to $2^+\text{NO}_3^-$ in chloroform. A smaller rate dependence upon dielectric constant was observed by Bard and co-workers for PhCN, PhCN$^-$ electron exchange, although the fact that their solution was 0.1 M in n-Bu$_4$NCIO$_4$ and over 5 M in PhCN made the actual effective dielectric constant change somewhat uncertain. The effect of counterion is negligible in Me$_2$SO and rather small even in chloroform, which has a dielectric constant of only 4.8.

Activation parameters for electron transfer were measured in CD$_3$Cl$_2$. Exchange broadening of 88.9, 33.1, 17.9, and 8.5 Hz for a solution of $2^+\text{NO}_3^-$ 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 $k_e^0 = 7.4 \text{ kcal/mol}$ and $\Delta S^\circ_e = -12.0 \text{ cal/(mol deg)}$. 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 $2^+$ and $2^+$ (a large internal reorganization energy in Marcus terms).

The reactivity of $2^+$ in the presence of $2^+$, favorable NMR properties of $2^+$, and large enough $k_e$ 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 (AG$_{\text{exc}}^*$, the value quoted is calculated by extrapolation to 0% methanol from samples containing 0.49-5.50% methanol. $\Delta$ = 20.1 °C, $\Delta$ = 1.12 $M^{-1}$ s$^{-1}$, $\Delta AG^\circ_e$ = 11.72 kcal/mol.

We have chosen the ligand substitution of pyridine on the Ru(NH$_3$)$_2$(H$_2$O)$_2^+$ complex (eq 1) as our system for study. In Ru(NH$_3$)$_2$(H$_2$O)$_2^+$ + pyr $\rightarrow$ Ru(NH$_3$)$_2$(pyr)$_2^+$ + H$_2$O (1) our experiments, the ruthenium complex is electrostatically bound to 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 yields a bimolecular rate for substitution of Ru(II) that is 10-fold greater than for pyridine, yet the activity of NC$_2$H$_4$COO$^-$ in aqueous solution, the electrostatic attraction of NC$_2$H$_4$COO$^-$ yields a bimolecular rate for substitution of Ru(II) that is 10-fold greater than for pyridine.

Acknowledgment. We thank the National Science Foundation for partial financial support of this work under Grants CHE-8026111 and 8451077.

Registry No. 2, 90046-42-7; $2^+\text{NO}_3^-$, 98920-52-6; $2^+\text{PF}_6^-$, 98920-53-7; $2^+\text{OTs}^-$, 98920-54-8.

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

Table I. Solvent and Counterion Effect on Self-Exchange Electron Transfer between $2^+$ and $2^+$

<table>
<thead>
<tr>
<th>solvent</th>
<th>X</th>
<th>dielectric const, $\epsilon$</th>
<th>temp.$^\circ$C</th>
<th>$10^{-4}k_e^0$</th>
<th>M$^{-1}$ s$^{-1}$</th>
<th>$\Delta AG^\circ_e$</th>
<th>kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD$_3$SO</td>
<td>NO$_3^-$</td>
<td>46.7</td>
<td>23.8</td>
<td>1.27</td>
<td>11.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PF$_6^-$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OTs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CD$_3$CN</td>
<td>NO$_3^-$</td>
<td>37.5</td>
<td>23</td>
<td>1.30</td>
<td>11.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CD$_3$CO$_2$</td>
<td>NO$_3^-$</td>
<td>20.7</td>
<td>24.2</td>
<td>2.91</td>
<td>11.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CD$_3$ClO$_4$</td>
<td>NO$_3^-$</td>
<td>8.9</td>
<td>22.9</td>
<td>5.42</td>
<td>10.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CDC$_3$</td>
<td>NO$_3^-$</td>
<td>4.8</td>
<td>23.0$^d$</td>
<td>1.22$^d$</td>
<td>11.79$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CD$_3$OD</td>
<td>NO$_3^-$</td>
<td>32.7</td>
<td>24.4</td>
<td>0.095</td>
<td>13.36</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Temperature of NMR probe controlled at $\pm$0.1 °C. $^b$T = 20.8 °C, $10^{-4}k_e^0$ = 1.170 kcal/mol, $\Delta S^\circ_e^a$ = 11.75 kcal/mol. Methanol was used to dissolve $2^+\text{NO}_3^-$, the value quoted is calculated by extrapolation to 0% methanol from samples containing 0.49-5.50% methanol. $^c$T = 20.1 °C, $10^{-4}k_e^0$ = 1.12 $M^{-1}$ s$^{-1}$, $\Delta AG^\circ_e$ = 11.72 kcal/mol.

Probing Polymer Effects on Chemical Reactivity: Ligand Substitution Kinetics of Ru(NH$_3$)$_2$(H$_2$O)$_2^+$ in Nafion Films

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Received June 4, 1985.

Several studies have addressed electron transport by outer-sphere electron-transfer processes for polymer-coated electrodes. 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 the rate and separability of the rate 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. 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(NH$_3$)$_2$(H$_2$O)$_2^+$ complex (eq 1) as our system for study. In Ru(NH$_3$)$_2$(H$_2$O)$_2^+$ + pyr $\rightarrow$ Ru(NH$_3$)$_2$(pyr)$_2^+$ + H$_2$O (1) our experiments, the ruthenium complex is electrostatically bound to 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 yields a bimolecular rate for substitution of Ru(II) that is 10-fold greater than for pyridine, yet the activity of NC$_2$H$_4$COO$^-$ in aqueous solution, the electrostatic attraction of NC$_2$H$_4$COO$^-$ yields a bimolecular rate for substitution of Ru(II) that is 10-fold greater than for pyridine.
the difference between the two dipolar pyridines and pyridine itself is mainly due to an entropic effect. It is likely that the significant results from the greater interactions (hydrogen bonding, electrostatic) 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.

Acknowledgment. We acknowledge helpful discussions with Dr. W. Tuma and Profs. J. I. Brauman and H. Taube of Stanford University. Support for this work was provided by the Gas Research Institute. N.S.L. also received support from an IBM Young Faculty Development Award and from the Exxon Educational Foundation, Mobil Co., and Monsanto Co. under the Presidential Young Investigator Program.

Table I. Kinetic Data for Substitution of L at Ru(NH₃)₆(H₂O)⁺⁺ in Nafion at 25 °C

<table>
<thead>
<tr>
<th>Ligand</th>
<th>k_{Kligand} a [M⁻¹ s⁻¹]</th>
<th>k_{H₂O} b [M⁻¹ s⁻¹]</th>
<th>ΔHᵢ c kcal/mol</th>
<th>ΔSᵢ d eu</th>
<th>ΔSᵢ(H₂O) e eu</th>
</tr>
</thead>
<tbody>
<tr>
<td>isonicotinamide</td>
<td>0.20</td>
<td>0.041</td>
<td>14.8</td>
<td>-15.2</td>
<td></td>
</tr>
<tr>
<td>pyridine</td>
<td>0.77</td>
<td>0.093</td>
<td>15.1</td>
<td>-12.0</td>
<td>-6.6</td>
</tr>
<tr>
<td>4-pyridylcarboxil</td>
<td>0.48</td>
<td>0.082</td>
<td>14.2</td>
<td>-16.4</td>
<td>-5.6</td>
</tr>
</tbody>
</table>

* Partition constant corrected concentration of L. b Partition corrected constant. c Values are from ref 5a. d Measured over 5-45 °C; e = cal mol⁻¹ deg⁻¹. e This work.

Figure 1. Substitution reaction of isonicotinamide with Nafion-bound Ru(NH₃)₆(H₂O)⁺⁺, as monitored with linear-sweep voltammetry. The scans (200 mV/s sweep rate) were made at 20-6 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.

The system is very low, and an upper limit on the activity is estimated as 0.029 M⁻¹ s⁻¹. This indicates a change of greater than 10⁶ in the selectivity of Ru(II) for pyridine vs. NC₄H₅COO⁻ 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(I⁺) sites react with comparable rates of polymer thickness (0.2-0.8 μm; constant RU(NH₃)₆(H₂O)⁺⁺ film concentration), indicating that the substitution rates are not varying with the extent of reaction, implying that the electrochemical activity of the Ru(II) ion is immobilized in Nafion films.

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. A summary of our kinetic data (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, electrostatic).

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 in an “anti-bent” or a “syn-bent” configuration, the former being slightly more stable due to a stronger π,π orbital mixing.³

In agreement with the experimental results, theoretical calculations⁴ 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, H₂NNH²⁺ 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.

Tetraaryl-¹ and tetraalkylhydrazines² cation radicals are 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 diphosphines can be isolated only if they are kinetically stabilized by large steric crowding.⁵