ligand Substitution Kinetics of Ru(NH₃)₅(H₂O)²⁺ in Nafion Films

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Several studies have addressed electron transport by outer-sphere electron-transfer processes for polymer-coated electrodes.¹⁻³ However, relatively little attention has been focused upon the effects that the polymer environment will have upon the intrinsic chemical reactivity of the reagent bound in the polymer phase. Difficulties in quantifying and separating the role of substrate and product diffusion from partition effects and from intrinsic changes in chemical reactivity have also been recognized in studies of catalysis by polymer-bound organometallic complexes.⁴ We report studies of a model catalyst-substrate system for which we have been able to address the independent kinetic effects of reaction site homogeneity, substrate diffusion into the polymer film, and changes in activation parameters.

We have chosen the ligand substitution of pyridine on the Ru(NH₃)₅(H₂O)²⁺ complex (eq 1) as our system for study.^{5,6} In Ru(NH₃)₅(H₂O)²⁺ + pyr → Ru(NH₃)₅(pyr)²⁺ + H₂O (1)

our experiments, the ruthenium complex is electrostatically bound⁷ into Nafion polyelectrolyte films, and variation of the electrode potential effects the conversion from the substitution-inert Ru(III) complex to the labile Ru(II) ion. A typical kinetic experiment is shown in Figure 1, in which the substitution of isonicotinamide for water in Ru(NH₃)₅(H₂O)²⁺ is monitored by linear sweep voltammetry.^{8,9} An analysis of these reaction kinetics yields first-order plots in [Ru(III)] which are linear for at least three half-lives. As represented in Table I, these reaction activities for substitution by the various pyridines are generally 2–8 times more rapid than the observed rates in aqueous solutions containing identical concentrations of L.

The effect of deliberate variation in the ligand activities is dramatically illustrated by the data for NC₅H₄COO⁻ substitution. In aqueous solution, the electrostatic attraction of NC₅H₄COO⁻ yields a bimolecular rate for substitution of Ru(II) that is 10-fold greater than for pyridine,¹⁰ yet the activity of NC₅H₄COO⁻ in

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(9) Polymer-coated electrodes were prepared by evaporation of dilute (0.5%) alcoholic solutions of Nafion (1100 equiv wt) onto pyrolytic graphite electrodes. The Ru site concentration was varied by equilibrating the film with solutions of differing [Ru(III)]. For all experiments, the film [Ru] was sufficiently low to ensure pseudo-first-order kinetics. Partition coefficients were determined in a separable optical cell of 10–20 μm thickness which had the Nafion film (0.5–2 μm) deposited on one of the windows before cell assembly. The entire cell volume was filled with solution, and absorption differences between cells with and without the film were performed with a Cary 17 Spectrophotometer. The Nafion film was in contact with the bathing solution during the measurement. All film concentrations are on the basis of the calculated swollen film volume and are not corrected for differences between the swollen volume and the polymer void volume. The observed activities were independent of the holding electrode potential provided that the potential was sufficient to completely reduce the Ru(III) complex.

Table I. Kinetic Data for Substitution of L at $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ in Nafion at 25 °C

	k_{activity}^a $\text{M}^{-1} \text{s}^{-1}$	partition coefficient [L] _{solution} = 0.1 M	$k_{\text{intrinsic}}^b$ $\text{M}^{-1} \text{s}^{-1}$	$k_{\text{H}_2\text{O}}^c$ $\text{M}^{-1} \text{s}^{-1}$	ΔH^\ddagger^d kcal/mol	$\Delta H^\ddagger_{(\text{H}_2\text{O})}$ kcal/mol	ΔS^\ddagger , eu ^d	$\Delta S^\ddagger_{(\text{H}_2\text{O})}$, eu
isonicotinamide	0.20	5.0	0.041	0.105 ^c	14.8		-15.2	
pyridine	0.77	7.0	0.11	0.093 ^c	15.1	16.9 ^c	-12.0	-6.6 ^c
4-pyridylcarbinol	0.48	6.9	0.070	0.082 ^e	14.2	17.3 ^e	-16.4	-5.6 ^e

^a Bimolecular rate constant calculated at 0.10 M solution concentration of L. ^b Partition corrected rate constant. ^c Values are from ref 5a. ^d Measured over 5–45 °C; eu = cal mol⁻¹ deg⁻¹. ^e This work.

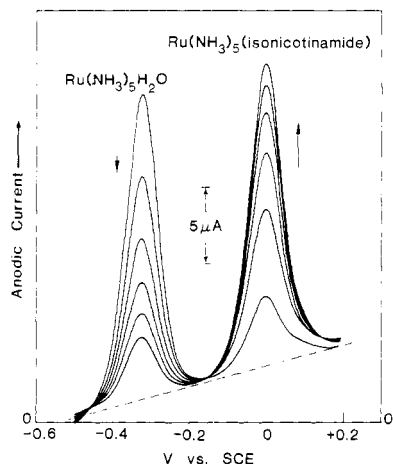


Figure 1. Substitution reaction of isonicotinamide with Nafion-bound $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$, as monitored with linear-sweep voltammetry. The scans (200 mV/s sweep rate) were made at 20-s intervals; the potential between scans was maintained at -0.6 V vs. SCE. The dashed line represents background current at the Nafion-coated pyrolytic graphite surface in aqueous solution.

our system is very low, and an upper limit on the activity is estimated as $0.029 \text{ M}^{-1} \text{s}^{-1}$. This indicates a change of greater than 10^2 in the selectivity of Ru(II) for pyridine vs. $\text{NC}_5\text{H}_4\text{COO}^-$ from aqueous media to the Nafion phase.

The full width at half-maximum of the voltammetric waves (approximately 120 mV) for both the reactant and product does not vary with the extent of reaction, implying that the electrochemically detectable Ru(II) sites react with comparable rates on our reaction time scale. Additionally, the rates are independent of polymer thickness (0.2–0.8 μm ; constant $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ film concentration), indicating that the substitution rates are not limited by substrate diffusion into the polymer phase. Substantial contribution from the poorly ligating, protonated pyridinium ions^{5a} is excluded because the partition coefficients and substitution activities were determined to be independent of pH in our measurement range (typically $\text{pH} > \text{p}K_{\text{ligand}} + 2$).

A direct comparison of intrinsic rates requires measurement of the actual concentration of ligand within the polymer film. Partition coefficients for L are found to vary with ligand polarity, and for a given L they are also dependent on its solution concentration. Utilizing the partition coefficient data, we find a first-order dependence of the substitution rate on the concentration of ligand inside the Nafion film. A summary of our kinetic data for the substitution of three pyridine ligands is given in Table I. A striking feature of these results is the contrast between the essentially constant reaction rate for substitution of the $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ ion with functionalized pyridine ligands in aqueous solution^{5,10} and the variation of reaction rate constants when the Ru(II) ion is immobilized in Nafion films.

Examination of ΔH^\ddagger and ΔS^\ddagger (Table I) for the substitution reactions of the three ligands indicates that the differences in intrinsic reactivity from the polymer and solution data are primarily due to an entropic effect. It is likely that the significant difference between the two dipolar pyridines and pyridine itself results from the greater interactions (hydrogen bonding, elec-

trostatic) possible between these two functionalized ligands and the Nafion environment. Exploitation of these interactions may thus lead to reactivity of polymer-bound reagents which is different than observed in aqueous solutions.

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Tetraaryldiphosphine Cation Radicals. Electrochemical Generation and ESR Study

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Tetraaryl-¹ and tetraalkylhydrazine² cation radicals have been extensively studied. These cation radicals prefer planar, olefin-like geometries, with coplanar p-rich lone pair orbitals forming a delocalized or a localized three-electron bond. In the case of tetraalkylhydrazine cation radicals, pyramidalization at nitrogen is relatively facile, and sterically constrained examples of these radicals can exist either in an "anti-bent" or a "syn-bent" configuration, the former being slightly more stable due to a more favorable σ, π orbital mixing.³

In agreement with the experimental results, theoretical calculations² predict the hydrazine cation radical to be planar or very nearly so, depending on the theoretical level used, with a rotation barrier of 31 kcal/mol. The N–N bond in the cation radical (1.292 Å) is calculated to be significantly shorter than that in hydrazine itself (1.413 Å). Therefore, H_2NNH_2^+ behaves as a typical two-center π bond with about half the π bond energy of ethylene. Since the nitrogen atoms are pyramidal in the preferred conformer of tetraalkylhydrazines, it is clear that in the corresponding cation radicals the energy required to make the nitrogen centers planar is largely compensated for by three-electron π stabilization.

Tricoordinate atoms in the second row of the periodic table are more highly pyramidalized than their first-row counterparts.⁴ On the other hand, the bond energy of a typical two-center P–P π bond is small, and diphosphenes can be isolated only if they are kinetically stabilized by large steric crowding.⁵

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