Measurement of Rates of Electron Transfer between $Ru(bpy)_3{}^{3+}$ and $Fe(phen)_3{}^{2+}$ and between $Ru(phen)_3{}^{3+}$ and $Ru(bpy)_3{}^{2+}$ by Differential Excitation Flash Photolysis

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Abstract: Flash photolysis of solutions containing $Fe(H_2O)_6{}^{3+}$, $Ru(bpy)_3{}^{2+}$, and $Fe(phen)_3{}^{2+}$ results in excitation to the CT excited state of $Ru(bpy)_3{}^{2+}$ followed by rapid quenching to give $Ru(bpy)_3{}^{3+}$ and $Fe(H_2O)_6{}^{2+}$. The quenching step is followed by rapid electron transfer between $Ru(bpy)_3{}^{3+}$ and $Fe(phen)_3{}^{2+}$ ($k(25\ °C) = 1.8 \times 10^9\ M^{-1}\ s^{-1}$ in 1.0 M $HClO_4$) and then return of the system to equilibrium by electron transfer between $Fe(phen)_3{}^{3+}$ and $Fe(H_2O)_6{}^{2+}$. Both reactions can be followed directly by observing transient spectral changes following flash photolysis. Flash photolysis of solutions containing $Ru(bpy)_3{}^{2+}$, $Ru(phen)_3{}^{2+}$, and $Fe(H_2O)_6{}^{3+}$ results in excitation and quenching of both the bpy and phen complexes. However, because of differences in spectral and excited state properties, in solutions in which initially there are equal amounts of $Ru(bpy)_3{}^{2+}$ and $Ru(phen)_3{}^{2+}$, an excess of $Ru(phen)_3{}^{3+}$ can be produced. Excitation and quenching are followed by a reaction between $Ru(bpy)_3{}^{2+}$ and $Ru(phen)_3{}^{3+}$ which takes the system to a position of transient equilibrium (see eq 12 in text), for which $K = 1.0$, and which is followed by the slower reductions of $Ru(phen)_3{}^{3+}$ and $Ru(bpy)_3{}^{3+}$ by $Fe(H_2O)_6{}^{2+}$. An appropriate analysis of the transient spectral changes following flash photolysis has given rate constant data for both the equilibration reaction and the back-reactions between $Fe(H_2O)_6{}^{2+}$ and $Ru(bpy)_3{}^{3+}$ and $Ru(phen)_3{}^{3+}$. At 25 °C, k_1, which is a measure of the $Ru(bpy)_3{}^{3+/2+}$ and $Ru(phen)_3{}^{3+/2+}$ self-exchange rates, is $1.2 \times 10^9\ M^{-1}\ s^{-1}$ in 1.0 M $HClO_4$. In 0.1 M $HClO_4$, $\Delta H^{\ddagger} = 7.7 \pm 1.5$ kcal/mol and $\Delta S^{\ddagger} = -6.6 \pm 0.4$ eu. It is concluded that the net reaction and, therefore, the self-exchange reactions are slightly below the diffusion-controlled limit and that a slight barrier to electron transfer exists arising from reorganization of outer coordination sphere solvent molecules.

Flash photolysis is an invaluable technique for observing photochemically generated transients and for measuring their rates of reaction. In properly designed chemical systems, flash photolysis can also be used as a kinetic device for obtaining electron transfer rate data which are otherwise inaccessible or difficult to obtain.[1-3] For example, in a solution containing $Ru(bpy)_3{}^{2+}$ (bpy is 2,2′-bipyridine) and $Fe(H_2O)_6{}^{3+}$, flash photolysis is followed by rapid quenching of the CT excited state $Ru(bpy)_3{}^{2+*}$ [4-6] (eq 2 in Scheme I) to give the redox products $Ru(bpy)_3{}^{3+}$ and $Fe(H_2O)_6{}^{2+}$. The subsequent back-electron transfer step (eq 3) can be followed directly using conventional flash photolysis.

Scheme I (in water)

$$Ru(bpy)_3{}^{2+} \xrightarrow{h\nu} Ru(bpy)_3{}^{2+*} \qquad (1)$$

$$Ru(bpy)_3{}^{2+*} + Fe(H_2O)_6{}^{3+} \rightarrow Ru(bpy)_3{}^{3+} + Fe(H_2O)_6{}^{2+} \qquad (2)$$

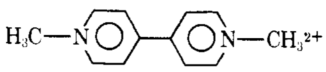
$$Ru(bpy)_3{}^{3+} + Fe(H_2O)_6{}^{2+} \rightarrow Ru(bpy)_3{}^{2+} + Fe(H_2O)_6{}^{3+} \qquad (3)$$

When used in this way, flash photolysis becomes a relaxation technique (eq 4) in which a reaction at equilibrium is rapidly perturbed by the light absorption–quenching sequence in eq 1 and 2.

$$Ru(bpy)_3{}^{3+} + Fe(H_2O)_6{}^{2+} \underset{h\nu}{\overset{\Delta G\,=\,-0.52\ V}{\rightleftarrows}} Ru(bpy)_3{}^{2+} + Fe(H_2O)_6{}^{3+} \qquad (4)$$

The rates of very rapid reactions can be measured, including the theoretically interesting case of reactions in the "abnormal" free energy region[7-9] where the chemical driving force is large and favorable (e.g., eq 5).[1,3]

$$P^+ + Ru(bpy)_3{}^{3+} \xrightarrow[CH_3CN]{\Delta G\,=\,-1.7\ V} P^{2+} + Ru(bpy)_3{}^{2+} \qquad (5)$$

(P^{2+} is paraquat; )

The technique can also be applied in more general ways. As shown by the sequence of reactions in Scheme II, by using two different one-electron transfer redox couples, the quenching and back-electron transfer steps can be separated and visible light used to perturb an equilibrium in which both of the reactants are transparent in the visible. The equilibrium-perturbing excited state is not involved in the net reaction.

Scheme II (in acetonitrile)

$$Ru(bpy)_3{}^{2+} \xrightarrow{h\nu} Ru(bpy)_3{}^{2+*} \qquad (6)$$

$$Ru(bpy)_3{}^{2+*} + P^{2+} \rightarrow Ru(bpy)_3{}^{3+} + P^+ \qquad (7)$$

$$Ru(bpy)_3{}^{3+} + NPh_3 \rightarrow Ru(bpy)_3{}^{2+} + NPh_3{}^+ \qquad (8)$$

$$P^{2+} + NPh_3 \underset{h\nu}{\overset{\Delta G\,=\,-1.49\ V}{\rightleftarrows}} P^+ + NPh_3{}^+ \qquad (9)$$

(Ph = phenyl)

The spin-paired, substitution inert polypyridine complexes of iron, ruthenium, and osmium(II) and -(III) have played an important role in testing the Marcus–Hush theory for outer-sphere electron transfer.[10-19] Previous work has shown that net reactions like eq 10 (phen is 1,10-phenanthroline),[20]

$$Ru(bpy)_3{}^{3+} + Fe(phen)_3{}^{2+} \xrightarrow{\Delta G\,=\,-0.184\ V} Ru(bpy)_3{}^{2+} + Fe(phen)_3{}^{3+} \qquad (10)$$

and self-exchange reactions like eq 11,[21,22]

$$Ru(bpy)_3{}^{2+} + Ru'(bpy)_3{}^{3+} \rightarrow Ru(bpy)_3{}^{3+} + Ru'(bpy)_3{}^{2+} \qquad (11)$$

are very rapid and difficult to measure using conventional techniques. The measurement of rates of self-exchange for these systems is especially important given the usefulness of the ions as electron transfer reagents. With properly designed experiments, it should be possible to apply the flash photolysis relaxation technique to both kinds of reactions and we report here the results of such experiments using the net reaction between $Ru(phen)_3^{3+}$ and $Ru(bpy)_3^{2+}$ as a model for the self-exchange process.

Experimental Section

Chemicals. $[Ru(bpy)_3](ClO_4)_2$ and $[Ru(phen)_3](ClO_4)_2$ were prepared and purified as reported previously.[23] $Fe(ClO_4)_3{\cdot}6H_2O$ and $Fe(ClO_4)_2{\cdot}6H_2O$ were purchased from G. F. Smith and Company. Water was deionized and distilled from alkaline $KMnO_4$. Complex concentrations were determined spectrophotometrically using a Bausch and Lomb 210UV spectrophotometer and known molar extinction coefficients.[16,23]

Flash Photolysis Experiments. The flash photolysis apparatus analyzing system consisted of a Xenon Corporation Model G low ripple analyzing lamp, two lenses, a Bausch and Lomb high-intensity UV-visible monochromator, and an EMI 6256 photomultiplier tube. A nonlinear capacitor coupled dynode chain was used on the PM tube with applied potentials from 500 to 650 V and the output was measured by a Tektronix 7514 storage oscilloscope across a 1.0 kΩ load resistor. The risetime of the analyzing system was shorter than 1 μs. The photolysis system was a Xenon Corporation fast extinguishing flash tube FP-10A through which a 2.0 μF capacitor (typically charged to 4 kV) was discharged. Triggering of the flash was accomplished by use of a Xenon Corporation Model C trigger which also reproducibly triggers the oscilloscope sweep with its radio frequency noise. The output of the PM was monitored while the flash was on for each PM potential setting to ensure that the output of the PM was kept well below its maximum current rating (0.5 mA). A set of aluminum tubing light baffles painted flat black enabled PM tube voltages of up to 650 V to be used with scattered light levels insignificant at 1-mm slit widths. These precautions were necessary as the experiment required photolyzing and monitoring in the same wavelength region. UV photolyzing light was filtered out with Corning 3-73 glass filters, ensuring photolysis of only the metal chelate charge transfer bands in the visible region.

Solutions were made up containing $[Ru(bpy)_3](ClO_4)_2$ and $[Ru(phen)_3](ClO_4)_2$, $[Fe(H_2O)_6](ClO_4)_3{\cdot}6H_2O$, and $[Fe(H_2O)_6](ClO_4)_2{\cdot}6H_2O$ in 1.0 M $HClO_4$ for $\mu = 1.0$ M, or 0.076 M $HClO_4$ for $\mu = 0.1$ M. The solutions were degassed through several cycles of freezing, evacuating, and thawing, and then 1.0 atm of N_2 was added. A jacketed 12-cm cell was used for the measurements. The cell was thermostated (±0.1 °C) using a Forma Model 2095 circulator-water bath.

Changes in optical density with time following flash photolysis were recorded from the oscilloscope trace by photography and digitized manually. A computer program was developed to analyze the data according to the kinetic analysis given below.

Treatment of Kinetic Data. After excitation to give the two excited states $Ru(phen)_3^{2+*}$ and $Ru(bpy)_3^{2+*}$ and quenching by $Fe(H_2O)_6^{3+}$, which occurs during the flash, a slight excess of $Ru(phen)_3^{3+}$ is produced. The first event which occurs following the quenching step is the reaction between $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{3+}$, which leaves the system in a state of transient equilibrium (eq 12)

$$Ru(bpy)_3^{2+} + Ru(phen)_3^{3+} \underset{k_2}{\overset{k_1}{\rightleftarrows}} Ru(bpy)_3^{3+} + Ru(phen)_3^{2+} \qquad (12)$$

followed by the slower back-reactions which involve Fe^{2+} (eq 13 and 14).

$$Ru(bpy)_3^{3+} + Fe^{2+} \xrightarrow{k_3} Ru(bpy)_3^{2+} + Fe^{3+} \qquad (13)$$

$$Ru(phen)_3^{3+} + Fe^{2+} \xrightarrow{k_4} Ru(phen)_3^{2+} + Fe^{3+} \qquad (14)$$

From reduction potential measurements, for eq 12, $K = k_1/k_2 = 1.0$ and $k_1 = k_2$. Also, from independent studies, $k_3 \sim k_4$,[3,15] and since Fe^{2+} was present in pseudo-first-order excess in the experiments, the first-order rate constants for each of the processes (eq 13) and (eq 14) can be represented as k_3' (= $k_3[Fe^{2+}]$).

If the concentrations at time t of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ are represented as B and B^+, and those of $Ru(phen)_3^{2+}$ and $Ru(phen)_3^{3+}$ as P and P^+, respectively, then $dB^+/dt = -k_1B^+P + k_2P^+B - k_3'B^+ = B^+(-k_1P - k_3') + k_1P^+B$. Similarly, $dP^+/dt = -k_1P^+B + k_2B^+P - k_4'P^+ = P^+(-k_1B - k_3') + k_1B^+P$. In terms of the total concentrations (Ru(II) + Ru(III)) of the bpy(C_T^B) and phen(C_T^P) complexes, and since $C_T^B = B + B^+$, $C_T^P = P + P^+$,

$$\frac{dB^+}{dt} = B^+(-k_1C_T^P - k_3') + k_1P^+C_T^B \qquad (15)$$

$$\frac{dP^+}{dt} = P^+(-k_1C_T^B - k_3') + k_1B^+C_T^P \qquad (16)$$

Equations 15 and 16 represent a linear system of differential equations, which can be solved by the use of the substitutions B^+ . constant$_1$ × $e^{\lambda t}$ and P^+ = constant$_2$ × $e^{\lambda t}$.[24]

The solutions of the resulting equations are $\lambda = -k_3'$ and $\lambda = -k_1(C_T^B + C_T^P) - k_3'$ which gives for the integrated forms of eq 15 and 16:

$$B^+ = C_1e^{-k_3't} + C_2e^{-\{k_3'+k_1(C_T^B+C_T^P)\}t} \qquad (17)$$

$$P^+ = (C_T^P/C_T^B)C_1e^{-k_3't} - C_2e^{-\{k_3'+k_1(C_T^B+C_T^P)\}t} \qquad (18)$$

If ϵ_B, ϵ_{B^+}, ϵ_P, ϵ_{P^+} represent the molar extinction coefficients of the four ions at a given wavelength ($Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$ are essentially transparent in the visible), then the absorbance A at any time t is given by

$$A = (\epsilon_BB + \epsilon_{B^+}B^+ + \epsilon_PP + \epsilon_{P^+}P^+)l$$

(l = path length), so that

$$A/l = (\epsilon_BC_T^B + \epsilon_PC_T^P) + B^+(\epsilon_{B^+} - \epsilon_B) + P^+(\epsilon_{P^+} - \epsilon_P)$$

or

$$(\epsilon_BC_T^B + \epsilon_PC_T^P) - A/l = B^+(\epsilon_B - \epsilon_{B^+}) + P^+(\epsilon_P - \epsilon_{P^+})$$

Since the factor $(\epsilon_BC_T^B + \epsilon_PC_T^P)l$ represents the absorbance of the reaction at completion (A_∞), the left-hand side of this equation = $(A_\infty - A_t)/l = \Delta A/l$. Substituting for B^+ and P^+ from eq 17 and 18,

$$\frac{\Delta A}{l} = C_1([\epsilon_B - \epsilon_{B^+}] + (C_T^P/C_T^B)[\epsilon_P - \epsilon_{P^+}])e^{-k_3't} + C_2([\epsilon_B - \epsilon_{B^+}] - [\epsilon_P - \epsilon_{P^+}])e^{-\{k_3'+k_1(C_T^B+C_T^P)\}t} \qquad (19)$$

At long t, the second term on the RHS rapidly becomes small so that the reaction is dominated by the first term, i.e.

$$\Delta A \sim lC_1(\Delta\epsilon_B + (C_T^P/C_T^B)\Delta\epsilon_P)e^{-k_3't} \qquad (20)$$

whence k_3' can be obtained from plots of ln ΔA vs. t. Furthermore, the contribution to ΔA at small t can be obtained by extrapolation. Consequently, rearranging eq 19 gives,

$$\Delta(\Delta A) = \Delta A - lC_1(\Delta\epsilon_B + (C_T^P/C_T^B)\Delta\epsilon_P)e^{-k_3't} = lC_2(\Delta\epsilon_B - \Delta\epsilon_P)e^{-\{k_3'+k_1(C_T^B+C_T^P)\}t} \qquad (21)$$

so that a plot of ln $(\Delta(\Delta A))$ vs. t at the early part of the reaction should give a first-order plot with slope $k_{obsd} = k_3' + k_1(C_T^B + C_T^P)$. Since k_3' is obtained from the data at long t, and C_T^B and C_T^P are known, k_1 (the rate of electron exchange) can be calculated using the formula in eq 22.

$$k_1 = \frac{k_{obsd} - k_3'}{C_T^B + C_T^P} \qquad (22)$$

For the reactions with $Fe(phen)_3^{2+}$ present, following flash photolysis and quenching, reaction 10 occurred followed by reaction 23.

$$Ru(bpy)_3^{3+} + Fe(phen)_3^{2+} \underset{\Delta G\,=\,-0.184\text{ V}}{\xrightarrow{k_5}} Ru(bpy)_3^{2+} + Fe(phen)_3^{3+} \qquad (10)$$

$$Fe(phen)_3^{3+} + Fe(H_2O)_6^{2+} \xrightarrow{k_6} Fe(phen)_3^{2+} + Fe(H_2O)_6^{3+} \qquad (23)$$

Under conditions where $Fe(phen)_3^{2+}$ and $Fe(H_2O)_6^{2+}$ are present in excess, the kinetic analysis simplifies to the conventional solution for a series of consecutive first-order reactions:

$$[Ru(bpy)_3^{3+}]_t = [Ru(bpy)_3^{3+}]_0e^{-k_5't} \qquad (24)$$

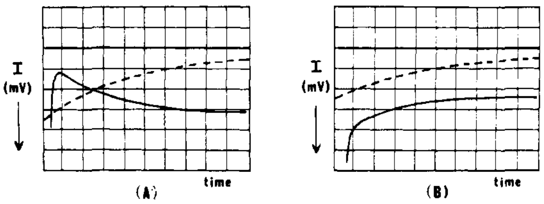


Figure 1. Oscilloscope trace following flash photolysis of a solution containing $Ru(bpy)_3^{2+}$ (3.0×10^{-6} M), $Fe(phen)_3^{2+}$ (2.5×10^{-6} M), $Fe(H_2O)_6^{3+}$ (4.0×10^{-3} M), and $Fe(H_2O)_6^{2+}$ (3.0×10^{-5} M at λ 510 nm (A) and λ 450 nm (B): - - -, 50 μs/div; —, 100 ms/div; T = 25 °C; μ = 1.0 M.

and

$$[Fe(phen)_3^{3+}]_t = \frac{[Ru(bpy)_3^{3+}]_0 k_5'}{k_6' - k_5'}(e^{-k_5't} - e^{-k_6't}) \quad (25)$$

where $k_5' = k_5[Fe(phen)_3^{2+}]$ and $k_6' = k_6[Fe(H_2O)_6^{2+}]$. Accordingly, k_5' can be directly measured and k_6' calculated, or if $k_5' \gg k_6'$ the two reactions can be observed as independent first-order processes.

Analysis of Kinetic Data. The transmittance data at each wavelength were converted to changes in absorbance (ΔA) and analyzed on a Raytheon 706 computer. The kinetic analysis described above for the $Ru(bpy)_3^{2+}$ + $Ru(phen)_3^{2+}$ system is a closed form equation describing two consecutive first-order reactions. Two important aspects of the rate law enabled analysis of the data to be accomplished without the use of Fourier transformation or the use of a Simplex program. Firstly, the two rate constants are separated into different exponential terms. Secondly, the preexponential factors are the difference and sum of two large numbers. Thus the first term appears as a small perturbation on the second term and the second reaction accounts for virtually all of the changes in absorbance after several half-lives of the first reaction have passed. In order to separate the two reactions as cleanly as possible, the experimental conditions were adjusted such that the rate of the second reaction was two or more orders of magnitude slower than the first. Thus the second reaction could be analyzed with a simple first-order (ln ΔA vs. t) plot (eq 20). To analyze the first reaction a theoretical baseline was calculated by extrapolation of absorbance changes due to the second reaction back to time zero. The difference between the theoretical and observed changes in absorbance was analyzed with an ln ΔA vs. t plot (eq 21). The rate constant for the first reaction is extremely sensitive to the extrapolated y intercept of the theoretical baseline. An iteration loop was written into the program which adjusted the theoretical baseline to give the best fit as determined by the correlation coefficient of a least-squares routine. In every case the standard deviation of the slope of the best fit was proportionately smaller than any other.

For the $Ru(bpy)_3^{3+}$ + $Fe(phen)_3^{2+}$ system, the basic analysis was the same except that after extrapolation of the slower reaction (k_6') back to zero, the ln ΔA vs. t plot of the faster reaction gave the rate constant k_5' directly.

A copy of the computer programs used is available upon request.

Results

Following flash photolysis of a solution containing $Ru(bpy)_3^{2+}$ (3.0×10^{-6} M), $Fe(phen)_3^{2+}$ (2.5×10^{-6} M), $Fe(H_2O)_6^{3+}$ (4.0×10^{-3} M), and $Fe(H_2O)_6^{2+}$ (3.0×10^{-5} M), typical transmittance-time plots at 510 and 450 nm are shown in Figure 1. Quenching of $Ru(bpy)_3^{2+*}$ and formation of redox intermediates occur during the lifetime of the flash. The signal in the first division of the fast scan is due mainly to the scattered light of the flash. At 510 nm, the 50 μs/division trace shows an absorbance decrease due to oxidation of $Fe(phen)_3^{2+}$ to $Fe(phen)_3^{3+}$ (reaction 10). The slower scan (absorbance increase) represents the back-reaction in which $Fe(phen)_3^{2+}$ is regenerated (reaction 23). The same experiment monitored at 450 nm (Figure 1) shows both reactions as absorbance increases, as at this wavelength the fast reaction is observed as mainly $Ru(bpy)_3^{3+}$ being reduced to $Ru(bpy)_3^{2+}$. The $Ru(bpy)_3^{3+}$ and $Fe(phen)_3^{3+}$ complexes are relatively transparent in the visible region. Qualitatively, the difference spectra for both processes in the region between 360 and 540 nm agreed with the difference spectra predicted by reactions 10 and 23. A solution made up without added $Ru(bpy)_3^{2+}$ showed no transient behavior following flash photolysis, indicating that the excited state or states of $Fe(phen)_3^{2+}$ arising from visible photolysis are too short-lived to undergo electron transfer quenching processes under the conditions of the experiment. Rate constants for the two processes obtained by flash photolysis are given in Table I.

Table I. Rate Constant Data for the Reactions between $Ru(bpy)_3^{3+}$ and $Fe(phen)_3^{2+}$ (k_5) and between $Fe(phen)_3^{3+}$ and $Fe(H_2O)_6^{2+}$ (k_6)

T (°C)	μ (M)	$[H^+]$ (M)	$k_5{}^a$ ($M^{-1} s^{-1}$)	$k_6{}^a$ ($M^{-1} s^{-1}$)
25.0	1.0	1.0	1.8×10^9	5.4×10^4
25.0	0.10	0.076	1.3×10^9	6.4×10^4

[a] Error limit estimated as ±10% from the standard deviation of the least-squares analysis at a 95% probability level.

Flash photolysis of a solution containing initially $Ru(bpy)_3^{2+}$, $Ru(phen)_3^{2+}$, $Fe(H_2O)_6^{3+}$, and $Fe(H_2O)_6^{2+}$ (Figure 2) results in electron transfer quenching of both $Ru(bpy)_3^{2+*}$ and $Ru(phen)_3^{2+*}$. However, at equal initial concentrations of $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$, an excess of $Ru(phen)_3^{3+}$ is produced and flash photolysis is followed by reaction 26.

$$Ru(phen)_3^{3+} + Ru(bpy)_3^{2+} \rightarrow Ru(phen)_3^{2+} + Ru(bpy)_3^{3+} \quad (26)$$

which takes the system to equilibrium (eq 12). Reduction potential measurements indicate that formal potentials for the $Ru(bpy)_3^{3+/2+}$ and $Ru(phen)_3^{3+/2+}$ couples are virtually the same (1.30 and 1.31 V vs. NHE at 25 °C)[25,26] so that K_{eq} = 1.0 and $k_1 = k_2$. The equilibration reaction is followed by the slower reductions or $Ru(bpy)_3^{3+}$ and $Ru(phen)_3^{3+}$ by $Fe(H_2O)_6^{2+}$, and as mentioned previously $k_3 \sim k_4$ from previous work.[3,15]

$$Ru(bpy)_3^{3+} + Fe(H_2O)_6^{2+} \xrightarrow{k_3} Ru(bpy)_3^{2+} + Fe(H_2O)_6^{3+} \quad (13)$$

$$Ru(phen)_3^{3+} + Fe(H_2O)_6^{2+} \xrightarrow{k_4} Ru(phen)_3^{2+} + Fe(H_2O)_6^{3+} \quad (14)$$

Evidence for the two independent processes is shown in the oscillographic trace in Figure 2.

The data treatment used to obtain k_1 and k_3 from oscillographic traces was presented in a previous section. For ease of calculation, the initial concentrations of $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ were made the same so that after the equilibration reaction the concentrations of $Ru(bpy)_3^{3+}$ and $Ru(phen)_3^{3+}$ were the same. In a typical experiment the concentrations of reagents used were $[Ru(phen)_3^{2+}]$ = $[Ru(bpy)_3^{2+}]$ = 3.0×10^{-6} M, $[Fe(H_2O)_6^{2+}]$ = 3.0×10^{-5} M and $[Fe(H_2O)_6^{3+}]$ = 4.0×10^{-3} M. Rate constant data for both the equilibration reaction k_1 and for the back-electron transfer reactions are given in Table II. The data for the back-electron transfer reactions are in good agreement with the results obtained earlier by flash photolysis and reproduce the unusual feature that the rate constants decrease slightly with an increase in temperature (Table II).[1,3,15]

From the data at μ = 0.10, the activation enthalpy ($\Delta H^{\ddagger}$) for the establishment of the equilibrium (eq 12) was obtained

Table II. Rate Constant Data for the Reaction between $Ru(phen)_3^{3+}$ and $Ru(bpy)_3^{2+}$ (k_1) and for the Reductions of $Ru(bpy)_3^{3+}$ and $Ru(phen)_3^{3+}$ by $Fe(H_2O)_6^{2+}$ (k_3)

T (°C)	μ (M)	$[H^+]$ (M)	$k_1{}^a$ (M^{-1} s^{-1})	$k_3{}^b$ (M^{-1} s^{-1})
50.0	0.10	0.076	9.6×10^8	1.3×10^6
35.0	0.10	0.076	7.6×10^8	1.4×10^6
25.0	0.10	0.076	4.2×10^8	1.4×10^6
15.0	0.10	0.076	2.0×10^8	1.5×10^6
5.0	0.10	0.076	1.4×10^8	1.5×10^6
25.0	1.0	1.0	1.2×10^9	1.2×10^6

[a] Error limit estimated as ±20% from the standard deviation of the least-squares analysis at a 95% probability level. [b] Estimated error ±10%.

from a plot of ln k_1/T vs. $1/T$. At each temperature the activation free energy ($\Delta G^{\ddagger}$) and activation entropy ($\Delta S^{\ddagger}$) were calculated. The activation parameters obtained were $\Delta G^{\ddagger}$(25 °C) = 5.7 ± 0.2 kcal/mol, $\Delta H^{\ddagger}$ = 7.7 ± 1.5 kcal/mol, and $\Delta S^{\ddagger}$ = −6.6 ± 0.4 eu. The error limit on $\Delta H^{\ddagger}$ is approximated by the maximum and minimum slopes that could reasonably be assigned in the plots of ln (k_1/T) vs. $1/T$. The error limit in $\Delta S^{\ddagger}$ indicates the spread of the values of $\Delta S^{\ddagger}$ calculated at all temperatures using the value $\Delta H^{\ddagger}$ = 7.7 kcal/mol.

Discussion

Application of the Flash Photolysis Relaxation Technique. The Use of Differential Excitation Flash Photolysis to Measure Rates of Self-Exchange. As mentioned above, with the proper design of chemical systems, flash photolysis can be used to measure the rates of rapid electron transfer reactions. Two different approaches were exploited here. Using low concentrations of $Ru(bpy)_3^{2+}$ and fairly high quencher concentrations, the diffusion-controlled quenching of $Ru(bpy)_3^{2+*}$ by $Fe(H_2O)_6^{3+}$ (eq 2)

$$Ru(bpy)_3^{2+*} + Fe(H_2O)_6^{3+} \rightarrow Ru(bpy)_3^{3+} + Fe(H_2O)_6^{2+} \quad (2)$$

$$k(25\ °C) = 2.9 \times 10^9\ M^{-1}\ s^{-1}\ {}^{1,3}$$

occurs during the flash to give the redox products $Fe(H_2O)_6^{2+}$ and $Ru(bpy)_3^{3+}$ in low concentration. For example, with $[Fe(H_2O)_6^{3+}] = 4 \times 10^{-3}$ M the half-time for reaction 2 is 0.06 μs while the duration of the flash in a typical experiment is ~20 to ~30 μs. The back-reaction between $Fe(H_2O)_6^{2+}$ and $Ru(bpy)_3^{3+}$ is slower by a factor of 3000 and occurs on a considerably longer time scale. If $Fe(phen)_3^{2+}$ is added to the solution initially, the more rapid reaction between $Fe(phen)_3^{2+}$ and $Ru(bpy)_3^{3+}$ (eq 10) intervenes

$$Ru(bpy)_3^{3+} + Fe(phen)_3^{2+} \xrightarrow{k_5} Ru(bpy)_3^{2+} + Fe(phen)_3^{3+} \quad (10)$$

and can be followed directly. Reaction 10 goes essentially to completion (K = 1300)[25,26] and is followed by eq 23 which returns the system to equilibrium.

$$Fe(phen)_3^{3+} + Fe(H_2O)_6^{2+} \rightarrow Fe(phen)_3^{2+} + Fe(H_2O)_6^{3+} \quad (23)$$

The value obtained for k_5 in 1.0 M $HClO_4$ (k(25 °C) = 1.8 × 10^9 M^{-1} s^{-1}) is in only fair agreement with the value obtained earlier by Holzwarth and Jurgensen in 1 M H_2SO_4 (3.3 × 10^9 M^{-1} s^{-1}) using a continuous flow method which involved several numerical approximations.[20] The rate of the back-reaction between $Fe(H_2O)_6^{2+}$ and $Fe(phen)_3^{3+}$ is in reasonable agreement with data obtained earlier by stopped-flow techniques.[14]

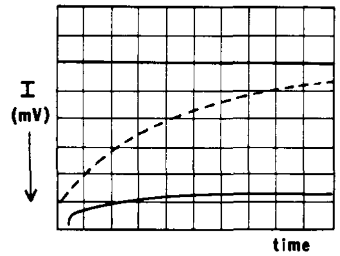


Figure 2. Oscilloscope trace following flash photolysis of a solution containing initially $Ru(bpy)_3^{2+}$ (3.0 × 10^{-6} M), $Ru(phen)_3^{2+}$ (3.0 × 10^{-6} M), $Fe(H_2O)_6^{2+}$ (3.0 × 10^{-5} M), and $Fe(H_2O)_6^{3+}$ (4.0 × 10^{-3} M) at λ 450 nm: - - -, 100 μs/div; —, 5 ms/div; T = 25 °C; μ = 1.0 M.

It is clear that the flash photolysis relaxation technique can be applied to reactions related to eq 10, where the limitations appear to include that the added reducing agent cannot itself undergo efficient visible photochemistry, and that its rate of reaction with $Ru(bpy)_3^{3+}$ must fall in the same or a shorter time range than the rate of the back-reaction with $Fe(H_2O)_6^{2+}$.

The approach taken for the estimation of the $Ru(bpy)_3^{3+/2+}$ self-exchange rate relied on differences in spectral and excited state properties between the bpy and phen systems. Electrochemical studies on a series of bpy and phen complexes have shown that in complexes which are structurally analogous, Ru(III)/Ru(II) reduction potentials are essentially identical. However, the optical spectra of the bpy and phen complexes are different and so reactions like eq 27 and 28 can be followed directly using stopped-flow techniques. Given the similarities in the bpy and phen ligand systems and the fact that K_{eq} = 1.0, rate constants for reactions like eq 27 and 28 provide a good estimate for rates of the corresponding self-exchange processes for the couples $Ru(bpy)(NH_3)_4^{3+/2+}$, $Ru(phen)(NH_3)_4^{3+/2+}$ and $Ru(bpy)_2(py)Cl^{2+/+}$, $Ru(phen)_2(py)Cl^{2+/+}$.

$$Ru(bpy)(NH_3)_4^{3+} + Ru(phen)(NH_3)_4^{2+} \rightarrow Ru(bpy)(NH_3)_4^{2+} + Ru(phen)(NH_3)_4^{3+} \quad (27)^{17}$$

$$Ru(phen)_2(py)Cl^{2+} + Ru(bpy)_2(py)Cl^{+} \rightarrow Ru(phen)_2(py)Cl^{+} + Ru(bpy)_2(py)Cl^{2+} \quad (28)^{27}$$

In a solution containing $Ru(bpy)_3^{2+}$, $Ru(phen)_3^{2+}$ and $Fe(H_2O)_6^{3+}$, flash photolysis in the visible gives both $Ru(bpy)_3^{2+*}$ and $Ru(phen)_3^{2+*}$ and both excited states are quenched by $Fe(H_2O)_6^{3+}$ at or near the diffusion-controlled limit.[1,3] However, molar extinction coefficients for $Ru(phen)_3^{2+}$ are greater than for $Ru(bpy)_3^{2+}$ throughout the visible. Following flash photolysis, an excess of $Ru(phen)_3^{2+*}$ over $Ru(bpy)_3^{2+*}$ can be produced when $Ru(phen)_3^{2+}$ and $Ru(bpy)_3^{2+}$ are present in equal amounts because of the higher absorptivity of $Ru(phen)_3^{2+}$. The lifetime of $Ru(phen)_3^{2+*}$ is also slightly greater than the lifetime of $Ru(bpy)_3^{2+*}$ under the conditions used in the experiments (0.8 vs. 0.6 μs).[3] The existence of both effects apparently leads to the production of an excess of $Ru(phen)_3^{3+}$ over $Ru(bpy)_3^{3+}$ following photolysis and quenching. Consequently, differential excitation and quenching leads to a situation where the Ru(III) components of the equilibrium in eq 12 are created rapidly in nonequilibrium amounts. The system then undergoes chemical relaxation to a state of transient equilibrium which is followed by the slower reduction of $Ru(phen)_3^{3+}$ and $Ru(bpy)_3^{3+}$ by $Fe(H_2O)_6^{2+}$. The latter reactions return the system to its initial state of equilibrium. The relaxation step can be followed directly because of the differences in spectral properties between the bpy and phen complexes.

The use of differential excitation flash photolysis which was exploited here should find application in related chemical problems involving rapid electron transfer.

The Self-Exchange Reaction. Earlier NMR[18] and stopped-flow[22] work by Wahl and co-workers has shown that M(II)/M(III) (Fe, Ru, Os) polypyridine self-exchange rates are in the range 3×10^6 to 3×10^7 M^{-1} s^{-1} at 25 °C in nonaqueous solvents like acetonitrile. The rate of the net reaction between $Ru(phen)_3^{3+}$ and $Ru(bpy)_3^{2+}$ in acidic aqueous solution measured by flash photolysis is considerably faster indicating that the self-exchange rates are sensitive to both the nature of the solvent and of added electrolyte which is to be expected. Using the transfer diffusion technique. Ruff and Zimonyi have reported that the self-exchange rate between $Fe(phen)_3^{2+}$ and $Fe(phen)_3^{3+}$ is $(3.3 \pm 1.4) \times 10^8$ M^{-1} s^{-1} at 25 °C in an aqueous solution saturated with Na_2SO_4.[21]

From the results of a series of electron transfer rate measurements by Holzwarth and Jurgensen[20] and from rate constants obtained for excited state quenching reactions,[1,3] a reasonable estimate for the diffusion-controlled limit in 1 M $HClO_4$ at 25 °C for the $Ru(bpy)_3^{2+}$-$Ru(bpy)_3^{3+}$ self-exchange is $k_D \sim 3 \times 10^9$ M^{-1} s^{-1}. Under the same conditions, the experimental value (measured as the net reaction between $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{3+}$ (eq 26) is 1.2×10^9 M^{-1} s^{-1} which appears to be significantly below the diffusion-controlled limit.

Corrections for diffusion effects can be made using eq 29[28]

$$\frac{1}{k_{obsd}} = \frac{1}{k_D} + \frac{1}{k_{act}} \tag{29}$$

which allows the rate constant for chemically activated electron transfer. k_{act} (the rate constant if diffusion were infinitely rapid), to be estimated. Using eq 29, k_{act} can be estimated to be 2.0×10^9 M^{-1} s^{-1} for the $Ru(bpy)_3^{3+/2+}$ self-exchange reaction.

The rate of the reaction between $Fe(phen)_3^{2+}$ and $Ru(bpy)_3^{3+}$ (k_{12}) can be estimated using the Marcus "cross reaction equation"

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2}$$

$$\log f = \frac{(\log K_{12})^2}{4 \log (k_{11}k_{22}/Z^2)}$$

and the activated self-exchange rates for $Ru(bpy)_3^{3+/2+}$ (2.0×10^9 M^{-1} s^{-1}) and $Fe(phen)_3^{3+/2+}$ (3.3×10^8 M^{-1} s^{-1}).[21] Using these values for k_{11} and k_{22}, $K_{12} = 1300$, and assuming that Z, the collision frequency between neutral molecules of the appropriate size in the reaction medium, is 10^{11} M^{-1} s^{-1}, gives $k_{12}(act) = 2.2 \times 10^{10}$. Using this value, $k_D = 3 \times 10^9$ M^{-1} s^{-1}. and eq 29, gives $k_{calcd} = 2.6 \times 10^9$ M^{-1} s^{-1} compared to the experimental value of 1.8×10^9 M^{-1} s^{-1}. Although the discrepancy between the two values is considerable it should be noted that if the actual value for the $Fe(phen)_3^{3+/2+}$ self-exchange under our conditions were 3.3×10^7 M^{-1} s^{-1}. k_{calcd} would be 2.2×10^9 M^{-1} s^{-1} which is nearly within experimental error of the measured value.

From Marcus theory the activation barrier for outer-sphere electron transfer is given by eq 30 where $\Delta G°_r{}'$ is the free energy change on electron transfer within the ion-pair of the reactants.

$$\Delta G^* = W_r + \frac{\lambda}{4}\left((1 + \frac{\Delta G°_r{}'}{\lambda}\right)^2 \tag{30}^{29}$$

In media of high ionic strength, the electrostatic repulsion term w_r is expected to be negligible and for a self-exchange reaction $\Delta G°_r{}' = 0$ which gives eq 31.

$$\Delta G^* = \frac{\lambda}{4} \tag{31}^{29}$$

The rate constant for reaction is given by

$$k = Z \exp[-(\lambda/4RT)] \tag{32}$$

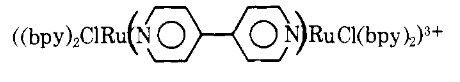
where Z was defined above and $\lambda/4$ is the reorganizational barrier, which includes contributions from rearrangements in both the inner- and outer-coordination spheres. Using $Z \sim 10^{11}$ M^{-1} s^{-1} [29] and $k = 2 \times 10^9$ M^{-1} s^{-1}, eq 32 gives for the activation barrier for electron transfer, $\lambda/4 = 2.3$ kcal/mol.

Contributions to $\lambda/4$ from inner-sphere reorganization should be negligible. M-N bond distances in $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_6^{3+}$ are nearly the same.[30] In $Fe(phen)_3^{2+}$ [31a] and $Fe(phen)_3^{3+}$,[31b] they are identical, and differences between $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ or between $Ru(phen)_3^{2+}$ and $Ru(phen)_3^{3+}$ should be negligible. The activation barrier to electron transfer must arise largely from changes in orientation and polarizability in outer-sphere solvent molecules giving $\lambda/4 \sim \Delta G_0^* \sim 2.3$ kcal/mol.

Using the dielectric continuum models of Hush[32] or Marcus,[29] ΔG_0^* can be estimated using eq 33 in which r_1 and r_2 are the molecular radii of the reacting ions, n^2 and D_s are the optical and static dielectric constants of the solvent, and e is the unit electron charge. For the reaction between $Ru(phen)_3^{3+}$ and $Ru(bpy)_3^{2+}$, using $r_1 = 7.1$ and $r_2 = 6.1$ Å and the values of n^2 and D_s for water, ΔG_0^* is calculated to be 3.5 kcal/mol.

$$\Delta G_0^* = \frac{e^2}{4}\left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{d}\right)\left(\frac{1}{n^2} - \frac{1}{D_s}\right) \tag{33}$$

ΔG_0^* has also been estimated to be ~4.0 kcal/mol in water for thermal electron transfer in the slightly smaller mixed-valence ion



(eq 34) using intervalence transfer measurements.[33]

$$((bpy)_2ClRu^{II}(4,4'\text{-}bpy)Ru^{III}Cl(bpy)_2)^{3+} \rightarrow ((bpy)_2ClRu^{III}(4,4'\text{-}bpy)Ru^{II}Cl(bpy)_2)^{3+} \tag{34}$$

The slightly lower value for ΔG_0^* calculated from the rate data (eq 32) can be attributed in part to the arbitrariness of using $Z = 10^{11}$. Better agreement would have been obtained if a slightly larger value had been used. However, three different approaches suggest the same conclusion. For the self-exchange reactions there is an activation barrier to electron transfer which arises from outer-sphere reorganization. Because of the large sizes of the reacting ions, the barrier is relatively small and the reactions have rates near the diffusion-controlled limit. If the conclusions reached here are correct, eq 29, 32, and 33 predict that the rates of $Ru(bpy)_3^{3+/2+}$ and $Ru(phen)_3^{3+/2+}$ self-exchange differ from the rate of the reaction between $Ru(phen)_3^{3+}$ and $Ru(bpy)_3^{2+}$ by only a few percent with the $Ru(phen)_3^{3+/2+}$ rate fastest and the $Ru(bpy)_3^{3+/2+}$ rate slowest.

There is considerable interest in electron transfer reactions involving $Ru(bpy)_3^{2+*}$ and related excited states.[1,3,34,35] The conclusions reached here are germane to the reactivity of the excited state and in particular to the excited state self-exchange reaction (eq 35).

$$\underset{(d^5)}{Ru(bpy)_3^{3+}} + \underset{(d^5\pi^*)}{Ru(bpy)_3^{2+*}} \rightarrow \underset{(d^5\pi^*)}{Ru(bpy)_3^{2+*}} + \underset{(d^5)}{Ru(bpy)_3^{3+}} \tag{35}$$

Excited state self-exchange differs from $Ru(bpy)_3^{3+/2+}$ self-exchange in that the exchanging electron and electron hole reside in a series of closely spaced, delocalized π^*(bpy) levels rather than in t_2(Ru) levels.[4,5]

Nonetheless, the outer-sphere reorganizational barrier should be identical for both reactions (eq 33) as should Z (eq 32). In the absence of long-range electron transfer in the excited state self-exchange or of significant structural differences either in Ru–N bonds or in the bpy ligands between $Ru(bpy)_3^{3+}$ and the excited state, the two self-exchange rates should be identical.

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Vibrational Spectra, Resonance Raman Spectra, and Electronic Spectra of the μ-Oxo-decachlorodiruthenium(IV) Ion

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Abstract: The infrared and Raman spectra of the complexes $K_4[Ru_2OCl_{10}]$, $Rb_4[Ru_2OCl_{10}]$, and $Cs_4[Ru_2OCl_{10}]$ have been recorded and the observed bands assigned. The $Ru_2OCl_{10}^{4-}$ ion displays the resonance Raman effect, most spectacularly for the potassium salt, when irradiated with an exciting line whose frequency falls within the contour of the lowest allowed band of the ion at ca. 20 000 cm^{-1}. These spectra are characterized by a large increase in the intensity of the Raman band arising from the ν_1(Ru–O–Ru), a_{1g}, stretching fundamental, together with the appearance of an overtone progression reaching $7\nu_1$ at room temperature and $12\nu_1$ at 100 K for the potassium salt. Six other progressions are also observed in the resonance Raman spectrum of this ion at room temperature (eight others at 100 K), in each of which it is ν_1 which acts as the progression forming mode. The observation of such progressions has permitted the determination of ω_1, x_{11}, and several cross terms x_{1n}. The ω_1 values decrease with increasing size of the cation (decreasing lattice energy), viz. 256.5 (K^+), 254.7 (Rb^+), and 249.9 (Cs^+) cm^{-1}. Excitation profiles for four of the Raman bands have been plotted. That for ν_1 reaches a maximum at ca. 20 000 cm^{-1}, from which observation it is concluded that the resonant electronic transition is the axially polarized, electric dipole allowed $^1A_{2u} \leftarrow {}^1A_{1g}$ component of the $(e_u^b)^4 (e_g)^3 (b_{2g})^2 (b_{1u})^2 (e_u^*)^1 \leftarrow (e_u^b)^4 (e_g^4) (b_{2g})^2 (b_{1u})^2$ transition of the Ru–O–Ru π-bond system; the observation that the depolarization ratio of ν_1 is $\approx 1/3$ at resonance confirms this conclusion. The results suggest the wider use of resonance Raman spectroscopy as a technique for the assignment of electric-dipole-allowed transitions.

There have been a number of recent reports of the observation of resonance Raman spectra from various inorganic molecules and ions.[1] Such spectra are characterized, among other things, by a very large enhancement to the intensity of a band arising from a totally symmetric fundamental of the molecule, together with the appearance of high intensity overtone progressions in this same mode. Several metal–metal bonded species which belong, or to a first approximation belong, to the D_{4h} point group, viz. the $Mo_2Cl_8^{4-}$ ion,[2] the $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ ions,[3] and the carboxylate-bridged species $Ru_2(O_2CR)_4Cl$ (R = CH_3 or n-C_4H_9),[4] have been particularly spectacular in this respect; irradiation within the contour of the lowest allowed transition of these formally multiply metal–metal bonded species has led, in each case, to the observation of long progressions in the (axial) metal–metal stretching fundamental, clearly demonstrating that the resonant electronic transition is also axially polarized, and thus of the $\delta^* \leftarrow \delta$ sort ($^1A_{2u} \leftarrow {}^1A_{1g}$).