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Kinetics and Mechanism of the Forward and Reverse Reactions between *N*,*N'*-Dimethyl-4,4'-bipyridinium and Hexacyanoferrate(II)[1a]

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Abstract: The kinetics of the hexacyanoferrate(III)-*N*,*N'*-dimethyl-4,4'-bipyridinium radical (MV^+) reaction was studied by a laser flash photolysis technique. The radical was generated, in the presence of $Fe(CN)_6^{3-}$, by quenching the excited state $^*Ru(bpy)_3^{2+}$ with MV^{2+}. The second-order rate constant for the $Fe(CN)_6^{3-}$–MV^+ reaction is $(7.6 \pm 0.5) \times 10^9$ M^{-1} s^{-1} at 23 °C and ionic strength 0.10 M. Comparison with the rate constants calculated for the diffusion-controlled reaction (4.7×10^9 M^{-1} s^{-1}) and the activation-controlled reaction (5.2×10^{12} M^{-1} s^{-1}, on the basis of self-exchange rate constants of 8.0×10^5 M^{-1} s^{-1} and 1.9×10^4 M^{-1} s^{-1} for the $MV^{2+/+}$ and $Fe(CN)_6^{3-/4-}$ couples, respectively) leads to the conclusion that the $Fe(CN)_6^{3-}$–MV^+ reaction is diffusion controlled. The rate constant for the $Fe(CN)_6^{4-}$–MV^{2+} reaction, calculated from the rate constant for the $Fe(CN)_6^{3-}$–MV^+ reaction and the appropriate equilibrium constant, is 2.4×10^{-5} M^{-1} s^{-1} at 23 °C and ionic strength 0.10 M. Microscopic reversibility considerations require that the $Fe(CN)_6^{4-}$–MV^{2+} reaction be controlled by the dissociation of the successor complex $Fe(CN)_6^{3-}|MV^+$. The thermal and optical electron transfers in the ion pair $Fe(CN)_6^{4-}|MV^{2+}$ and in related systems are analyzed and discussed.

In a recent paper,[2] Curtis, Sullivan, and Meyer calculated the internal electron-transfer rate constant (k_{et}) in the ion pair $MV^{2+}|Fe(CN)_6^{4-}$ (eq 1), where MV^{2+} is *N*,*N'*-dimethyl-4,4'-bipyridinium, using the properties of the outer-sphere, optical charge transfer band of the ion pair.[3,4] From the rate constant k_{et} and auxiliary thermodynamic information, the second-order rate constant for the overall reaction 2 was calculated as $(2-3) \times 10^{-4}$ M^{-1} s^{-1} in water at 23 °C and ionic strength 0.10 M. The value of k_2 calculated in this manner was found[2] to be in reasonable agreement with the value ~10^{-3} M^{-1} s^{-1} estimated from the Marcus cross-reaction equation and the values 8×10^6 M^{-1} s^{-1}[5] and 1.9×10^4 M^{-1} s^{-1}[6] for the self-exchange rate constants of the $MV^{2+/+}$ and $Fe(CN)_6^{3-/4-}$ couples, respectively.

$$MV^{2+}|Fe(CN)_6^{4-} \underset{k_{-et}}{\overset{k_{et}}{\rightleftharpoons}} MV^{+}|Fe(CN)_6^{3-} \qquad (1)$$

$$MV^{2+} + Fe(CN)_6^{4-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MV^{+} + Fe(CN)_6^{3-} \qquad (2)$$

In order to evaluate the validity of rate constants for electron transfer estimated from optical transitions,[7] it is important to compare, in as many systems as possible,[8] the estimated rate constants with the values determined experimentally. Therefore, we sought to measure the rate constant for reaction 2. Since the reaction is highly endoergonic ($K = 3.1 \times 10^{-15}$), it is necessary to measure the rate of the reverse reaction. This was accomplished by generating the methylviologen radical, MV^+, via the quenching of the excited state of tris(bipyridine)ruthenium(II) by methyl viologen, eq 3, possibly the most extensively[9-11] studied reaction in recent years. Hexacyanoferrate(III) was added in sufficient concentrations to prevent the occurrence of the back reaction, eq 4, and therefore the M^+–$Fe(CN)_6^{3-}$ reaction proceeded and its kinetics were measured.

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

$$Ru(bpy)_3^{3+} + MV^{+} \xrightarrow{k_4} Ru(bpy)_3^{2+} + MV^{2+} \qquad (4)$$

Experimental Section

Materials. Methyviologen chloride was purified as follows. The commercial material (BDH or Aldrich) was dissolved in hot methanol and treated with activated charcoal to remove a yellow impurity. After filtration and cooling of the resulting solution, white crystals formed and were collected and then air-dried. The measurements at 450 nm proved to be very sensitive to the presence of the yellow impurity. In contrast, measurements at 605 and 395 nm did not seem to be affected. $Ru(bpy)_3Cl_2{\cdot}6H_2O$, $K_3Fe(CN)_6$, and $K_4Fe(CN)_6{\cdot}2H_2O$ were purified by recrystallization from water. The amount of $Fe(CN)_6^{3-}$ present in solutions of $Fe(CN)_6^{4-}$ was determined by measuring the decrease in absorbance at 420 nm upon addition of ascorbic acid. The purification of the water and of the argon was described previously.[12] All other chemicals were reagent grade and were used as received.

Flash Photolysis Measurements. A solution containing the desired concentrations of $Ru(bpy)_3^{2+}$, MV^{2+}, buffer (phosphate, pH 6.8), and sufficient sodium chloride to maintain a 0.10 M ionic strength was placed in a 1-cm^2 fluorescence cell equipped with a Rotoflow valve. Dioxygen was removed by purging the solution with argon for about 30 min. Flash photolysis measurements were carried out in an apparatus similar to one described previously.[13] Monitoring wavelengths were 395, 450, and 605 nm. The molar absorbance of MV^+ at 395 nm was estimated by measuring the absorbance of a MV^+ solution at 605 and 395 nm by use of the interrogating system of the flash photolysis apparatus and taking the molar absorbance at 605 nm as 1.18×10^4 M^{-1} cm^{-1}.[14] Solutions containing MV^+ were obtained by steady-state irradiation of deaerated solutions 2.0×10^{-2} M in MV^{2+} and 0.65 M in 2-propanol with a 450-W xenon lamp.[12,15]

Results

Immediately following the laser pulse, solutions containing 4.2×10^{-5} $Ru(bpy)_3^{2+}$, 1.0×10^{-2} MV^{2+}, and $(1.6-5.1) \times 10^{-5}$ M $Fe(CN)_6^{3-}$ (pH 6.8, ionic strength 0.10 M, 23 ± 1 °C) were found to exhibit the characteristic absorption[16] of MV^+ at 605 and 395 nm and to have lost some of the $Ru(bpy)_3^{2+}$ absorbance at 450

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(2) Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 3833.

(3) Nakahara, A.; Wang, J. H. *J. Phys. Chem.* **1963**, *67*, 496.

(4) Toma, H. E. *Can. J. Chem.* **1979**, *57*, 2079.

(5) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K *Chem. Phys. Lett.* **1979**, *61*, 522; *J. Am. Chem. Soc.* **1979**, *101*, 4815.

(6) Haim, A.; Sutin, N. *Inorg. Chem.* **1976**, *15*, 476.

(7) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086.

(8) Meyer, T. *Chem. Phys. Lett.* **1979**, *64*, 417.

(9) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 4710.

(10) Kalyanasundaram, K.; J.; Grätzel, M. *Helv. Chim. Acta* **1978**, *61*, 2720.

(11) Keller, P.; Maradpour, A.; Amonyal, E.; Kagan, H. B. *Nouv. J. Chem.* **1980**, *4*, 377.

(12) Leopold, K.; Haim, A. *Inorg. Chem.* **1978**, *17*, 3138.

(13) Brunschwig, B.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *100*, 7568.

(14) Trudinger, P. A. *Anal. Biochem.* **1970**, *36*, 222.

(15) Hopkin, A. S.; Ledwith, A.; Stam, M. F. *Chem. Commun.* **1970**, 494.

(16) Kosower, E. M.; Cotter, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 5524.

0002-7863/82/1504-3363$01.25/0

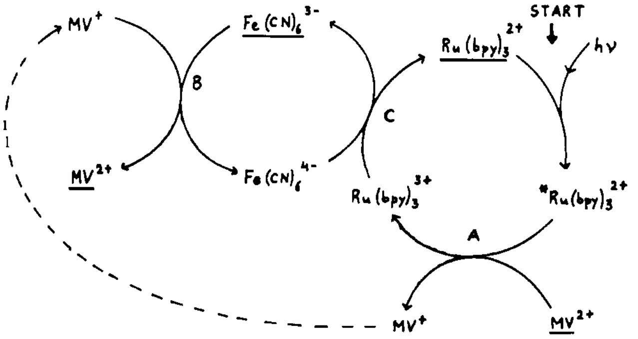

Figure 1. Reactions involving the $Ru(bpy)_3^{2+/3+}$, $Fe(CN)_6^{4-/3-}$, $MV^{+/2+}$, and $^*Ru(bpy)_3^{2+}$–$Ru(bpy)_3^{3+}$ couples. The species underlined are present initially. The sequence of events is initiated by the flash (start). The reactions occur in the order A, B, C, which correspond to reaction 3, the reverse of reaction 2, and reaction 5, respectively.

nm. Then two successive reactions were observed in the microsecond time scale. The first reaction corresponds to the disappearance of MV^+ (decrease in absorbance at 605 and 395 nm) and is followed by the recovery of $Ru(bpy)_3^{2+}$ (increase in absorbance at 450 nm). The formation and disappearance of MV^+ are associated with reaction 3 and the reverse of reaction 2, respectively. The return of $Ru(bpy)_3^{2+}$ is caused by the reaction (eq 5) of the $Fe(CN)_6^{4-}$ produced in the reverse of reaction 2 with

$$Fe(CN)_6^{4-} + Ru(bpy)_3^{3+} \xrightarrow{k_5} Fe(CN)_6^{3-} + Ru(bpy)_3^{2+} \quad (5)$$

the $Ru(bpy)_3^{3+}$ produced in the quenching step in the reverse of reaction 2 with the $Ru(bpy)_3^{3+}$ produced in the quenching step (eq 3). For clarification of the sequence of events following the flash, the compete reaction scheme is presented in Figure 1 utilizing the format analogous to that applicable to catalytic cycles. It will be seen that, at the completion of the sequence of reactions initiated by the laser pulse (eq 3, –2, and 5, or A, B, and C in the figure), the system returns to the initial state. The complete reversibility of the system was established by measuring the absorption spectrum of the solution before and after repeated laser flashes; no changes in absorbance were observed.

The measurements at 605 nm are the simplest to interpret, because at this wavelength only MV^+ has any absorbance. Plots of ln $(A_t - A_\infty)$ vs. t were linear, and the slopes yielded (least-squares analysis) pseudo-first-order rate constants, which are listed in Table I. These constants were found to increase linearly with $[Fe(CN)_6^{3-}]$, the slope of k_{obsd} vs. $[Fe(CN)_6^{3-}]$ being $(7.0 \pm 0.5) \times 10^9$ M^{-1} s^{-1}. The observation of first-order absorbance plots and a first-order dependence with respect to $Fe(CN)_6^{3-}$ are surprising when it is recognized that, under our experimental conditions, each laser pulse yields approximately 1.5×10^{-5} M MV^+ and $Ru(bpy)_3^{3+}$ (calculated from the measured $A_0 - A_\infty$ value at 605 nm and the molar absorbance of MV^+). Since the concentration of $Fe(CN)_6^{3-}$ in our experiments varied between 1.1 and 4.5×10^{-5} M, it is apparent that pseudo-first-order conditions with respect to MV^+ did not obtain even at the highest $[Fe(CN)_6^{3-}]$ used. However, as the reverse of reaction 2 takes place, $Fe(CN)_6^{4-}$ is produced, which in turn reacts with $Ru(bpy)_3^{3+}$ to regenerate $Fe(CN)_6^{3-}$. Thus it is conceivable for $Fe(CN)_6^{3-}$ to reach a constant steady-state concentration and, therefore, for the kinetics of disappearance of MV^+ to be effectively pseudo first order. In fact, this situation obtains, as shown by a numerical simulation of the system. The differential rate equations for the system of reactions given by the reverse of eq 2 and eq 5 and 4 were integrated by using the Runge–Kutta approximation.[18] Values of the rate constants and of initial concentrations were taken to be representative of our experimental conditions: k_{-2} = 8.5×10^9 M^{-1} s^{-1}, $k_5 = 8.9 \times 10^9$ M^{-1} s^{-1} (see below), $k_4 = 4.0 \times 10^9$ M^{-1} s^{-1},[17] $[Ru(bpy)_3^{3+}]_0 = [MV^+]_0 = 1.5 \times 10^{-5}$ M, $[Ru(bpy)_3^{2+}]_0 = 2.5 \times 10^{-5}$ M, $[Fe(CN)_6^{3-}]_0 = (1.6–5.1) \times 10^{-5}$ M, and $[Fe(CN)_6^{4-}]_0 = 0$. The calculations showed that after a rapid, initial decrease (for example, for $[Fe(CN)_6^{3-}]_0 = 2.5 \times 10^{-5}$ M, after 3.6 μs the concentration reaches the value 1.97×10^{-5} M), the concentration of $Fe(CN)_6^{3-}$ remained essentially constant at a value 10–30% lower than the initial value (from 1.93×1^{-5} M to 2.08×10^{-5} M between 4.8 and 21.6 μs) during the period of time when useful kinetic data of the disappearance of MV^+ are obtained. Moreover, calculated ln $(A_t - A_\infty)$ vs. time curves from the MV^+ concentration yielded excellent straight lines. The slopes of the lines $(1.83 \times 10^5$ $s^{-1})$ when divided by the effective concentration of $Fe(CN)_6^{3-}$ $(1.98 \times 10^{-5}$ M) gave back values $(9.2 \times 10^9$ M^{-1} $s^{-1})$ within 7% of the input constant of 8.5×10^9 M^{-1} s^{-1}. On the basis of the Runge–Kutta calculations, it is evident that our measured values of k_{-2} have to be corrected for the effective concentration of $Fe(CN)_6^{3-}$, and in this manner we estimate that $k_{-2} = (7.6 \pm 0.5) \times 10^9$ M^{-1} s^{-1}. Turning to the measurements at 395 nm, we found that the absorbance decreased, went through a minimum, then increased, and finally reached the initial value. This observation is readily interpreted on the basis of the reverse of reaction 2, reaction 5, and the relative magnitudes of the molar absorbances of $Ru(bpy)_3^{3+}$ and $Ru(bpy)_3^{2+}$ at 395 nm (2.2×10^3 and 5.5×10^3 M^{-1} cm^{-1}, respectively). Reaction 5 is not sufficiently rapid to keep up with the reverse of eq 2, and therefore as the MV^+ concentration reaches a value near 0, a significant fraction of the ruthenium is still present as $Ru(bpy)_3^{3+}$, and the absorbance of the solution is lower than the initial value. As reaction 5 proceeds to completion, then the absorbance change associated with the convertion of $Ru(bpy)_3^{3+}$ to $Ru(bpy)_3^{2+}$ is seen as a tail-end increase. Plots of ln $(A_t - A_\infty)$, where A_∞ was taken to be the minimum in the absorbance vs. t curves, yielded reasonably good straight lines, and the corresponding values of k_{obsd} are listed in Table I. It will be seen that the values of k_{obsd} at 395 nm are 20–30% higher than the values of k_{obsd} at 605 nm. Again, by using the Runga–Kutta method, the concentrations of all the species were calculated, and from the known molar absorbances, plots of ln $(A_t - A_\infty)$ vs. t were constructed. Reasonably good linear plots, although noticeably concave downward, were obtained, and values of k_{obsd} were calculated. These were found to be 15–25% higher (for the simulation indicated above, $k_{obsd} = 2.14 \times 10^5$ s^{-1}) than the k_{obsd} values calculated from the 605-nm data, as found for the experimental measurements. We conclude, therefore, that the 395-nm data are perfectly compatible with the 605-nm data but utilize the latter data to obtain the value of k_{-2}.

Table I. Rate Constants for $Fe(CN)_6^{3-}$–MV^+ and $Fe(CN)_6^{4-}$–$Ru(bpy)_3^{3+}$ Reactions[a]

10^5-$[Fe(CN)_6^{3-}]$, M	$10^{-5}k_{obsd}$, s^{-1} [b]	$10^{-5}k_{obsd}$, s^{-1} [c]	$10^{-5}k_{obsd}$ [d]
1.62[e]	1.16 ± 0.04, 1.17 ± 0.17	1.34 ± 0.05, 1.15 ± 0.03	6.98 ± 0.72
	1.04 ± 0.08, 1.23 ± 0.04	1.41 ± 0.11	
2.59[f]	1.61 ± 0.29, 1.62 ± 0.11	2.14 ± 0.15, 2.21 ± 0.15	
	1.88 ± 0.15	2.22 ± 0.08	
3.36[g]	2.50 ± 0.13, 2.03 ± 0.19	2.87 ± 0.19	7.14 ± 0.44
5.08[h]	3.43 ± 0.20	3.79 ± 0.14	
20.0[i]		3.5 ± 0.6[j]	7.96 ± 0.77

[a] At 23 °C, $[Ru(bpy)_3^{2+}] = 4.2 \times 10^{-5}$ M, $[MV^{2+}] = 1.0 \times 10^{-2}$ M, ionic strength 0.10 M, pH 6.8. Each entry is the average of 3–8 replicate determinations. [b] $Fe(CN)_6^{3-}$–MV^+ reaction; measurements at 605 nm. [c] $Fe(CN)_6^{3-}$–MV^+ reaction; measurements at 395 nm. [d] $Fe(CN)_6^{4-}$–$Ru(bpy)_3^{3+}$ reaction, measurements at 450 nm. [e] Effective $[Fe(CN)_6^{3-}]$ is 1.14×10^{-5} M. [f] Effective $[Fe(CN)_6^{3-}]$ is 2.10×10^{-5} M. [g] Effective $[Fe(CN)_6^{3-}]$ is 2.89×10^{-5} M. [h] Effective $[Fe(CN)_6^{3-}]$ is 4.50×10^{-5} M. [i] Concentration of $Fe(CN)_6^{4-}$ added. [j] Observed rate coefficient in units of cm s^{-1}. Average of 30 replicate determinations.

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(17) A variety of values in the range $(1–8) \times 10^9$ M^{-1} s^{-1} has been reported for k_4. The value 4.0×10^9 M^{-1} s^{-1} is measured in our laboratories under the same conditions as the $Fe(CN)_6^{3-}$ studies.

(18) Carnahan, B.; Luther, H. A.; Wilks, J. O. "Applied Numerical Methods"; Wiley: New York, 1969; p 360.

The absorbance increases at 450 nm, associated with reaction 5, were found to be second order, as plots of $1/(A_t - A_\infty)$ vs. t were linear. If the concentrations of Fe(CN)$_6^{4-}$ and Ru(bpy)$_3^{3+}$ are equal, the slopes of such plots are equal to $k_5/\Delta A_m$, where ΔA_m is the difference between the molar absorbances of Ru(bpy)$_3^{2+}$ and Ru(bpy)$_3^{3+}$ at 450 nm, 1.21 × 10^4 M^{-1} cm^{-1}. The slopes of such plots, listed in Table I, were found to increase with increasing [Fe(CN)$_6^{3-}$], in contrast with what was expected for second-order, equal concentration kinetics. The Runga–Kutte calculations indicated that the assumption of equal concentrations was not valid at the lower [Fe(CN)$_6^{3-}$]. Thus, by using the rate constants and initial concentrations given above, it was found that the Fe(CN)$_6^{4-}$ and Ru(bpy)$_3^{3+}$ concentrations became equal to each other within about 5% only after 34 μs, when the reaction was within 20% of completion. At the highest Fe(CN)$_6^{3-}$ concentration, the values of [Fe(CN)$_6^{4-}$] and [Ru(bpy)$_3^{3+}$] became equal to each other to within 5% after 10 μs, when about 50% of the reaction had taken place. On the basis of these calculations, we conclude that only the data at the highest [Fe(CN)$_6^{3-}$] yield reliable values of k_{obsd}, and therefore $k_5 = (9.8 \pm 1.0) \times 10^9$ M^{-1} s^{-1}.

Because pseudo-first-order conditions were not exactly obeyed in the measurements of k_{-2}, an alternate approach, based on second-order conditions, was also utilized. This approach, similar to that utilized previously to measure the rate of the NPh$_3^+$–MV$^+$ reaction,[19] is based on the excitation of Ru(bpy)$_3^{2+}$ in the presence of an oxidant and a reductant. The oxidant, present at relatively high concentrations, serves to quench *Ru(bpy)$_3^{2+}$, while the reductant, present at relatively low concentrations, serves to reduce the Ru(bpy)$_3^{3+}$ produced in the quenching step. Under these circumstances, the order of events is given by the reaction sequence A, C, B (see figure). For the purpose of measuring k_{-2}, we utilized 1.0 × 10^{-2} M MV^{2+} and 2.0 × 10^{-4} M Fe(CN)$_6^{4-}$. MV$^+$ (eq 3) and Fe(CN)$_6^{3-}$ (eq 5) are produced in equal concentrations and react according to the reverse of eq 2. Plots of $1/(A_t - A_\infty)$ at 395 nm were linear and yielded slopes equal to (3.6 ± 0.6) × 10^5 cm s^{-1}. In order to calculate k_{-2}, it is necessary to have the molar absorbances of Fe(CN)$_6^{4-}$, Fe(CN)$_6^{3-}$, and MV$^+$ at 395 nm. The first two values are easily determind, but literature values for MV$^+$ exhibit serious discrepancies (for example, 3.37 × 10^4 [20] and 4.5 × 10^4 [21]). Several attempts were made to measure to molar absorbance of MV$^+$ at 395 nm by preparing solutions of MV$^+$ via reduction with zinc amalgam or dithionite, but the absorbance of solutions prepared in this manner was irreproducible and changed rapidly. Photolysis of MV^{2+} in the presence of 2-propanol[15] yielded stable solutions, and the absorbance of such solutions at 395 and 605 nm was measured. From the molar absorbance at 605 nm,[14] we calculated a value of (4.41 ± 0.09) × 10^4 M^{-1} cm^{-1} at 395 nm. From this value, we obtain k_{-2} = (1.6 ± 0.3) × 10^{10} M^{-1} s^{-1}. This value differs by a factor of 2 from the value measured by the first approach. We were quite surpised at the discrepancy because the two approaches involve the same chemical systems. However, the second approach yields constants which are very sensitive to traces of Fe(CN)$_6^{3-}$ that may be present in the system before flash excitation. Thus, a simulation using the Runge–Kutta approximation shows that, with Fe(CN)$_6^{4-}$ initially at 2.0 × 10^{-4} and [Fe(CN)$_6^{3-}$]$_0$ = 2.0 × 10^{-6} M, the plots of $1/(A_t = A_\infty)$ yield slopes which are a factor of 2 larger than the slopes when [Fe(CN)$_6^{3-}$]$_0$ = 0. Two possible sources of Fe(CN)$_6^{3-}$ may be considered. The first one is the reductive quenching[22] of Ru(bpy)$_3^{2+}$ by Fe(CN)$_6^{4-}$, eq 6. Although Fe(CN)$_6^{4-}$ is at much lower concentration than MV^{2+}, k_6 (3.5 × 10^9 M^{-1} s^{-1})[22] is larger than k_3 (1.0 × 10^9 M^{-1} s^{-1}),[23] and we calculate that about 1 × 10^{-6} M Fe(CN)$_6^{3-}$ is produced by reaction 6. However, it appears that the Fe(CN)$_6^{3-}$ produced does not escape the solvent cage, and essentially 100% escape as compared to recombination would be necessary to account for our results. Another source of Fe(CN)$_6^{3-}$ is oxidation of Fe(CN)$_6^{4-}$ during the manipulations necessary to prepare the necessary solutions. In fact, a measurement of the Fe(CN)$_6^{3-}$ concentration present in solutions of Fe(CN)$_6^{4-}$ prepared under the same conditions as those utilized to prepare solutions for flash photolysis showed the presence of ~0.5% Fe(CN)$_6^{3-}$. We conclude that although the second approach to measuring k_{-2} is sound in principle, difficulties with trace oxidation of Fe(CN)$_6^{4-}$ render the measurements less reliable than those based on the first approach.

$$^*\text{Ru(bpy)}_3^{2+} + \text{Fe(CN)}_6^{4-} \xrightarrow{k_6} \text{Ru(bpy)}_3^{+} + \text{Fe(CN)}_6^{3-} \qquad (6)$$

Discussion

Combining the value of k_{-2} measured in the present work, 7.6 × 10^9 M^{-1} s^{-1}, with the equilibrium constant 3.1 × 10^{-15} for reaction 2 calculated from electrochemical measurements,[2] we compute k_2 = 2.4 × 10^{-5} M^{-1} s^{-1} at 23 °C and ionic strength 0.10 M. The value calculated from the properties of the outer-sphere optical charge transfer band and auxiliary thermodynamic information[2] is (2–3) × 10^{-4} M^{-1} s^{-1}. Upon consideration of the approximations and assumptions necessary to calculate the rate constant from the spectral data, the agreement between the optical and kinetic values might be considered satisfactory. However, we believe the agreement to be fortuitous because the kinetic value is diffusion controlled whereas the optical value is, to be sure, activation controlled. Consider the three elementary steps in the mechanism of outer-sphere reactions: formation of precursor complex (eq 7), internal electron transfer (eq 1), and dissociation of successor complex (eq 8). The formation of the precursor (k_7) and successor (k_{-8}) complexes from the separate ions are diffusion-controlled processes. The rate constants k_7 and k_{-8}, calculated from the Debye equation corrected to 0.10 M ionic strength,[23] are 1.4 × 10^9 and 4.7 × 10^9 M^{-1} s^{-1}, respectively. From the agreement between the calculated value of k_{-8} and the measured value of k_{-2}, we infer that the overall Fe(CN)$_6^{3-}$–MV$^+$ reaction is controlled by diffusion of Fe(CN)$_6^{3-}$ and MV$^+$, the reverse of eq 8. On the basis of microscopic reversibility, the Fe(CN)$_6^{4-}$–MV^{2+} reaction must also have eq 8 as the rate-determining step, and therefore the reaction is controlled by the dissociation of the successor complex. On the basis of eq 7, 1, and 8, the value of k_2 is given by $(k_7/k_{-7})(k_{\text{et}}/k_{-\text{et}})k_8$. The values of k_7/k_{-7} and $k_{\text{et}}/k_{-\text{et}}$ were measured or estimated[2] as 220 M^{-1} and 1.2 × 10^{-16}. Therefore, k_8 = 9.1 × 10^8 s^{-1}. In order for dissociation of the successor complex to be rate determining, it is necessary that $k_{-\text{et}}$ be considerably larger than 9.1 × 10^8 s^{-1}. It will be seen below that this condition is obeyed.

$$\text{MV}^{2+} + \text{Fe(CN)}_6^{4-} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} \text{MV}^{2+}|\text{Fe(CN)}_6^{4-} \qquad (7)$$

$$\text{MV}^{+}|\text{Fe(CN)}_6^{3-} \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} \text{MV}^{+} + \text{Fe(CN)}_6^{3-} \qquad (8)$$

Additional evidence for the contention of a dissociation-controlled reaction comes from calculations of the rate constant for the activation-controlled reaction utilizing Marcus' cross relationship. In order to perform the calculations, it is necessary to have values for the self-exchange rate constants of Fe(CN)$_6^{3-/4-}$ and MV$^{2+/+}$. The value for the former couple is 1.9 × 10^4 M^{-1} s^{-1},[6] but no measurements are available for the MV$^{2+/+}$ couple. However, an estimate of 8.4 × 10^6 M^{-1} s^{-1} in acetonitrile has been made[2,5] for the self-exchange rate constant from measurements of electron-transfer quenching of *Ru(bpy)$_3^{2+}$ by a series of bipyridinium quenchers of varying reduction potential. From these measurements, it was estimated that a hypothetical quencher for which the free-energy change was zero had a quenching rate constant of 8.4 × 10^6 M^{-1} s^{-1}, and this was taken to be similar to the self-exchange rate constant for viologens. However, it

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(19) Meyer, T. J., Whitten, D. G.; Young, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 16.

(20) Steckhan, E.; Kuwana, T. *Ber. Bunsenges. Phys. Chem.* **1974**, *78*, 253.

(21) Farrington, J. A.; Ebert, M.; Land, E. J. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 665.

(22) Creutz, C.; Sutin, N. *Inorg. Chem.* **1976**, *15*, 496.

(23) Miralles, A. J.; Armstrong, R. E.; Haim, A. *J. Am. Chem. Soc.* **1977**, *99*, 1416.

Table II. Experimental and Calculated Rate Constants for Reaction of $MV^{2+/+}$ [a]

reactant	k_{ex}, $M^{-1}\ s^{-1}$	$E°$, V	r, nm	k_{exptl}, $M^{-1}\ s^{-1}$	k_{calcd}, $M^{-1}\ s^{-1}$	ref
Cr^{2+}	5.1×10^{-10}	-0.41	0.35	4.3×10^{-2}	1.2×10^{-2}	*b*
V^{2+}	1.2×10^{-2}	-0.24	0.35	2.3	2.5	*b*
$^*Ru(bpy)_3{}^{2+}$	1.0×10^{8}	-0.84	0.65	1.0×10^{9}	3.3×10^{9}	*c*
$Ru(bpy)_3{}^{3+}$	4.0×10^{9}	1.26	0.65	4×10^{9}	1.1×10^{4}	*d*

[a] In the first three entries the reactant is MV^{2+}; in the last two entries the reactant is MV^{+}. $E°$ of the $MV^{2+/+}$ couple is -0.44 V, and the rate constant for self-exchange is $8.0 \times 10^{5}\ M^{-1}\ s^{-1}$. [b] Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* 1977, *16*, 2516. [c] Reference 11. [d] Present work.

appears that a better interpretation of the quenching rate constant for a zero free-energy quencher is $(k_{MV}k_{Ru})^{1/2}$, where k_{MV} is the self-exchange rate constant of the viologen and k_{Ru} is the self-exchange rate constant for the $^*Ru(bpy)_3{}^{2+}/Ru(bpy)_3{}^{3+}$ couple. Since $k_{Ru} = 1 \times 10^{8}\ M^{-1}\ s^{-1}$,[24] $k_{MV} = 8 \times 10^{5}\ M^{-1}\ s^{-1}$. The reliability of this estimate[25] can be verified by calculation of the few known cross reactions involving $MV^{2+/+}$ and comparison of the results with experimental values. Such comparison is presented in Table II, where calculated values have been obtained by utilizing Marcus' reactive collision model.[26] There is good agreement between calculated and experimental values for the Cr^{2+}–MV^{2+}, V^{2+}–MV^{2+}, and $^*Ru(bpy)_3{}^{2+}$–MV^{2+} reactions, but there is a serious discrepancy for the $Ru(bpy)_3{}^{3+}$–MV^{+} reaction. The disagreement is not surprising, since the enormous exoergonicity[27] of the reaction ($K \sim 5 \times 10^{28}$) places it in the inverted region where the theoretically predicted decrease in rate is not observed experimentally. On the basis of these comparisons, the value of $8 \times 10^{5}\ M^{-1}\ s^{-1}$ appears reasonable.

The calculated value of the rate constant for the MV^{2+}–$Fe(CN)_6{}^{4-}$ reaction is, on the basis of the ion-pair model,[26] $1.6 \times 10^{-2}\ M^{-1}\ s^{-1}$. This is considerably faster than the experimental value $k_{-2} = 2.4 \times 10^{-5}\ M^{-1}\ s^{-1}$, and the comparison reinforces the interpretation of a dissociation-controlled reaction. For the reverse reaction, the calculated rate constant is $5.2 \times 10^{12}\ M^{-1}\ s^{-1}$, to be compared with the experimental value $7.6 \times 10^{9}\ M^{-1}\ s^{-1}$, and the contention of a diffusion-controlled mechanism is further supported. From the activation-controlled rate constants calculated by using the ion-pair model and the theoretical ion-pair formation constants, we calculate values of k_{et} and k_{-et} of 1.7×10^{-4} and $1.0 \times 10^{12}\ s^{-1}$, respectively. As indicated above, k_{-et} is considerably larger than k_8, as required for a dissociation-controlled reaction. It is noteworthy that the MV^{2+}–$Fe(CN)_6{}^{4-}$ reaction represents an additional example of the important role played by the separation of products in determining the kinetics of highly endoergonic reactions.[28]

Since the rate of $Fe(CN)_6{}^{4-}$–MV^{2+} reaction is controlled by the dissociation of the successor complex, it is not possible to make a comparison between a measured, thermal, activation-controlled rate constant with the rate constant derived from the charge transfer, optical transition. However, a comparison between the latter and a thermal rate constant calculated from the self-exchange rate constants and thermodynamic data is feasible. The comparison is not encouraging: k_2 is $1.9 \times 10^{-5}\ M^{-1}\ s^{-1}$ from optical measurements[29] and $1.6 \times 10^{-2}\ M^{-1}\ s^{-1}$ from the cross-reaction calculation. However, since the value calculated for the thermal reaction is based on an estimate of the self-exchange rate constant for the $MV^{2+/+}$ couple, it might be argued that the comparison between optical and thermal rates is not meaningful in the present system. Therefore, we attempted to find other systems where *experimental* information on thermal and optical electron transfer is available.[30] The only systems that we are aware of are the $Fe(CN)_6{}^{4-}$–$Ru(NH_3)_5py^{3+}$ (py = pyridine) and $(NH_3)_5RupzRuEDTA^{+}$ (pz = pyrazine) systems for which measurements of the thermal rates[24,34] and of the intervalence outer-sphere and inner-sphere charge transfer bands[31,34] are available. By utilization of the experimental results and eq 9–11,

$$E_{th} = E_{op}{}^2/[4(E_{op} - \Delta E)] \tag{9}$$

$$\nu_{et} = 9.76 \times 10^{10}(\tilde{\nu}_{max})^{1/2}\epsilon_{max}\Delta\nu_{1/2}/r^2 \tag{10}$$

$$k_{et} = \nu_{et} \exp(-E_{th}/RT) \tag{11}$$

where E_{th} and E_{op} are the thermal and optical electron transfer barriers (31.3 kcal), respectively, ΔE is the energy change associated with electron transfer within the ion-pair $Fe(CN)_6{}^{4-}|Ru(NH_3)_5py^{3+}$, (2.65 kcal) ν_{et} is the electron hopping frequency in the activated complex,[32] $\tilde{\nu}_{max}$ and ϵ_{max} are the wavenumber and extinction coefficient ($10.9 \times 10^{3}\ cm^{-1}$, $40\ M^{-1}\ cm^{-1}$), respectively, of the maximum for the charge-transfer band, r is the distance (in pm) (800) over which the electron is transferred in the optical transition, and k_{et} is the internal electron transfer within the ion pair, we calculate $E_{th} = 8.5$ kcal, $\nu_{et} = 4.1 \times 10^{12}\ s^{-1}$, and $k_{et} = 2.3 \times 10^{6}\ s^{-1}$. We previously[23] reported a value of $4.3 \times 10^{6}\ M^{-1}\ s^{-1}$ for the second-order rate constant ($k = Q_{1P}k_{et}$) of the $Fe(CN)_6{}^{4-}$–$Ru(NH_3)_5py^{3p}$ reaction. From k and $Q_{1P} = 2.4 \times 10^{3}\ M^{-1}$,[23,33] we obtain $k_{et} = 1.8 \times 10^{3}\ s^{-1}$, which is in very poor agreement with the $2.3 \times 10^{6}\ s^{-1}$ value derived from the optical transition. For the $(NH_3)_5RupzRuEDTA^{+}$ system, thermal and optical values are $8 \times 10^{9}\ s^{-1}$ and $1.9 \times 10^{12}\ s^{-1}$, respectively.[35] Again the comparison is not encouraging, and it is evident that the investigation of more systems, where thermal and optical measurements can be carried out, is necessary before any confidence can be placed on the validity of calculations of thermal electron transfer rates from properties of optical charge transfer transitions.

Finally, our value of k_5, $9.8 \times 10^{9}\ M^{-1}\ s^{-1}$ at 23 °C and 0.10 M ionic strength, compares favorably with the value $6.3 \times 10^{9}\ M^{-1}\ s^{-1}$ measured under the same conditions for the similar $Os(bpy)_3{}^{3+}$–$W(CN)_8{}^{4-}$ and $Fe(CH_3\text{-}phen)_3{}^{3+}$–$Mo(CN)_8{}^{4-}$ reactions.[36] All these reactions are diffusion controlled. The activation-controlled rate, calculated from the self-exchange rate constants by utilizing the ion-pair model, is $1.7 \times 10^{14}\ M^{-1}\ s^{-1}$, for reaction 5, and to be sure, the calculation reinforces the conclusion that the measured value represents the diffusion-controlled process. From the calculated ion-pair formation constant[23] between $Ru(bpy)_3{}^{3+}$ and $Fe(CN)_6{}^{4-}$ ($127\ M^{-1}$ at 25 °C and $\mu = 0.10$ M) and the calculated, activation-controlled rate constant for reaction 5, we compute an internal electron-transfer rate constant within the ion pair $Ru(bpy)_3{}^{3+}|Fe(CN)_6{}^{4-}$ of $1.4 \times 10^{12}\ s^{-1}$. This is considerably higher than the previously measured value ($2 \times 10^{8}\ s^{-1}$)[37] for the analogous ion pair $^*Os(5\text{-}Cl\text{-}phen)_3{}^{2+}|Fe(CN)_6{}^{4-}$. The difference in reactivity is almost entirely associated with the difference in the driving forces of the reactions, $^*Os(5\text{-}Cl\text{-}phen)_3{}^{2+}$ ($E^0 = 0.72$ V) being a considerably weaker oxidant than $Ru(bpy)_3{}^{3+}$ ($E^0 = 1.28$ V).

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Registry No. $Ru(bpy)_3{}^{2+}$, 15158-62-0; $Fe(CN)_6{}^{3-}$, 13408-62-3; $Fe(CN)_6{}^{4-}$, 13408-63-4; MV^{2+}, 4685-14-7; MV^{+}, 25239-55-8.

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[24] Sutin, N.; Creutz, C. *Adv. Chem. Ser.* **1978**, *No 168*, 1.

[25] This value is applicable to acetonitrile solutions. However, the value in water is expected to be within 5% since the outer-sphere term $(1/D_{op}) - (1/D_s)$ difference between water and acetonitrile is ~5%.

[26] Brown, G.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.

[27] Bottcher, W.; Zahir; Haim, A., work in progress.

[28] Stanbury, D. M.; Wilmarth, W. K.; Khalaf, S.; Po, H. N.; Bryd, J. E. *Inorg. Chem.* **1980**, *19*, 2716.

[29] This value differs from that reported previously ($\sim 1 \times 10^{-6}\ s^{-1}$)[2] because we obtained ν_{et} from eq 10 rather than eq 19 in ref 2.

[30] Toma, H. E. *J. Chem. Soc., Dalton Trans.* **1980**, 471.

[31] Curtis, J. C.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 6284.

[32] Sutin, N. Section 12.2 of "Inorganic Reactions and Methods"; Zuckerman, J. J., Ed.; Verlag Chemie; Weinheim, Germany, in press.

[33] This is the value of the ion-pair formation constant of $Co(NH_3)_5py^{3+}|Fe(CN)_6{}^{4-}$.

[34] Creutz, C.; Kroger, P.; Matsubara, T.; Netzel, T. L.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 5442.

[35] Our value $1.9 \times 10^{12}\ s^{-1}$ differs from that reported previously[34] ($5 \times 10^{11}\ s^{-1}$) because we obtained ν_{et} from eq 10 rather than by utilizing kT/h.

[36] Holtzwarth, J.; Jürgensen, H. *Ber. Bunsges. Phys. Chem.* **1974**, *78*, 526.

[37] Rybak, W.; Haim, A.; Netzel, T. L.; Sutin, N. *J. Phys. Chem.* **1981**, *85*, 2856.