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Measurement of Both the Equilibrium Constant and Rate Constant for Electronic Energy Transfer by Control of the Limiting Kinetic Regimes

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Electronic energy transfer can fall into two limiting cases. When the rate of the energy transfer back reaction is much faster than relaxation of the acceptor excited state, equilibrium between the donor and acceptor excited states is achieved and only the equilibrium constant for the energy transfer can be measured. When the rate of the back reaction is much slower than relaxation of the acceptor, the energy transfer is irreversible and only the forward rate constant can be measured. Herein, we demonstrate that with *trans*-$[Cr(d_4\text{-cyclam})(CN)_2]^+$ as the donor and either *trans*-$[Cr([15]\text{ane-ane-}N_4)(CN)_2]^+$ or *trans*-$[Cr(\text{cyclam})(CN)_2]^+$ as the acceptor, both limits can be obtained by control of the donor concentration. The equilibrium constant and rate constant for the case in which *trans*-$[Cr([15]\text{ane-ane-}N_4)(CN)_2]^+$ is the acceptor are 0.66 and 1.7×10^7 M^{-1} s^{-1}, respectively. The equilibrium constant is in good agreement with the value of 0.60 determined using the excited state energy gap between the donor and acceptor species. For the thermoneutral case in which *trans*-$[Cr(\text{cyclam})(CN)_2]^+$ is the acceptor, an experimental equilibrium constant of 0.99 was reported previously, and the rate constant has now been measured as 4.0×10^7 M^{-1} s^{-1}.

Introduction

Electronic energy transfer between transition metal complexes often involves spin and symmetry forbidden transitions and thus proceeds through the exchange mechanism, prompting the application of Marcus–Hush theory in order to understand the reaction dynamics.[1,2] A number of studies of energy transfer have been analyzed to determine the relative importance of thermodynamics, electronic factors, and nuclear factors in these bimolecular reactions.[3–11] The majority of these studies have involved Cr(III) donor and/or acceptor molecules due to the large body of existing knowledge on Cr(III) photophysics and photochemistry[12,13] Our interest in this area is to discover systems for which energy transfer self-exchange can be studied so that cross-exchange and self-exchange dynamics can be compared in a manner similar to what has been done for electron transfer.[14] Several investigations of reactions approximating energy transfer self-exchange[14–16] utilized a method first described by Maharaj and Winnik[15] involving flash photolysis of mixtures of cleverly designed chromophores. The chomophores are designed such that slight structural modifications substantially affect the excited state lifetime of the molecule but leave the electronic energy levels relatively unchanged. In these cases, the longer-lived analogue is used as the donor with the shorter lived species as the acceptor. Figure 1 depicts the energy transfer and relaxation processes when the donor and acceptor have overlapping absorptions, and thus, the donor cannot be selectively excited. Here, $k_D = 1/\tau_D$ and $k_A = 1/\tau_A$ are the intrinsic rate constants for the decay of D* and A*, respectively, exclusive of energy transfer, and k_{EnT} and k_{-EnT} are the forward and reverse second order rate constants for energy transfer.

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[1] (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966–978. (b) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557. (c) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

[2] (a) Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152–2163. (b) Scandola, F.; Balzani, V. *J. Chem. Educ.* **1983**, *60*, 814–823. (c) Parola, A. J.; Pina, F.; Ferreira, E.; Maestri, M.; Balzani, V. *J. Am. Chem. Soc.* **1996**, *118*, 11610–11616.

[3] Endicott, J. F.; Heeg, M. J.; Gaswick, D. C.; Pyke, S. C. *J. Phys. Chem.* **1981**, *85*, 1777–1779.

[4] Gamache, R. E.; Rader, R. A.; McMillin, D. R. *J. Am. Chem. Soc.* **1985**, *107*, 1141–1146.

[5] Endicott, J. F.; Tamilarasan, R.; Brubaker, G. R. *J. Am. Chem. Soc.* **1986**, *108*, 5193–5201.

[6] Balzani, V.; Indelli, M. T.; Maestri, M.; Sandrini, D.; Scandola, F. *J. Phys. Chem.* **1980**, *84*, 852–855.

[7] Endicott, J. F. *Acc. Chem. Res.* **1988**, *21*, 59–66.

[8] Tamilarasan, R.; Endicott, J. F. *J. Phys. Chem.* **1986**, *90*, 1027–1033.

[9] Endicott, J. F.; Ramasami, T.; Gaswick, D. C.; Tamilarasan, R.; Heeg, M. J.; Brubaker, G. R.; Pyke, S. C. *J. Am. Chem. Soc.* **1983**, *105*, 5301–5310.

[10] Gandolfi, M. T.; Maestri, M.; Sandrini, D.; Balzani, V. *Inorg. Chem.* **1983**, *22*, 3435–3439.

[11] Endicott, J. F. *Coord. Chem. Rev.* **1985**, *64*, 293–310.

[12] Forster, L. S. *Chem. Rev.* **1990**, *90*, 331–353.

[13] Kirk, A. D. *Chem. Rev.* **1999**, *99*, 1607–1640.

[14] Wagenknecht, P. S.; Kane-Maguire, N. A. P.; Speece, D. G.; Helwic, N. *Inorg. Chem.* **2002**, *41*, 1229–1235.

[15] Majaraj, U.; Winnik, M. A. *Chem. Phys. Lett.* **1981**, *82*, 29–32.

[16] (a) Maestri, M.; Sandrini, D.; Balzani, V.; Belser, P.; Von Zelewski, A. *Chem. Phys. Lett.* **1984**, *110*, 611–614. (b) Balzani, V.; Juris, A. *Coord. Chem. Rev.* **2001**, *211*, 97–115.

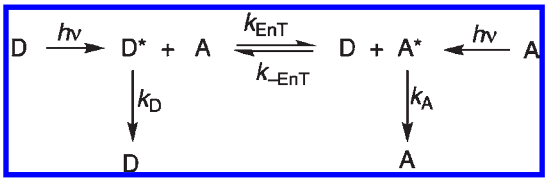

Figure 1. Energy transfer between a donor (D) and acceptor (A). Herein, the species with the longer lived excited state will always be defined as the donor.

There are two limiting kinetic regimes for energy transfer. In case I, $k_A \ll k_{-\mathrm{EnT}}[\mathrm{D}]$ and the excitation energy will be transferred many times between D and A (that is, equilibrium will be established) before deactivation of either excited state occurs. Maharaj and Winnik[15] have demonstrated that in this case a single exponential decay of the emission signal is experimentally observed with a lifetime that is a weighted average of the two intrinsic lifetimes (eq 1) and only the equilibrium constant for energy transfer, K_{EnT}, can be determined.

$$1/\tau = k_D + K_{\mathrm{EnT}}([\mathrm{A}]/[\mathrm{D}])(k_A - 1/\tau) \qquad (1)$$

In case II, $k_A \gg k_{-\mathrm{EnT}}[\mathrm{D}]$ and energy transfer in the forward direction is irreversible. Under such conditions, the Stern−Volmer equation (eq 2) for the quenching of D* emission by A applies and the rate constant for energy transfer can be determined.

$$1/\tau = k_D + k_{\mathrm{EnT}}[\mathrm{A}] \qquad (2)$$

Note that if both donor and acceptor emit at similar wavelengths, the decay profile will be biexponential.

Previous investigations of energy transfer self-exchange using such an analysis have been limited to measuring only the rate constant or equilibrium constant for energy transfer, not both. For example, in the electronic energy "self-exchange" experiment between *trans*-$[\mathrm{Cr}(d_4\text{-cyclam})(\mathrm{CN})_2]^+$ (τ > 1500 μs) and *trans*-$[\mathrm{Cr(cyclam)(CN)}_2]^+$ (τ = 350 μs), the pulsed emission studies resulted in single-exponential decay, indicative of reversible energy transfer (see Figure 2).[14] Plotting the data according to eq 1 resulted in a straight line and a value for $K_{\mathrm{EnT}} = 0.99$. An equilibrium constant close to unity is indicative of a thermoneutral process, as anticipated for the self-exchange system. Because this energy transfer had occurred in the case I limit, in which $k_A \ll k_{-\mathrm{EnT}}[\mathrm{D}]$, only a lower limit of $k_{\mathrm{EnT}} \gg 7 \times 10^6\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ could be placed on the rate constant.

We have now determined that it is possible in such a situation to also measure the energy transfer rate constant by careful control of the donor concentration. Note that whether the case I or II kinetic regime applies depends on the relative magnitudes of k_A and $k_{-\mathrm{EnT}}[\mathrm{D}]$. Thus, judicious control of the concentration of the longer-lived donor species may prompt a shift between these kinetic regimes and make possible the measurement of both the rate constant and equilibrium constant for energy transfer.[17] Herein, we demonstrate that by substantially lowering the donor concentration in the energy transfer between *trans*-$[\mathrm{Cr}(d_4\text{-cyclam})(\mathrm{CN})_2]^+$ and *trans*-$[\mathrm{Cr(cyclam)(CN)}_2]^+$, case II kinetics are achieved and a rate constant can be measured. We have also demonstrated that by similar control of the donor concentration, both the rate constant and equilibrium constant for energy transfer between *trans*-$[\mathrm{Cr}(d_4\text{-cyclam})(\mathrm{CN})_2]^+$ and *trans*-$[\mathrm{Cr([15]ane\text{-}N_4)(CN)}_2]^+$ can be measured and that the equilibrium constant agrees with that calculated from the spectroscopic energy gap between the excited states.

Experimental Section

Materials and Methods. All materials were reagent grade and were used as received. *trans*-$[\mathrm{Cr(cyclam)(CN)}_2]\mathrm{ClO}_4$ was synthesized according to the literature procedure.[18] Elemental analyses were performed by Midwest Microlabs in Indianapolis, IN. *Caution! Perchlorate salts of metal complexes are potentially explosive and should be handled with extreme caution and only in very small quantities.*

Characterization of *trans*-$[\mathbf{Cr([15]ane\text{-}N_4)(CN)_2]ClO_4}$. The synthesis was performed according to the procedure by Lessard et al.[19] However, the elemental analysis of the *trans*-$[\mathrm{Cr([15]ane\text{-}N_4)(CN)}_2]\mathrm{ClO}_4$ complex did not indicate the presence of a formula unit of cocrystallized sodium perchlorate as had been reported in the literature. Anal calcd (found) for $\mathrm{C_{13}H_{26}N_6CrClO_4}$: C, 37.37 (37.39); N, 20.11 (19.90); H, 6.27 (6.50). The absorption maxima at 348 nm (ε = 82 $\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$) and 452 nm ($\varepsilon$ = 80 $\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$) were consistent with the literature (molar absorptivities previously unreported), although the room temperature excited state lifetime was measured as 230 μs, higher than the published value of 190 μs.[19]

Energy Transfer Studies. All measurements were performed in acidified aqueous solution (0.01 M HCl) which efficiently suppresses amine N−D exchange of *trans*-$[\mathrm{Cr}(d_4\text{-cyclam})(\mathrm{CN})_2]^+$ with solvent protons. Stock solutions of the donors and acceptors were prepared and the concentrations determined by UV−vis spectroscopy using molar absorptivity values of $\varepsilon_{414} = 62.5\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ for deuterated and undeuterated *trans*-$[\mathrm{Cr(cyclam)(CN)}_2]\mathrm{ClO}_4$,[18] and $\varepsilon_{452} = 80.0\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ for *trans*-$[\mathrm{Cr([15]ane\text{-}N_4)(CN)}_2]\mathrm{ClO}_4$. To dissolve the perchlorate salts at the higher concentrations necessary for several of the measurements, the samples were shaken vigorously in 0.01 M HCl along with Dowex chloride exchange resin beads (2-X8, 20−50 mesh) and, then, filtered to remove any insoluble materials.

A series of solutions for analysis was prepared by adding a variable volume of the acceptor stock solution to a fixed volume of donor stock solution, then diluting the solutions to achieve a uniform total volume. The emission lifetime of each solution was measured using as the excitation source a Photon Technology International (PTI) GL-3300 pulsed-nitrogen laser fed into a PTI GL-302 dye laser. The dye laser was operated at 440 nm, corresponding to $^4\mathrm{A}_{2g} \rightarrow {}^4\mathrm{T}_{2g}$ (O_h) excitation of the *trans*-$[\mathrm{Cr(N_4)(CN)}_2]^+$ complexes. The samples were thermostatted to 20 °C using a Quantum Northwest TLC 50, and emission was monitored at right angles using a Hamamatsu R928 photomultiplier tube connected to a monochromator. To maximize the $^2\mathrm{E}_g \rightarrow {}^4\mathrm{A}_{2g}$ (O_h) emission signal from the solutions of low concentration the monochromator was removed and a Corning CS 2-64 cutoff filter was placed prior to the photomultiplier to limit stray light. The signal from the photomultiplier was fed into a LeCroy 9350 digital oscilloscope and stored for further analysis. Under conditions of biexponential decay, decay traces were analyzed beyond the value of 5τ for the shorter lived acceptor, allowing for selective monitoring of the donor lifetime. Correlation coefficients for the exponential fits of the emission

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(17) For a treatment of the two-state model for reversible monomer/excimer kinetics with pyrene see Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970; pp 301−371.

(18) (a) Kane-Maguire, N. A. P.; Bennett, J. A.; Miller, P. K. *Inorg. Chim. Acta* **1983**, *76*, L123–L125. (b) Kane-Maguire, N. A. P.; Crippen, W. S.; Miller, P. K. *Inorg. Chem.* **1983**, *22*, 696–698.

(19) Lessard, R. B.; Heeg, M. J.; Buranda, T.; Perkovic, M. W.; Schwarz, C. L.; Yang, R.; Endicott, J. F. *Inorg. Chem.* **1992**, *31*, 3091–3103.

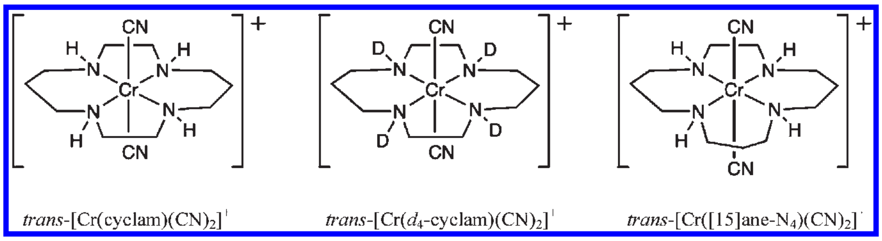

Figure 2. Macrocyclic complexes utilized in the energy transfer experiments.

decay curves were typically 0.999 or greater. All studies were carried out under air-saturated solution conditions, since it has been previously demonstrated that the emission intensities and excited state lifetimes of the complexes studied are insensitive to dissolved oxygen.[18]

N−H Deuteration of *trans*-[Cr(cyclam)(CN)$_2$]ClO$_4$. A 100 mg sample (0.235 mmol) of *trans*-[Cr(cyclam)(CN)$_2$]ClO$_4$ was dissolved in 40 mL D$_2$O, and one drop of triethylamine was added to the solution. The solution was stirred at 45 °C for 24 hours under vacuum. The solvent was reduced to approximately 6 mL under vacuum, and the deuterated product was precipitated with anhydrous lithium perchlorate and washed with ether. Deuteration was determined to be ~99% by IR spectroscopy.

Results and Discussion

Serial Dilution Experiments. In order to make measurements of both the rate constant and equilibrium constant for energy transfer, i.e., in order to access both the case I and II limits, two requirements must be met: (1) The donor and acceptor must have significantly different emission lifetimes; otherwise, the addition of the acceptor molecule will not significantly alter the lifetime of the mixture. (2) The lifetime of the acceptor molecule must be long enough such that the bimolecular back energy transfer process could potentially out-compete the unimolecular relaxation of the acceptor by addition of reasonable amounts of the donor. The systems that we suspected would fit these criteria involved using *trans*-[Cr(d_4-cyclam)(CN)$_2$]$^+$ as the donor and either *trans*-[Cr(cyclam)-(CN)$_2$]$^+$ or *trans*-[Cr([15]ane-N$_4$)(CN)$_2$]$^+$ as the acceptor. Initial tests of whether or not the Case I and Case II limits could be accessed with these complexes involved serial dilution experiments of a donor/acceptor sample according to the following analysis. If eq 1 is rearranged to solve for $1/\tau$ (eq 3), it is clear that the excited state lifetime of a mixture of chromophores in the Case I limit depends only on the ratio of donor and acceptor concentrations.

$$1/\tau = \frac{k_D + K_{EnT}([A]/[D])(k_A)}{K_{EnT}([A]/[D]) + 1} \qquad (3)$$

In contrast, in the case II limit, the Stern−Volmer equation (eq 2) demonstrates that the lifetime of the longer-lived donor species depends exclusively on the concentration of the acceptor.

This experiment was conducted with a solution of *trans*-[Cr([15]ane-N$_4$)(CN)$_2$]ClO$_4$ as the acceptor and *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$ as the donor prepared with an acceptor-to-donor ratio of 0.8. The initial concentration of donor in the solution was 4.6×10^{-3} M, and the emission decay lifetime (or the lifetime of the longest-lived component in cases of biexponential decay) was monitored as the solution was diluted to a donor concentration of 5.0×10^{-6} M (Figure 3). The plot is relatively flat at high concentrations, whereas there is a steep linear relationship between $1/\tau$ and concentration at low donor concentrations, consistent with theoretical expectations. The region of curved transition between the two limits of this plot exists at donor concentrations between approximately 1×10^{-3} and 5×10^{-5} M.

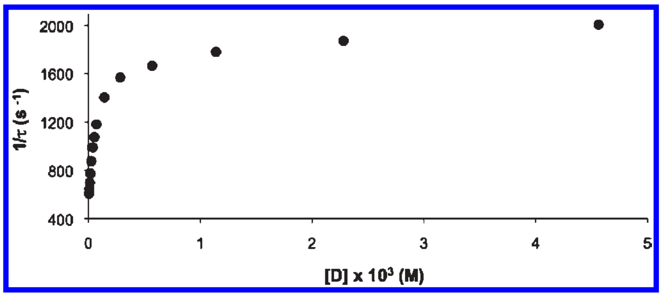

Figure 3. $1/\tau$ vs [D] for *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$ as the donor and *trans*-[Cr([15]ane-N$_4$)(CN)$_2$]ClO$_4$ as the acceptor, where [A]/[D] = 0.8.

The serial dilution experiment was also performed with *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$ as the donor and *trans*-[Cr(cyclam)(CN)$_2$]ClO$_4$ as the acceptor (Supporting Information), and the plot shows an analogous transition between case I and II limiting kinetics. Both experiments demonstrate a shift from case I behavior to case II behavior as the donor concentration is reduced. In addition, both experiments demonstrated the expected single exponential behavior at the high concentration limits and biexponential behavior at the low concentration limit. The plots also give an indication of what donor concentrations to use in order to achieve the case I and II limits. Note also, though, that these plots do not completely flatten out at high concentration as the model predicts. This is likely due to the slight concentration dependence of the donor lifetime at high concentration (vide infra).

Determination of the Rate Constant and Equilibrium Constant for Energy Transfer between *trans*-[Cr(d_4-cyclam)-(CN)$_2$]ClO$_4$ and *trans*-[Cr([15]ane-N$_4$)(CN)$_2$]ClO$_4$. Case I Limiting Kinetics. Mixtures of *trans*-[Cr(d_4-cyclam)(CN)$_2$]-ClO$_4$ donor and *trans*-[Cr([15]ane-N$_4$)(CN)$_2$]ClO$_4$ acceptor were prepared, in which the total concentration of donor was 4.3×10^{-3} M (well within the case I limit). The ratio of [A] to [D] was increased systematically in the sample solutions to yield a maximum of 0.6. The pulsed emission studies resulted in single-exponential decay, indicative of case I energy transfer. Plotting the data according to eq 1 resulted in a straight line with a slope (K_{EnT}) of 0.66 (Figure 4). A Stern−Volmer plot of this data is curved, offering further evidence that case I kinetics predominates.

The theoretical equilibrium constant can be calculated using the energy gap between the ^2E_g (O_h) excited states of

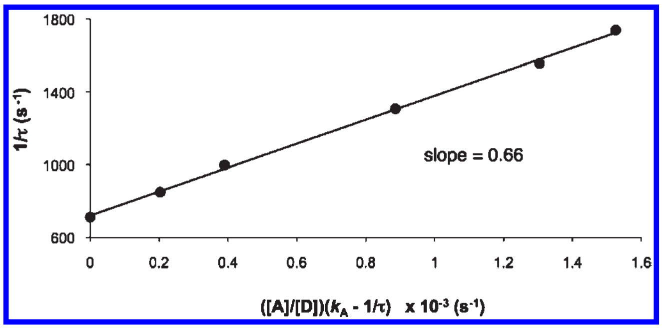

Figure 4. Case I plot for *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$ as the donor ([D] = 4.34×10^{-3} M) and *trans*-[Cr([15]ane-N$_4$)(CN)$_2$]ClO$_4$ as the acceptor (R^2 = 0.998).

the donor and acceptor. The ^2E_g energy of *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$ is 13 936 cm^{-1} at 77 K in glass DMSO/water, while that of *trans*-[Cr([15]ane-N$_4$)(CN)$_2$]ClO$_4$ is 14 039 cm^{-1},[19] an uphill energy difference of +103 cm^{-1} which corresponds to an equilibrium constant for forward energy transfer of 0.60 at 293 K. This value is in good agreement with the value of 0.66 determined from this experiment. In order to enter the case II limit and obtain the rate constant, the donor concentration was reduced for the subsequent experiment.

Case II Limiting Kinetics. Mixtures of *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$ and *trans*-[Cr([15]ane-N$_4$)(CN)$_2$]ClO$_4$ were prepared, in which the total concentration of donor was 1.0×10^{-5} M (well within the case II limit as demonstrated by the serial dilution experiment). The maximum value of [A]/[D] in the sample solutions was 7.0. The pulsed emission studies revealed biexponential decay, indicative of case II energy transfer. The lifetime of the longer lived donor component was determined for each sample and this data was plotted according to eq 2. A linear fit of the data yielded a slope (k_{EnT}) of 1.7×10^7 M^{-1} s^{-1} (Figure 5). Plotting according to the reversible exchange equation (eq 1) yielded a curved plot, further confirming the case II behavior. In addition, analysis of the case II region of the serial dilution plot (Figure 3) gives nearly the same rate constant (1.6×10^7 M^{-1} s^{-1}).

"Intermediate" Energy Transfer Kinetics. For cases in which $k_{-\mathrm{EnT}}$[D] is comparable in magnitude with k_A, the energy transfer scheme above is complex and falls between the two limiting cases. An energy transfer experiment was performed in which the concentration of donor in each sample solution was held at 1.2×10^{-4} M. The ratio of [A] to [D] was increased systematically in the sample solutions to yield a maximum of 7.7. The emission decay traces in this case are predicted to be complex[15] and indeed cannot be fit to a single exponential decay. Nevertheless, good biexponential fits can be obtained and analysis of the decay trace beyond 3τ of the acceptor yielded single exponential fits with correlation coefficients of 0.999 or greater. However, plotting this data according to either the case I limit (Figure 6) or the Stern–Volmer equation (Figure 7) yielded distinctly nonlinear plots, confirming that the energy transfer in this scenario falls between the two limiting kinetic regimes.

This experiment was also performed at a donor concentration of 2.25×10^{-4} M, with similar results. The hooked shape of the case I plot (Figure 6) is peculiar but has occurred repeatedly in situations that fall into this intermediate kinetic region.

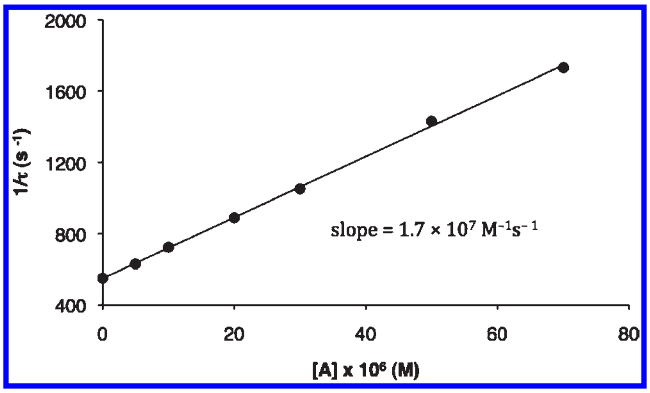

Figure 5. Stern–Volmer plot for *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$ as the donor ([D] = 1.0×10^{-5} M) and *trans*-[Cr([15]ane-N$_4$)(CN)$_2$]ClO$_4$ as the acceptor (R^2 = 0.999).

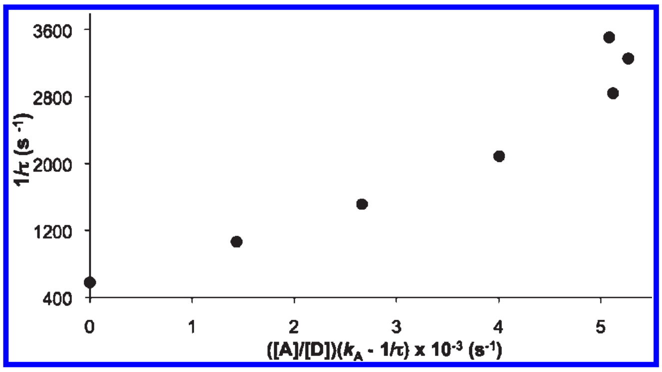

Figure 6. Case I plot for *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$ as the donor ([D] = 1.2×10^{-4} M) and *trans*-[Cr([15]ane-N$_4$)(CN)$_2$]ClO$_4$ as the acceptor.

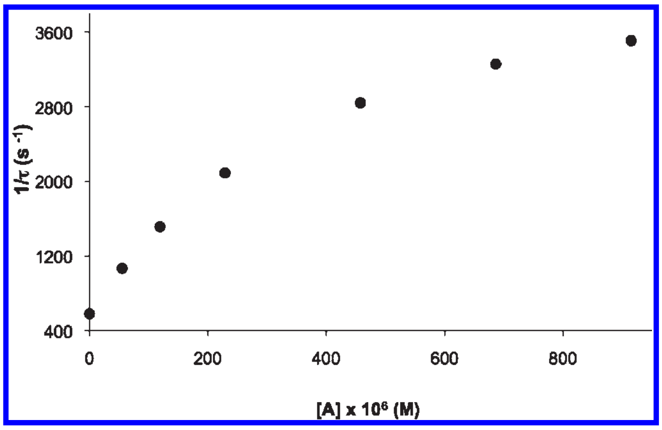

Figure 7. Stern–Volmer plot for *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$ as the donor ([D] = 1.2×10^{-4} M) and *trans*-[Cr([15]ane-N$_4$)(CN)$_2$]ClO$_4$ as the acceptor.

Determination of the Rate Constant for Energy Transfer Self-Exchange between *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$ and *trans*-[Cr(cyclam)(CN)$_2$]ClO$_4$. We had previously reported electronic energy self-exchange for this system in the case I limit, in which only a lower limit of $k_{\mathrm{EnT}} \gg 7 \times 10^6$ M^{-1} s^{-1} could be placed on the rate constant.[14] We have now performed an energy transfer experiment between *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$ and *trans*-[Cr(cyclam)(CN)$_2$]ClO$_4$ with a much lower donor

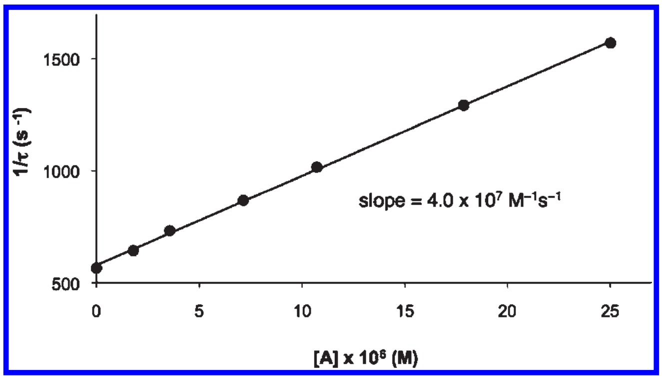

Figure 8. Stern–Volmer plot for *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$ as the donor ([D] = 5.0×10^{-6} M) and *trans*-[Cr(cyclam)(CN)$_2$]ClO$_4$ as the acceptor (R^2 = 0.999).

concentration, 5.0×10^{-6} M, well within the case II limit as demonstrated in the serial dilution experiment. In this experiment, the maximum ratio of acceptor to donor achieved in the sample solutions was 5.0.

The pulsed emission studies revealed biexponential decay, indicative of the case II limit. Plotting the lifetime of the long-lived donor component according to eq 2 (Figure 8) gave an energy transfer rate constant, k_{EnT}, of 4.0×10^7 M^{-1} s^{-1}. Analysis of the case II region of the serial dilution plot gives an identical rate constant. This experimental rate constant is nearly six times greater than the lower limit of $k_{\mathrm{EnT}} \gg 7 \times 10^6$ estimated from the case I kinetics study.[14,20] Also, the plot generated using eq 1 is nonlinear, offering additional evidence that this system is in the case II kinetic regime.

Complications. It appears problematic that the $1/\tau$ values in the serial dilution plots (e.g., Figure 3) do not level off with increasing donor concentration, but instead appear to gradually increase. This phenomenon is likely due to variations in k_{D} with concentration. We have found that at concentrations above 5×10^{-4} M, the lifetime of *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$ decreases with increased concentration, i.e., a sample with a lifetime of 1700 μs at 4.8×10^{-4} M has a lifetime of about 1400 μs at 4.3×10^{-3} M. A plot of $1/\tau$ vs concentration appears linear. (Below 5×10^{-4} M, the lifetime does not vary systematically with concentration.) This may be part of the reason for the slight variation of the excited state lifetime for this complex in the literature[18,19]—though incomplete N-deuteration would also be suspect. The quenching of the excited state lifetime at high concentrations may be due to a *trans*-[Cr([15]ane-N$_4$)(CN)$_2$]ClO$_4$ impurity (< 5%) in the *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$ sample, which has been detected in our group by mass spectrometry and has also been reported by Endicott.[19,21] Although self-quenching by doublet–doublet annihilation has been reported for Cr(III) polypyridine complexes,[22] this explanation is unlikely for *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$. A 1% transmittance neutral density filter applied to the laser aperture resulted in no significant increase in the excited state lifetime of a sample at a concentration of 1.24×10^{-3} M. A third explanation is that under the acidic conditions necessary for the experiment, a protonated complex may quench the excited state of the unprotonated species, which would also be more evident at higher [Cr].[23]

If k_{D} increases with [D], then the case I limiting value of $1/\tau$ for the mixture should also increase with solution concentration (eq 3). To avoid any errors due to the concentration dependence of the donor lifetime, all experiments other than the serial dilution experiment were performed with a constant concentration of the *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$ donor.

Summary and Analysis

Measurements on these systems demonstrate that both the rate constant and equilibrium constant can be measured by judicious control of the donor concentration. It should be noted that apparent biexponential behavior does not by itself establish that the case II limit is applicable since even in the intermediate region between the case I and II limits the decay traces we observe can be satisfactorily fit to a biexponential function. However, in this intermediate region, plotting according to either eqs 1 or 2 yields nonlinear plots.

Measurements on these systems also demonstrate that the equilibrium constant for the energy transfer can be estimated directly from the energy difference between the ^2E_g excited states involved in the energy transfer, indicating that the spectroscopic energy gap (ΔE in Table 1) is a good approximation of $\Delta G°$ for these energy transfer reactions. Table 1 summarizes the data in this manuscript. Note also, that because both an equilibrium constant and a rate constant for forward energy transfer have been determined, the rate constant for back energy transfer, $k_{-\mathrm{EnT}}$, can be calculated. This is trivial in the case of the self-exchange but in the case of the cross-exchange energy transfer between *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$ and *trans*-[Cr([15]ane-N$_4$)(CN)$_2$]ClO$_4$, the calculation gives a value of 2.6×10^7 M^{-1} s^{-1}. Thus, it appears that the rate constant for thermoneutral energy transfer is faster than either the slightly uphill case (+103 cm^{-1}) or the calculated downhill case.

In order to discuss the observed differences in the rate constants, one must consider that, for energy transfer, the solvent reorganization energy is nearly zero, a factor that has allowed the determination of the role that internal reorganization and electronic factors have on the rate.[3-6,24] Thus, the observed rate differences could simply be electronic in origin. The fact that even the fastest (thermoneutral) rate constant measured here falls considerably lower than the diffusion controlled rate constant highlights the importance of electronic factors in energy transfer reactions. We have previously demonstrated the importance of electronic factors for a series of self-exchange energy transfer reactions of Cr(III) complexes.[14] However, given the homogeneous nature of the energy transfer reactions studied herein, namely where energy transfer occurs from the same excited state to electronically and structurally similar acceptors, electronic differences between the energy transfer processes studied herein should be minimized. This leads us to also consider internal

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(20) Conclusions in ref 14 used a conservative estimate that the much greater than inequality was at least a factor of 5. Thus, this work does not invalidate any of the conclusions drawn in that publication.

(21) Samples of cyclam are potentially contaminated with [15]aneN$_4$ due to the synthetic method, and the resulting complexes would be very difficult to separate as discussed in ref 19.

(22) Indelli, M. T.; Ballardini, R.; Bignozzi, C. A.; Scandola, F. *J. Phys. Chem.* **1982**, *86*, 4284–4286.

(23) We thank a reviewer for this suggestion.

(24) Place, I.; Farran, A.; Deshayes, K.; Piotrowiak, P. *J. Am. Chem. Soc.* **1998**, *120*, 12626–12633.

Table 1. Summary of Rate and Equilibrium Constants[a]

	ΔE (0−0′)[b]	K_{EnT} (calc)	K_{EnT} (exp)	k_{EnT} (M^{-1} s^{-1})	$k_{-\mathrm{EnT}}$ (M^{-1} s^{-1})[c]
self-exchange	≤ 10 cm^{-1}	~1	0.99[d]	4.0×10^7	4.0×10^7
cross-exchange	103 cm^{-1}	0.60	0.66	1.7×10^7	2.6×10^7

[a] Error estimates on rate and equilibrium constants are ±10%, and errors on ΔE are ±20 cm^{-1}. [b] Difference between the donor and acceptor ^2E_g (0−0′) energies in ref 19. [c] Calculated from $k_{-\mathrm{EnT}} = k_{\mathrm{EnT}}/K_{\mathrm{EnT}}(\mathrm{exp})$. [d] Reference 14.

reorganization. Because the ^2E_g excited state and $^4A_{2g}$ ground states of Cr(III) complexes are well-known to have very similar nuclear coordinates,[12,13] one might expect the D*/A reactant potential well and the D/A* product potential well to be nested and therefore weakly coupled. However, since the energy transfer processes considered here are thermoneutral, or nearly so, the potential wells can be considered to intersect. Note that, in such a case, the very small displacement along the nuclear coordinate should result in a crossing point (activation barrier) that is very sensitive to small changes in the donor−acceptor energy gap.[25] However, discriminating between an electronic vs nuclear origin of the rate differences reported herein will require additional measurements in this energy region. We have recently prepared several new complexes of the type *trans*-$[\mathrm{Cr(N_4)(CN)_2}]^+$ which should allow for the study of additional energy transfer "cross-reactions" in the energy range within 100 cm^{-1} of thermoneutrality.[26]

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Supporting Information Available: Plot of $1/\tau$ vs [D] for the serial dilution of a mixture of *trans*-[Cr(d_4-cyclam)(CN)$_2$]ClO$_4$ as the donor and *trans*-[Cr(cyclam)(CN)$_2$]ClO$_4$ as the acceptor. This material is available free of charge via the Internet at http://pubs.acs.org

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(25) Such small displacement−small gap behavior is discussed in refs 5 and 11 as one of four categories for energy transfer. Therein, the authors highlight the theoretical difficulty involved in addressing this situation.

(26) Grisenti, D. L.; Smith, M. B.; Fang, L.; Bishop, N.; Wagenknecht, P. S. *Inorg. Chim. Acta* **2010**, *363*, 157–162.