previously determined for inhibitors containing the proton,[25,26] carbon-13,[27] and fluorine-19[24,28-31] probe nuclei. The −39.8 ppm shift observed for this exchange can arise from a combination of polar field[2] or polarizability[11,32] effects, conformational restrictions imposed by the active-site producing possible differences in the γ-effect,[4,11] and a chemically different intermediate(s) upon binding of (phenylselenyl)acetate to the enzyme. Clearly, the results of this investigation establish the capabilities of this multinuclear technique and provide precedent for similar selenium-77 NMR applications.

Supplementary Material Available: A Table of observed chemical shifts, line widths, and predicted chemical shifts as a function of inhibitor concentration (1 page). Ordering information is given on any current masthead page.

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Measurement of Hydrazine, Hydrazine Radical Cation Self-Exchange Electron-Transfer Rates by ¹H NMR

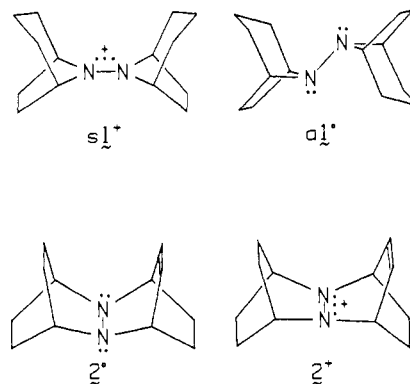Stephen F. Nelsen* and Silas C. Blackstock

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Electron loss from a hydrazine is accompanied by a large geometry change at the nitrogens, making hydrazine self-exchange electron-transfer reactions much slower than those for most other organic systems.[1] Although we have known for years that homogeneous electron transfer between hydrazines and hydrazine radical cations is unusually slow,[2] measurement of the rate constant, k_{et} in eq 1, has proven difficult. We recently exploited the

$$R_4N_2^+ + \underline{R_4N_2^0} \xrightleftharpoons[]{k_{et}} R_4N_2^0 + \underline{R_4N_2^+} \qquad (1)$$

unusual conformational properties of 8,8'-bi-8-azobicyclo[3.2.1]octane[3] to give the first determination of a k_{et} value[3b] for a hydrazine. Electron transfer between the syn cation **s1⁺** and the anti neutral isomer **a1⁰** is exothermic by about 1.6 kcal, and k_{et} was estimated at 4.5×10^3 M⁻¹ s⁻¹ (22 °C, CH₃CN with 0.15 M *n*-Bu₄NClO₄) by simulation of cyclic voltammograms for oxidation of **1**. In the present work we report the first measurement of hydrazine, hydrazine radical cation self-exchange electron-

transfer rates and provide a brief study of solvent and counterion effects.

2,7-Diazatetracyclo[6.2.2.2³,⁶.0²,⁷]tetradec-4-ene (**2**) is prepared by the recently discovered proton-driven Diels–Alder reaction of 1,3-cyclohexadiene with protonated 2,3-diazabicyclo[2.2.2]oct-2-ene[4] and proves to be especially well suited for electron-transfer rate studies. Silver(I) oxidation of hydrazine **2** affords isolably stable radical cation salts **2⁺X⁻** (X = NO₃, PF₆, OTs). The electron pairs of **2** are held at the electronically most destabilizing 0° dihedral angle, and only one **2⁰** and one **2⁺** conformation are observed by magnetic resonance, making the electron-transfer process far simpler than in the case of **1**. The **2, 2⁺** electron transfer is rapid enough to cause substantial broadening of the ¹H NMR spectrum of **2⁰** in the presence of **2⁺**; such broadening is not observed for **1, 1⁺** mixtures or their analogues.[1a] The vinyl hydrogen of **2⁰** provides a convenient signal for quantitative determination of the amount of broadening because it is well separated from the other signals and is a sharp AA'BB' multiplet, allowing accurate determination of the amount of exchange broadening, $\Delta\nu_{1/2} = (\nu_{1/2})_{2,2^+} - (\nu_{1/2})_2$, by simulation. Values of k_{et} are determined according to the slow exchange eq 2, introduced

$$k_{et} = \pi\Delta\nu_{1/2}/[2^+] \qquad (2)$$

by McConnell and by Weissman almost 30 years ago.[5] Decomposition of hydrazine radical cations by neutral hydrazines can be a problem even for Bredt's Rule protected compounds, but ¹H NMR studies prove that **2⁺** is not decomposed by **2** on the time scale of the kinetic experiments (ca. 30 min). Plots of broadening vs. [**2⁺**] fit eq 2 very precisely; all *r* values determined in this work for such a plot are above 0.999. All peaks qualitatively broaden to the same extent, and no chemical shift dependence upon radical cation concentration was observed, as required for slow exchange. Table I summarizes k_{et} in six solvents near room temperature. The rate constants are reproducible to 5% and the $\Delta G_{et}^{\ddagger}$ values to 0.3%.

The largest effect seen in our data is a decrease in k_{et} in methanol by a factor of 13 compared to non-hydroxylic solvents of similar dielectric constant, ϵ. Hydrogen bonding to the neutral form is clearly implicated for this lowering of k_{et}. The k_{et} values observed do not follow the Marcus dielectric parameter[6] ($1/n^2 - 1/\epsilon$) at all. Except for CDCl₃ and CD₃OD, there is a modest increase in k_{et} with decreasing ϵ, but the effect is an order of magnitude smaller than predicted by Marcus theory at reasonable distances for electron transfer. We note that CDCl₃ gives the smallest k_{et} for non-hydroxylic solvents despite having the lowest dielectric constant. Increased ion pairing effects relative to solvents of higher dielectric constant or the relatively weak hydrogen bonding of chloroform might be responsible. A modest decrease in k_{et} is observed as tetra-*n*-butylammonium perchlorate is added

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

solvent	X	dielectric const, ϵ	temp,[a] °C	$10^{-4}k_{et}$, $M^{-1}\,s^{-1}$	$\Delta G^{\ddagger}$, kcal/mol
(CD₃)₂SO	NO₃	46.7	23.8	1.27	11.80
	PF₆		22.4	1.11	11.82
	OTs		22.4	1.31	11.71
CD₃CN	NO₃	37.5	23.5[b]	1.30[b]	11.77[b]
(CD₃)₂CO	NO₃	20.7	24.2	2.91[c]	11.18
CD₂Cl₂	NO₃	8.9	22.9	5.42	10.91
CDCl₃	NO₃	4.8	23.0[d]	1.22[d]	11.79[d]
	OTs		24.8	0.55	12.33
CD₃OD	NO₃	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-workers[9] 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 **2⁰** 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 ($\Delta G_{et}^{\circ} = 0$) 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.

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 0915 M).

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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

$$Ru(NH_3)_5(H_2O)^{2+} + pyr \rightarrow Ru(NH_3)_5(pyr)^{2+} + H_2O \quad (1)$$

our experiments, the ruthenium complex is electrostatically bound[7] 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 kintic 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(II)] 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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