

Modulation of Outer-Sphere Electron Transfer Reactivity via Primitive Molecular Recognition Effects: $\text{Ru}(\text{NH}_3)_5(4\text{-methyl-pyridine})^{3+/2+}$ Self-Exchange Kinetics in the Presence of Macrocylic Polyether Species

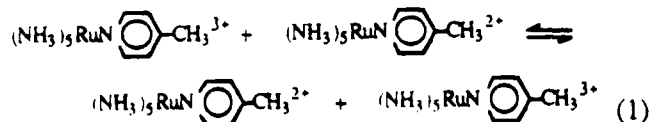
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Rates of outer-sphere electron transfer (ET) reactions, particularly self-exchanges, are typically only marginally influenced by environmental factors (e.g., changes in solvent identity, ion pair or ion triple formation, etc.).¹ We report here an example where self-exchange rates are instead enormously affected by very small changes in bulk solvent composition—specifically, millimolar additions of macrocylic polyether species (“crowns”). The rate effects, while apparently unprecedented, can nevertheless be qualitatively understood by considering corresponding effects in optical electron transfer reactions.

The self-exchange process examined was



in nitromethane-*d*₃ as solvent. Note that an outer-sphere mechanism is mandated by the coordinative saturation and resistance to substitution of both redox partners.² Kinetic parameters were determined by analysis of ¹H NMR line broadening in the slow exchange limit.³

Figure 1 shows that addition of dibenzo-30-crown-10 (DB-30-C-10) to a solution of $\text{Ru}(\text{NH}_3)_5(\text{Me-py})^{3+/2+}$ (1) causes a substantial decrease in the self-exchange rate constant, k_{ex} . Further crown addition largely restores the initial reactivity. Interestingly, the minimum in the reactivity plot occurs when the crown concentration equals the concentration of 1^{3+} . Prior work has shown that crowns can readily associate with metal am(m)ine complexes via multiple am(m)ine hydrogen–ether oxygen interactions.^{4–6} The available data additionally show that (a) crown association with 1^{3+} is strongly preferred over association with 1^{2+} and (b) association with the former will occur essentially quantitatively in this concentration range.^{6b} Thus, the minimum self-exchange rate in Figure 1 occurs when the electron acceptor and donor are $1^{3+}\cdot\text{crown}$ and 1^{2+} , i.e., when ET is also accompanied by crown transfer (Scheme 1).

The subsequent increase in k_{ex} occurs in the crown concentration range where $1^{2+}\cdot\text{crown}$ is formed. (Note that $[1^{2+}]$ exceeds $[1^{3+}]$ by ~10-fold; consequently, $1^{2+}\cdot\text{crown}$ formation occurs over a broader macrocycle concentration range than $1^{3+}\cdot\text{crown}$

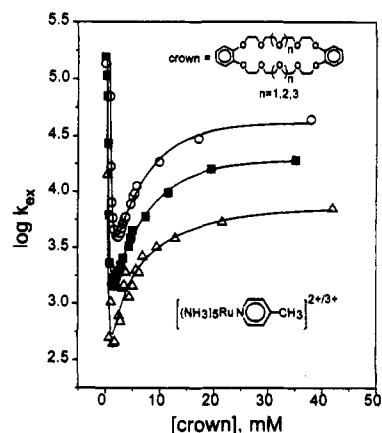
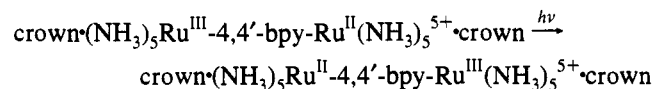
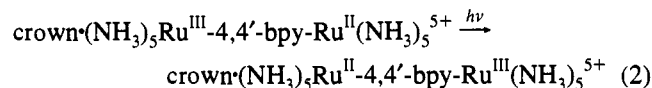
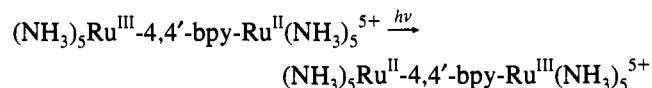


Figure 1. Log of self-exchange rate constant (eq 1) versus crown concentration. $[1^{3+}] = 0.74\text{--}1.5$ mM; $[1^{2+}] = 12.7\text{--}13.0$ mM. Key to crowns: (○) DB-30-C-10, $[1^{3+}]$; (■) DB-36-C-12; (△) DB-42-C-14.

formation.) At high crown concentrations, the reactants are $1^{3+}\cdot\text{crown}$ and $1^{2+}\cdot\text{crown}$, and ET is decoupled from crown transfer.

Additional kinetics studies with DB-36-C-12 and DB-42-C-14 show that similar patterns of reactivity exist but that the rate modulation effects are greater with the larger crowns (for example, decreases of up to 300-fold in k_{ex} in the presence of DB-42-C-14). The kinetic effects are paralleled in the redox half-reaction thermodynamics: the formal potential (E_f) for reduction of 1^{3+} is displaced by progressively larger amounts (–150, –179, and –236 mV) in the presence of progressively larger crowns.⁷ The kinetic effects are also paralleled in the recognition thermodynamics, where $1\cdot\text{crown}$ formation constants in both oxidation states increase with increasing crown size.⁸

The profound reactivity effects clearly are associated with recognition and binding of the redox active species by the crown ethers. Insight into the energetics of electron exchange in the presence of crowns can be gained by examining optical electron transfer processes, e.g.,



We have previously shown that selective binding of DB-30-C-10 to the Ru^{III} site increases the optical barrier (E_{op}) by rendering the donor and acceptor sites inequivalent by an amount (ΔE) that corresponds precisely to the incipient energy release for crown transfer (from Ru^{II} to Ru^{III}) in the redox product state.^{6a} For weakly coupled systems, ΔE can be equated with the change in E_f that accompanies crown binding. The energetic asymmetry is eliminated—and E_{op} decreases—when both redox sites are encapsulated.^{6a} Figure 2 illustrates the effect, where again larger effects are seen for larger crowns.

(7) The reported limiting shifts in E_f correspond to differences in potential for $1^{3+} + e^- \rightleftharpoons 1^{2+}$ vs $1^{3+}\cdot\text{crown} + e^- \rightleftharpoons 1^{2+}\cdot\text{crown}$. Also, $\Delta E_f = -(RT/F) \ln\{K(1^{3+}\cdot\text{crown})/K(1^{2+}\cdot\text{crown})\}$.

(8) $K(1^{2+}\cdot\text{DB-30-C-10}) = 640 \text{ M}^{-1}$; $K(1^{3+}\cdot\text{DB-30-C-10}) = 2 \times 10^5 \text{ M}^{-1}$; $K(1^{2+}\cdot\text{DB-36-C-12}) = 740 \text{ M}^{-1}$; $K(1^{3+}\cdot\text{DB-36-C-12}) = 8 \times 10^5 \text{ M}^{-1}$; $K(1^{2+}\cdot\text{DB-42-C-14}) = 1200 \text{ M}^{-1}$; $K(1^{3+}\cdot\text{DB-42-C-14}) = 1.2 \times 10^6 \text{ M}^{-1}$.

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(1) Representative work: Wherland, S. *Coord. Chem. Rev.* **1993**, *123*, 169 and references therein.

(2) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.

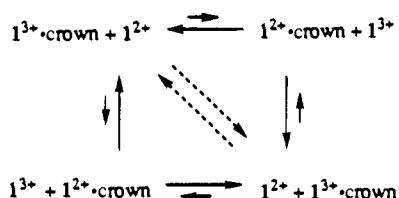
(3) See, for example: Nielson, R. M.; Wherland, S. *Inorg. Chem.* **1984**, *23*, 1338.

(4) For a review, see: Colquhoun, H. M.; Stoddart, J. F.; Williams, D. *J. Angew. Chem.* **1986**, *25*, 487.

(5) Representative reports: (a) Alston, D. R.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J.; Zarzycki, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 693. (b) Ando, I.; Ishimura, D.; Ujimoto, K.; Kurihara, H. *Inorg. Chem.* **1994**, *33*, 5010.

(6) (a) Todd, M. D.; Yoon, D. I.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 4685. (b) Todd, M. D.; Dong, Y.; Horney, J.; Yoon, D. I.; Hupp, J. T. *Inorg. Chem.* **1993**, *32*, 2001.

Scheme 1



If eq 2 is accepted as a model for reaction 1, then Marcus-Hush theory⁹ predicts that the barrier to thermal ET will increase by approximately $\Delta E/2$ (sequential electron and crown transfer; "square" pathway in Scheme 1) or $\Delta E/4$ (synchronous electron and crown transfer; "diagonal" pathway in Scheme 1) when only one of the two redox partners is encapsulated.^{11,12} Regardless of whether optical or electrochemical estimates for ΔE are used, the observed rate effects are much too large to accommodate a diagonal reaction pathway. They are also, however, somewhat too large for the square pathway, at least if rates are compared to those found in the absence of crown. Equally appropriate, however, would be comparisons to rates obtained in the presence of excess crown (i.e., both redox partners encapsulated). Better yet would be *averaged* comparisons. The average ΔE values required to describe the rate attenuation effects in Figure 2 via the square pathway are 160 (DB-30-C-10), 190 (DB-36-C-12), and 220 mV (DB-42-C-14). These are remarkably close to independent electrochemical (see above) and optical (Figure 2) estimates; we conclude that a square pathway (ET, then host transfer) is followed here.¹³

When donor and acceptor sites are both encapsulated, the supramolecular symmetry is restored, and ΔE is necessarily zero. Figure 2 suggests that reorganization energies (λ), and therefore optical and thermal barriers to electron transfer ($E_{\text{op}} \approx \lambda$ and $\Delta G^* \approx \lambda/4$, respectively), should be smaller for the fully crown encapsulated species than for the free reactant pair. Furthermore, barrier diminution should be greater with larger crowns. Rates alone (Figure 1) do not reflect this. Activation parameters, on the other hand, do. While considerable caution is required when interpreting parameters obtained in the absence of added inert electrolyte (a necessity, given reactant solubilities), the ΔH^* values in Table 1 tell a story that is qualitatively consistent with the foregoing description. Thus ΔH^* increases (as expected) when k_{ex} decreases (i.e., when $1^{3+} \cdot \text{crown}$ assemblies are formed and Scheme 1 can be invoked). Conversely, ΔH^* decreases (as expected from Figure 2) when $1^{2+} \cdot \text{crown}$ adduct formation (in addition to $1^{3+} \cdot \text{crown}$ formation) occurs. Furthermore, the barrier decrease is more pronounced with larger crowns. Nevertheless, quantitative agreement between measured thermal

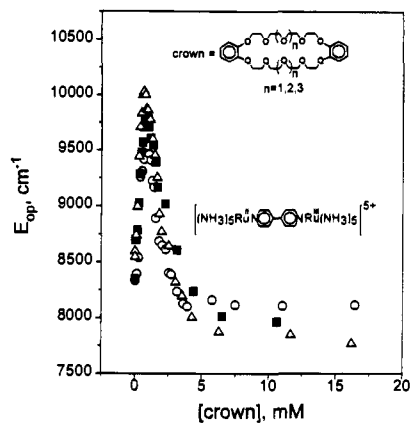


Figure 2. Optical barrier to electron transfer (eq 2) versus crown concentration, in nitromethane as solvent. Mixed valence ion concentration, 0.95–1.0 mM. Key as in Figure 1.

Table 1. Activation Parameters for Electron Exchange ($1^{3+}/2^{+}$)

crown	[crown], mM	[1^{3+}], mM	[1^{2+}], mM	ΔH^* , ^a kcal mol ⁻¹	A, s ⁻¹	temp range, °C
no crown	0	1.1	12.6	5.4 ± 0.5	1.4×10^9	-19–46
DB-30-C-10	2.3	1.2	11.9	7.9 ± 1.5	2.7×10^9	8–65
	42.1	1.3	13.0	2.3 ± 0.5	2.6×10^6	8–50
DB-36-C-12	2.1	1.6	11.9	8.9 ± 1	1.0×10^{10}	17–62
	36.0	0.80	14.7	1.5 ± 0.5	2.4×10^5	17–62
DB-42-C-14	1.7	0.70	13.1	12.4 ± 2	7×10^{11}	17–64
	42.0	0.63	11.1	1.5 ± 1	6×10^4	18–62

^a Calculated from variable temperature rate data by assuming $k_{\text{ex}} = A \exp(-\Delta H^*/RT)$. (See: Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.)

barrier modulation effects (Table 1) and optical predictions is lacking, particularly when excess crown is present. The disparities could reflect genuine differences in the way reorganization energies for intramolecular vs intramolecular ET are influenced by crown association; alternatively, the disparities might be related to uncorrected work terms and ion pairing artifacts presumably present in the bimolecular case.¹⁴ Also worth noting are the substantial decreases in preexponential factor (A) that accompany complete reactant encapsulation. These might be indicative of decreases in reaction adiabaticity in the encapsulated state.

Although the rate modulation effects described here are limited to crowns as hosts, they should exist whenever (a) guest recognition or encapsulation displays a strong oxidation state dependence and (b) the host concentration is appropriately limited. Similar effects can also be expected in mixed solvents, when preferential solvation is strongly dependent on reactant oxidation state.¹⁵ Indeed, such effects have recently been observed by Curtis et al. for eq 1 in DMSO/CH₃CN mixtures.¹⁶

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Supporting Information Available: Further description of the line broadening experiment and 2 figures (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(10) The energy relationships are approximate because small differences in reorganization energy (see Figure 2) for electron exchange between the free reactants vs the fully encapsulated reactants are neglected. These differences (as well as differences in prefactors) are incorporated in the subsequent "averaged" energy/rate comparisons (see text).

(11) In equating the change in thermal barrier height with $\Delta E/4$, we implicitly assume parabolic energy surfaces.

(12) The diagonal pathway incorporates crown transfer as an additional reorganizational energy (λ) component. The square pathway treats the incipient transfer as a source of redox asymmetry (i.e., an unfavorable thermodynamic driving force component, ΔG) for the isolated ET step.

(13) The diagonal pathway should, of course, offer a lower activation barrier than the square pathway. That is apparently *not* followed is indicative of additional (presumably dynamical) impediments. Unpublished electrochemical data for **1** with substoichiometric amounts of crown demonstrate that crown release from 1^{3+} is slow, even on a cyclic voltammetry (10 mV/s) time scale. Partial dissociation presumably is the dynamical impediment to the diagonal pathway. We note that related issues have been discussed in the context of gated ET reactions (Brunschwig, B. S.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 7454). The voltammetry experiments also permit us to exclude, as dynamically and kinetically uncompetitive, an alternate square pathway (Scheme 1) in which guest(1^{3+}):host(crown) dissociation precedes ET.

(14) Temperature effects upon $K(1^{3+} \cdot \text{crown})$ and $K(1^{2+} \cdot \text{crown})$,⁸ or more importantly, their ratio,⁷ could also influence activation parameters.

(15) Hupp, J. T.; Weydert, J. *Inorg. Chem.* **1987**, *26*, 2657.

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