The rate constants for trapping of the $Ru_3(CO)_{11}$ intermediate by CO or THF are each close to that calculated for a diffusion-limited reaction in the isooctane solvent.[14] Thus, this unsaturated cluster must be but weakly solvated by the isooctane. In contrast, but not surprising, the reactivity of the "THF solvate" is orders of magnitude less. Comparable high reactivity has been reported for the mononuclear unsaturated intermediate $(\eta^5\text{-}C_5H_5)Co(CO)$ formed by CO photodissociation from the dicarbonyl in cyclohexane, which reacts with various two-electron donors with second-order rate constants $>10^9$ M^{-1} s^{-1}.[3f] However, hydrocarbons appear to stabilize the $Cr(CO)_5$ intermediate (formed from $Cr(CO)_6$) more strongly; in cyclohexane this species reacts with CO with a rate constant (3×10^6 M^{-1} s^{-1}) about 3 orders of magnitude faster than in more weakly binding fluorocarbon solvents.[15] Among the few examples of dinuclear intermediates which have been analogously studied, both $Mn_2(CO)_9$[16] and $[(\eta^5\text{-}C_5H_5)Fe_2(\mu\text{-}CO)_3]$[17] (prepared, respectively, by CO photodissociation from $Mn_2(CO)_{10}$ and $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$) react with two-electron donors in cyclohexane solutions relatively slowly, i.e., with second-order rate constants near 10^6 M^{-1} s^{-1}. These intermediates each displayed IR spectra consistent with the unsaturation resulting from CO photodissociation being in part compensated by movement of one terminal carbonyl to a bridging or semibridging position. Similar rearrangement is available to $Ru_3(CO)_{11}$ and indeed has been proposed above to be the case. Thus, the surprising observation that this intermediate is so reactive with two-electron donors in alkane solutions suggests that any stabilization from such carbonyl bridging in the triruthenium cluster has but a minor effect on the dynamics of the bimolecular reactivity.

In summary, the mechanism described by Scheme I appears to be valid for S = THF and the medium being isooctane solution. The $Ru_3(CO)_{11}$ species must be but weakly solvated by the isooctane given that the rate constants k_{CO} and k_S have the values $2.4 \pm 0.4 \times 10^9$ M^{-1} s^{-1} and $6.1 \pm 1.2 \times 10^9$ M^{-1} s^{-1}, respectively, values which are less than 1 order of magnitude smaller than the calculated diffusion limit in this medium.

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Reductive Quenching of Ruthenium Polypyridyl Sensitizers by Cyanometalate Complexes

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Laser flash photolysis/transient absorbance and emission spectroscopy were used to probe the nature of the reductive quenching of ruthenium polypyridyl sensitizers by cyanometalate electron donors in aqueous solution. Quenching rate constants and approximate cage escape efficiencies were measured for a number of donor/sensitizer pairs; octacyanometalates ($Mo(CN)_8^{4-}$, $W(CN)_8^{4-}$) exhibit much higher cage escape efficiencies, typically 40–80%, than do hexacyanometalates ($Fe(CN)_6^{4-}$, $Os(CN)_6^{4-}$). Cage escape efficiencies vary with the overall charge of the sensitizer; geminate ion pair recombination competes most efficiently with cage escape when the electron donor and acceptor have 4+ and 4− overall charges, respectively. No dependence of cage escape efficiency on thermodynamic driving force for the back-electron-transfer reaction is observed. Little or no dependence on ionic strength or counterion is observed. Steady-state and time-resolved luminescence experiments with $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) show that the quenching process is dynamic at low cyanometalate concentrations and that association of the cationic sensitizer with the anionic cyanometalates occurs at higher concentrations. Even under these conditions, quantum yields for charge separation approach unity with octacyanometalate electron donors.

Since Adamson and Gafney first proposed electron-transfer quenching experiments involving tris(2,2′-bipyridine)ruthenium(II) in 1972, this molecule has been widely studied by photochemists.[1] Its strong electronic transitions in the visible and near-ultraviolet regions of the spectrum, strong luminescence in solution, relatively long metal to ligand charge-transfer (MLCT) state lifetime (670 ns),[2] and disinclination to undergo unimolecular photoreactions make it a superior photosensitizer.[3]

Since the first oxidation potential of $Ru(bpy)_3^{2+}$ is +1.29 V vs SCE (saturated calomel electrode) in acetonitrile[4a] and the excess free energy of the excited state over that of the ground state is 2.10 eV, it is apparent that the excited-state species $^*Ru(bpy)_3^{2+}$ must be a strong reducing agent. Accordingly, many electron-transfer studies involving $Ru(bpy)_3^{2+}$ have entailed oxidative quenching of the excited state:[1,5-7]

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

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

In an analogous manner, the first reduction potential for $Ru(bpy)_3^{2+}$, −1.33 V vs SCE in acetonitrile,[4a] indicates that $^*Ru$-

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$(bpy)_3^{2+}$ is also a rather powerful oxidizing agent. Reductive quenching of $^*Ru(bpy)_3^{2+}$ has been studied by Creutz and Sutin, Toma and Creutz,[4] Juris et al.,[8] and Meyer and co-workers:[9]

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

Both the oxidative and reductive quenching processes must be well-understood if a given photosensitizer is to be used in an electron-transfer chain that separates charge for the purpose of energy conversion.[10] An essential consideration in the design of such a chain is the nature of the reductive quencher. Recent work on microheterogeneous systems involving sensitizers bound by polymers[11] and zeolites[12] has required donor quenchers that are "nonsacrificial" (i.e., for which the oxidation is electrochemically reversible in aqueous solution), stable, and nonabsorbing in both their oxidized and reduced forms. Clearly, the donor must possess an oxidation potential that is sufficiently negative for rapid electron transfer to the photoexcited sensitizer, in order that reductive quenching of the excited state be efficient. Additionally, the quantum yield for separation of the oxidized donor-reduced sensitizer geminate ion pair must be high. For $Ru(bpy)_3^{2+}$ and related sensitizers, octacyano complexes of W and Mo are efficient electron donor quenchers. Interestingly, we find these octacyanometalates exhibit much higher cage escape efficiencies than do hexacyanometalate donors ($Fe(CN)_6^{4-}$, $Os(CN)_6^{4-}$). An examination of this difference is the subject of the present paper.

We report here the quenching rate constants and cage escape efficiencies for a number of donor/sensitizer combinations in aqueous solution. Four different quenchers were used: $K_4Mo(CN)_8{\cdot}2H_2O$, $K_4W(CN)_8{\cdot}2H_2O$, $K_4Fe(CN)_6{\cdot}3H_2O$, and $K_4Os(CN)_6{\cdot}3H_2O$. Four different sensitizers were used, each one having a different overall charge in solution: $RuL_3(PF_6)_2$ (where L = 4,4′-dicarboxy-2,2′-bipyridine), $Ru(bpy)_2L(PF_6)_2$, $Ru(bpy)_3Cl_2{\cdot}6H_2O$, and $[Ru(bpy)_2(Mebpy\text{-}Mebpy)Ru(bpy)_2](PF_6)_4$ (where Mebpy-Mebpy is a ligand prepared by dimerization of 4,4′-dimethyl-2,2′-bipyridine[13,14]). These sensitizers have charges ranging from 4− to 4+ in aqueous solutions more alkaline than pH 5–6. Thus, control of the overall charge on the sensitizers is accomplished by adjusting the number of dicarboxybipyridyl ligands on the molecule. We postulate that the considerable difference in cage escape efficiencies between octa- and hexacyanometalate electron donors is a consequence of different rates of geminate ion pair electron transfer in the two cases. This reverse-electron-transfer rate is expected to be slower in the case of the larger octacyanometalate ions.

Experimental Section

Materials. All cyanometalates were recrystallized several times from water/methanol. $K_4Fe(CN)_6{\cdot}3H_2O$ was obtained from Fisher. $K_4Os(CN)_6{\cdot}3H_2O$ was prepared by the method of Krauss and Schrader.[15] $K_4W(CN)_8{\cdot}2H_2O$ was prepared as described by Leipoldt et al.,[16] and $K_4Mo(CN)_8{\cdot}2H_2O$ was prepared according to the method of Furman and Miller.[17] $Li_4Fe(CN)_6$ and $Cs_4Fe(CN)_6$ solutions were prepared by eluting a column of appropriately exchanged Dowex cation-exchange resin with a solution 5 mM in $K_4Fe(CN)_6{\cdot}3H_2O$ and 100 mM in K_2HPO_4.

Table I. Emission Lifetimes (ns) and Quenching Rate Constants (M^{-1} s^{-1}) in 100 mM K_2HPO_4

sensitizer (lifetime)	$Os(CN)_6^{4-}$	$Fe(CN)_6^{4-}$	$W(CN)_8^{4-}$	$Mo(CN)_8^{4-}$
RuL_3^{4-} (680)	3.3×10^6	2.0×10^7	2.0×10^8	1.6×10^8
$Ru(bpy)_2L^0$ (545)	4.1×10^9	1.1×10^{10}	1.7×10^{10}	2.9×10^9
$Ru(bpy)_3^{2+}$ (585)	3.0×10^9	6.4×10^9	1.1×10^{10}	1.6×10^9
$[Ru(bpy)_2(L{\cdots}L)\text{-}Ru(bpy)_2]^{4+}$ (560)[a]	2.1×10^9	9.9×10^9	2.0×10^{10}	1.2×10^9

[a] L···L = Mebpy-Mebpy.

$RuL_3(PF_6)_2$ (L = 4,4′-dicarboxy-2,2′-bipyridine) was prepared as follows: 4,4′-dicarboxy-2,2′-bipyridine was prepared by the method of Whitten and co-workers[18] and esterified by refluxing 5.0 g of the dicarboxybipyridine in 25 mL of $SOCl_2$ for 3 h. Excess $SOCl_2$ was removed under vacuum, and the intermediate acyl chloride of bipyridine was dried in vacuo and then refluxed in 150 mL of absolute ethanol for 4 h. Half of the ethanol was removed under vacuum, whereupon white crystals of the diethyl ester of 4,4′-dicarboxyl-2,2′-bipyridine precipitated. A 0.5-g amount of $RuCl_3{\cdot}2H_2O$ and 2.0 g of the diethyl ester of 4,4′-dicarboxy-2,2′-bipyridine were refluxed for 4 days in absolute ethanol. Following filtration and removal of two-thirds of the solvent under vacuum, addition of aqueous NH_4PF_6 precipitated $Ru(4,4'\text{-}(EtO_2C)_2\text{-}2,2'\text{-}bpy)_3(PF_6)_2$. A 0.5-g amount of $Ru(4,4'\text{-}(EtO_2C)_2\text{-}2,2'\text{-}bpy)_3(PF_6)_2$ was suspended in 50 mL of water, and 6 equiv of NaOH was added; warming this mixture for several hours at 70–80 °C gave the sodium carboxylate form of the complex. Filtration, followed by acidification with aqueous HCl solution, precipitated $RuL_3(PF_6)_2$. $Ru(bpy)_2L(PF_6)_2$ was prepared by combining stoichiometric amounts of *cis*-dichlorobis(bipyridine)ruthenium, $Ru(bpy)_2Cl_2$ (0.060 g, prepared by Whitten's method[25]), 4,4′-dicarboxy-2,2′-bipyridine (0.055 g), and $NaHCO_3$ (0.150 g) in 10 mL of a 1/1 (v/v) ethanol/water solution. The solution was refluxed for 30 min, and about half the solvent was removed in vacuo. Aqueous HCl was then added to give a pH 1–2 solution, and NH_4PF_6 was added to precipitate the product. $Ru(bpy)_2L(PF_6)_2$ was isolated by filtration and washed with cold water. $[Ru(bpy)_2(Mebpy\text{-}Mebpy)Ru(bpy)_2](PF_6)_4$ was made according to the method of Rillema and co-workers.[14] $Ru(bpy)_3Cl_2{\cdot}6H_2O$ and K_2HPO_4 were obtained from Aldrich and used as received. Water was purified to a resistivity of 18.3 MΩ cm in a Barnstead Nanopure II system.

Apparatus. UV/visible spectra were collected on a Hewlett-Packard HP8451A diode array spectrophotometer. Steady-state fluorescence spectra were recorded on a SPEX Fluorolog fluorometer. Laser flash photolysis experiments were done at the Center for Fast Kinetics Research, University of Texas at Austin; this equipment has been described previously.[19] Nanosecond time scale experiments were performed with a Quantel YG 481 Nd:YAG Q-switched laser, which generates an 11-ns pulse at 532 nm; the laser was focused through a 1-cm solution, while the analyzing light was focused through a 1-mm pinhole normal to the incident laser beam. Picosecond time scale experiments were done in the pulse-probe mode with a mode-locked Nd:YAG laser that generates 30-ps pulses at 532 nm. The probe beam was generated from the pulse beam by means of a beam splitter and an optical delay line and was focused through a cell containing phosphoric acid and D_2O in order to generate white analyzing light. The picosecond apparatus has been described in detail elsewhere.[20]

Procedures. All experiments were carried out at ambient temperature (22–23 °C). Typically, 10 mg of sensitizer was dissolved in 100 mL of a 100 mM K_2HPO_4 solution. During spectroscopic experiments, donors were added in solid form directly to a cuvette containing the chromophore solution. Occasionally, the donor was introduced in aqueous form via a microliter syringe. For time-resolved experiments, all solutions were purged with nitrogen. Quantum yields reported represent the average of at least five laser shots and are estimated to be accurate to ±10% for $Ru(bpy)_3^{2+}$. These yields were determined from transients recorded at the absorbance maximum for $Ru(bpy)_3^{+}$ extrapolated to zero time. Since this extinction coefficient is known from pulse radiolysis experiments for only $Ru(bpy)_3^{+}$ ($\Delta\epsilon_{510} = 8.0 \times 10^3$ M^{-1} cm^{-1}),[21] quantum yields reported in Table I for the other sensitizers should be regarded as approximate. The ground- and excited-state spectra of $[Ru(bpy)_2(Mebpy\text{-}Mebpy)Ru(bpy)_2]^{4+}$ and $Ru(bpy)_2L$ in 100 mM K_2HPO_4, as well as transient

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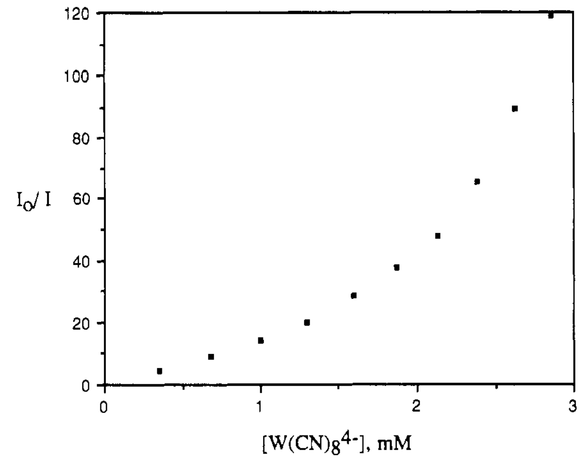

Figure 1. Stern–Volmer plot for quenching of 0.1 mM $Ru(bpy)_3^{2+}$ by $K_4W(CN)_8{\cdot}2H_2O$ in 100 mM K_2HPO_4 (excitation wavelength 460 nm; emission monitored at 630 nm).

visible spectra obtained in the presence of donor quenchers, are nearly identical with those of $Ru(bpy)_3^{2+}$. Spectral features of RuL_3^{4-} are similar under these conditions but are displaced about 10 nm to longer wavelengths; for this compound the calculated cage escape efficiencies are likely to be least reliable. For all sensitizers except RuL_3^{4-}, the concentration of cyanometalate quencher used (10–20 mM) was sufficient to quench >99% of the sensitizer luminescence; for RuL_3^{4-}, the concentration of quencher used was higher (0.2–1.0 M) and the fraction of luminescence quenched was typically ≥70%. Actinometry was performed before and after each experiment by measuring the MLCT-state transient absorbance, at 360 nm, of an aqueous $Ru(bpy)_3^{2+}$ solution, assuming a quantum yield of unity for formation of the MLCT state and $\Delta\epsilon_{360} = 2.2 \times 10^4\ M^{-1}\ cm^{-1}$. Cage escape efficiencies (Φ_{CE}) were then calculated simply from the absorbance of the sample and actinometer solutions at the laser wavelength by using eq 4.

$$\Phi_{CE} = \frac{(\Delta A_{510}/\Delta\epsilon_{510})_{sample}}{(\Delta A_{360}/\Delta\epsilon_{360})_{actinometer}} \frac{(1 - 10^{-A_{532}})_{actinometer}}{(1 - 10^{-A_{532}})_{sample}} \frac{1}{\text{fraction quenched}} \tag{4}$$

Results and Discussion

Table I summarizes the quenching rate constants as calculated from Stern–Volmer plots of steady-state emission data (excitation wavelength 460 nm; emission monitored at 630 nm). In the calculation of quenching rate constants (k_q), the slope of the Stern–Volmer plot was divided by the emission lifetime for $^*Ru(bpy)_3^{2+}$ and other derivatives;[2] measured lifetimes in 100 mM K_2HPO_4 are listed in Table I. The estimated error in these lifetimes is ±20 ns, and that of the k_q values is ±5%. The most immediately noticeable trend in Table I is the tendency toward a larger k_q value as donor/sensitizer pairs become more nearly opposite in charge. Quenching rate constants for $Ru(bpy)_3^{2+}$, at low cyanometalate quencher concentrations, are in agreement with those determined by Balzani and co-workers.[8]

For high concentrations of quencher and neutral or positively charged sensitizers, Stern–Volmer plots are nonlinear. For these sensitizers, the quenching rate constants reported in Table I refer to the linear portion of the curve at very low quencher concentrations. A typical plot of this kind is shown in Figure 1. The upward curvature of the plot indicates an association of the sensitizer with the quencher. Time-resolved emission studies confirm previous reports[8,22] that the quenching is dynamic in the $Ru(bpy)_3^{2+}$ system at low quencher concentration; that is, for all the cyanometalate quenchers studied, the $Ru(bpy)_3^{2+}$ emission intensity, extrapolated to zero time, is independent of quencher concentration. These time-resolved luminescence decays could be accurately measured for lifetimes ≥50 ns, or under conditions where $I_0/I \leq 10$ in steady-state experiments. This is the linear regime of the Stern–Volmer plots. At higher quencher concentrations, where the plots are nonlinear, our time-resolved luminescence data were uninformative; however, transient absorbance experiments (vide infra) indicate that the quantum yield for formation of charge-separated products can approach unity under these conditions.

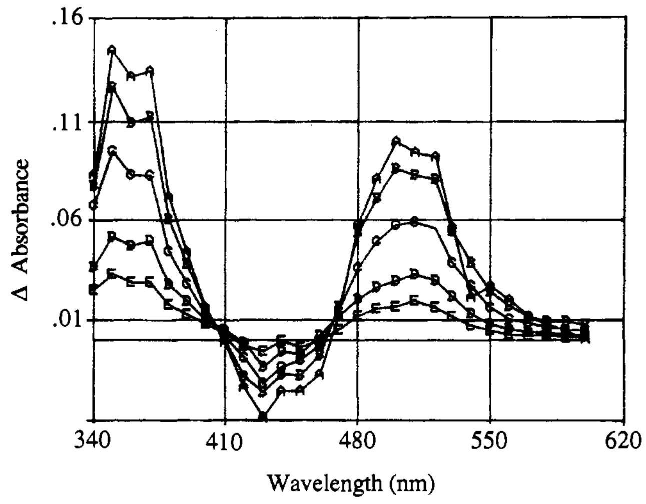

Figure 2. Transient absorbance spectra of a 0.1 mM $Ru(bpy)_3^{2+}$/5 mM $K_4W(CN)_8{\cdot}2H_2O$ solution in 100 mM K_2HPO_4. Spectra A–E were recorded 0.4–13.5 μs after an 11-ns, 532-nm laser flash and show the formation and decay of $Ru(bpy)_3^+$ (maxima at 360 and 510 nm).

Laser flash photolysis/transient absorbance experiments with ruthenium polypyridyl complexes and cyanometalate donors gave spectra like that shown in Figure 2. Positive changes in optical density at 360 and 510 nm and a negative change at 450 nm are attributable, respectively, to formation of the reduced complex $Ru(bpy)_3^+$ and bleaching of the $Ru(bpy)_3^{2+}$ MLCT absorbance. Both the reduced and oxidized forms of the donor absorb weakly, relative to the absorbance of the ruthenium complex, so oxidation of the donor is not observable in the transient difference spectra. Formation of a $Ru(bpy)_3^+$ transient and decay back to zero ΔOD via second-order/equal-concentration kinetics are consistent with electron donor quenching, charge recombination within the solvent cage, cage escape, and diffusion-controlled recombination via reactions 5–8.

$$Q^{4-} + {}^*Ru(bpy)_3^{2+} \xrightarrow{k_5} [Q^{3-}\cdots Ru(bpy)_3^+] \tag{5}$$

$$[Q^{3-}\cdots Ru(bpy)_3^+] \xrightarrow{k_6} Q^{4-} + Ru(bpy)_3^{2+} \tag{6}$$

$$[Q^{3-}\cdots Ru(bpy)_3^+] \xrightarrow{k_7} Q^{3-} + Ru(bpy)_3^+ \tag{7}$$

$$Q^{3-} + Ru(bpy)_3^+ \xrightarrow{k_8} Q^{4-} + Ru(bpy)_3^{2+} \tag{8}$$

Since significant quantities of reduced sensitizer are detected by the transient absorbance for RuL_3^{4-} with all the electron donors studied, and since the absorption and emission spectra of all the sensitizers are similar, it is reasonable to conclude that the quenching occurs predominantly or exclusively by electron transfer in all cases. It is noteworthy that the transient absorbance features of the reduced sensitizer are already at maximum absorbance immediately following the 11-ns pulse of the laser, so that conclusions regarding the dynamics of charge recombination (eq 6) and separation of geminate ion pairs (eq 7) cannot be drawn from these data. Under these conditions only the quantum efficiency for cage escape Φ_{CE} ($=k_7/(k_6 + k_7)$) can be determined. Picosecond laser flash photolysis experiments were carried out in the hope of directly observing solvent cage dynamics; similar experiments have been successfully conducted with donor/acceptor pairs in nonaqueous solutions.[23,24] However, in the case of both systems studied by picosecond methods ($Fe(CN)_6^{4-}/Ru(bpy)_3^{2+}$ and $W(CN)_8^{4-}/Ru(bpy)_3^{2+}$), the maximum transient absorbance was again seen on the shortest time scale observable following the laser

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Table II. Approximate Cage Escape Efficiencies (%) in 100 mM K_2HPO_4, for Cyanometalate Electron Donors and Ruthenium Polypyridyl Sensitizers

	$Os(CN)_6^{4-}$	$Fe(CN)_6^{4-}$	$W(CN)_8^{4-}$	$Mo(CN)_8^{4-}$
RuL_3^{4-}	6	27	67	74
$Ru(bpy)_2L^0$	6	11	80	48
$Ru(bpy)_3^{2+}$	5	3	86	87
$[Ru(bpy)_2(L\cdots L)\text{-}Ru(bpy)_2]^{4+}$ [a]	4	2	41	52

[a] L···L = Mebpy-Mebpy.

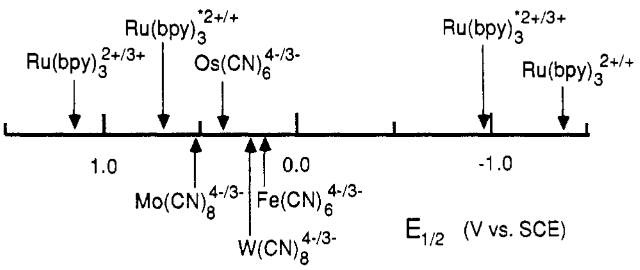
flash, ca. 100 ps. Furthermore, no significant migration of transient features (i.e., shift in location of maxima) was observed. Such a shift might have been attributed to a charge-transfer state of the geminate ion pair.[23,24] These data indicate that the branching of geminate ion pairs via pathways 6 and 7 occurs on a time scale shorter than 100 ps and that only the cage escape yields can be determined from our transient absorbance data.

Table II lists approximate values of Φ_{CE} for various donor/sensitizer pairs, calculated from transient absorbance data with the assumption that $\Delta\epsilon_{510}$ is 8.0×10^3 M^{-1} cm^{-1} for all the sensitizers. Two trends are immediately observable in this table: first, for a given donor, the cage escape efficiency is lowest when the sensitizer has a 4+ overall charge. This observation is explainable simply on the basis of the electrostatic attraction of ions within the solvent cage and its expected effect on the rate of reaction 7. It is surprising that there appears to be no dramatic trend, particularly for the octacyanometalates, toward higher cage escape efficiency as the charge on the sensitizer is changed from 2+ to 0 to 4−; for these quenchers the highest yields (approaching unity) are obtained with $Ru(bpy)_3^{2+}$ and not with RuL_3^{4-}. The second trend is the striking difference between octa- and hexacyanometalate donors. Cage escape yields are high with octacyanometalates, regardless of the overall charge on the sensitizer. In contrast, formation of charge-separated products does not occur efficiently with the hexacyanometalates, especially when the donor and sensitizer bear opposite overall charges. This conclusion differs from that drawn previously[8] from steady-state photolysis studies with solutions containing $Ru(bpy)_3^{2+}$ and $Mo(CN)_8^{4-}$ or $Os(CN)_6^{4-}$.

Varying the counterion from K^+ to Li^+ or Cs^+ had no discernible effect on cage escape efficiency. From the concentrations of K^+ and donor anions used in these experiments and published equilibrium constants,[25,26] we calculate that virtually all of the quenching species are in the monopotassium form in solution, that is, $KM(CN)_n^{3-}$, where $n = 6$ or 8 and M = Fe, Os, W, or Mo. It is therefore unlikely that differences among the quenchers in the number of counterions associated in solution could account for the large observed differences in cage escape yields. Moreover, cage escape efficiencies for both the octa- and hexacyanometalates were relatively independent of ionic strength. For $W(CN)_8^{4-}/Ru(bpy)_3^{2+}$, Φ_{CE} increased smoothly by 10–11% as the ionic strength was increased from 0.12 to 1.32 M; for $Fe(CN)_6^{4-}/Ru(bpy)_3^{2+}$, the cage escape efficiency did not change detectably as the ionic strength was varied within these limits. In all these experiments the quencher was present in large excess over the sensitizer, so variation of the ionic strength does not affect the concentration of free quencher.

Chart I shows the relative formal potentials in aqueous solution of couples involving $Ru(bpy)_3^{2+}$, $^*Ru(bpy)_3^{2+}$, and the donors used in this study. The potentials of the donors were determined by cyclic voltammetry in aqueous 100 mM K_2HPO_4. What is apparent from the relative ordering of these formal potentials is that there is no energetic basis for a difference in cage escape yields between the octa- and hexacyanometalates. That is, variation of the rate of reaction 6 with the difference between the $Ru(bpy)_3^{2+/+}$ and $M(CN)_n^{4-/3-}$ potentials would not be expected to produce the observed trends; for example, $W(CN)_8^{4-/3-}$ and $Fe(CN)_6^{4-/3-}$ have essentially identical driving forces for (6).

Chart I



An obvious difference between the two ions is their size.[27] It is possible that the larger diameter of the octacyanometalates is the chief reason for their larger cage escape efficiencies, relative to those of the hexacyano quenchers. The larger metal center to metal center distance involved with an octacyanometalate could make back electron transfer (6) slower within the solvent cage. All other things being equal, this effect should increase Φ_{CE}. The situation is reminiscent of "loose" and "tight" geminate ion pairs observed by Mataga and co-workers;[24] the former give rise to predominantly charge-separated products, while the latter predominantly undergo charge recombination. Gould, Farid, and co-workers[28] have also reported effects of varying the size of aromatic electron donors on geminate ion pair cage escape efficiency. The electronic structure of the geminate ion pair will of course change as well as one substitutes a d^1 octacyanometalate for a d^5 hexacyanometalate, and substantial differences in the rates of back electron transfer within the cage are therefore not surprising. Recent ab initio calculations of electron self-exchange reactions between octahedral transition-metal complexes show a strong dependence of the rate on both ligand electronic structure and the relative orientation of the two octahedra.[29] It is possible that favorable conformations for the back-electron-transfer reaction are more accessible with the hexacyanometalates than they are with octacyanometalates.

The picture which begins to emerge is that of an electron-transfer process which is relatively insensitive to substantial variation of solution parameters and, surprisingly, to the overall charge on the sensitizer as well. Additionally, there appears to be no dependence of cage escape yield on thermodynamic driving force for back electron transfer. The efficiency of charge separation with ruthenium polypyridyl sensitizers and cyanometalate quenchers is directed by the size, geometry, and/or electronic structure of the latter.

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