J. Am. Chem. Soc. 1992, 114, 430–438

Photoinduced Electron Transfer in Linked Ruthenium(II) Diimine–Diquat Complexes: Linkage Dependence

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Abstract: Intramolecular photoinduced electron transfer in a series of linked ruthenium(II) diimine donor–diquat acceptor complexes was examined as a function of the nature of the bridge between the donor and acceptor centers. Bridging groups include polymethylene chains ($-(CH_2)_n-$, $n = 2$–7, 12) and phenyl- or cyclohexyl-containing spacers (p-($-CH_2-Ph-CH_2-$), p-($-CH_2-$*trans*-cyclohexyl$-CH_2-$), and p-($-CH_2-$*cis*-cyclohexyl$-CH_2-$)). The rate constant for electron transfer decreases sharply as the number of methylenes separating the donor and acceptor increases in straight chain alkyl bridged complexes. An odd–even alternation in the electron-transfer rate constant is observed in the straight chain series. Rate constants for electron transfer in the series of complexes bridged by the cyclic spacers having a fixed number of bonds but differing steric environments varied by only a factor of 2. Results are discussed in terms of possible through-space and through-bond interactions. The combined results suggest that the bridging ligands may serve to mediate the electron transfer in these systems.

Introduction

Intramolecular electron-transfer reactions have been widely examined for a variety of reasons including (1) predictions of electron-transfer theories can be tested by appropriate synthetic variation and kinetic studies,[1–13] (2) effects of geometry and molecular organization on electron-transfer rates can be examined in detail,[1,3,4,14–20] and (3) artifical photosynthetic systems can be prepared in which long-lived charge-separated radical ions are generated upon photolysis.[3,7,8b,15] Artificial photosynthetic systems, if successfully developed and exploited, may prove useful in the development of novel energy conversion and storage devices or molecular electronic materials.[2a,7b,m,21a] In this regard ruthenium(II) bipyridyl complexes have been widely investigated as both electron-donating and -accepting sensitizers in both covalently linked donor–acceptor (D–A) systems[6d,7,8,16,21–23] and in various organized assemblies such as micelles, zeolites, clays, vesicles, and monolayer films and assemblies.[24–30] These systems are attractive because they have metal to ligand charge-transfer transitions (MLCT) in the visible, relatively long lived excited states and they are generally stable upon one-electron oxidation or reduction.[31–33]

The examination of ruthenium(II) diimine chromophores covalently linked to either electron donors or acceptors has shown that the behavior of such complexes cannot be quantitatively understood from studies of bimolecular reactions of the Ru(II) complex with the excited-state quencher. Two reactions can be examined in linked donor–acceptor complexes which do not exhibit permanent photochemical changes: electron-transfer quenching of the excited Ru(II) complex and the thermal back electron transfer to regenerate the starting complex (eq 1a, b). In bimolecular photoredox reactions involving $[(bpy)_3Ru]^{2+}$ and series of viologens and diquats as electron-accepting quenchers, the rate of the electron-transfer quenching process can be related to the free energy using classical electron-transfer theories.[33] Recent work of Cooley et al. showed that intramolecular electron-transfer quenching of linked ruthenium(II) bipyridyl–diquat complexes, shown below (L = 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, 4,4′,5,5′-tetramethyl-2,2′-bipyridine), exhibit rates which depend on both the driving force and partitioning of the excited-state

$$[(L)_2Ru(III)(bpy^{-}\text{-}A)]^{n+*} \xrightarrow{k_{et}} [(L)_2Ru(III)(bpy\text{-}A^{-})]^{n+} \tag{1a}$$

$$[(L)_2Ru(III)(bpy\text{-}A^{-})]^{n+} \xrightarrow{k_b} [(L)_2Ru(II)(bpy\text{-}A)]^{n+} \tag{1b}$$

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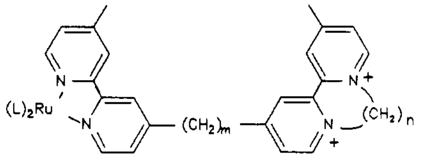
energy of the Ru(II) complex between ligands adjacent and remote to the diquat quencher.[8a]



4mn-DQ^{2+}

m = 2 ; n = 2, 3, 4

Evidence was obtained for electron transfer exclusively from the adjacent ligand. Back electron transfer in homogeneous so-

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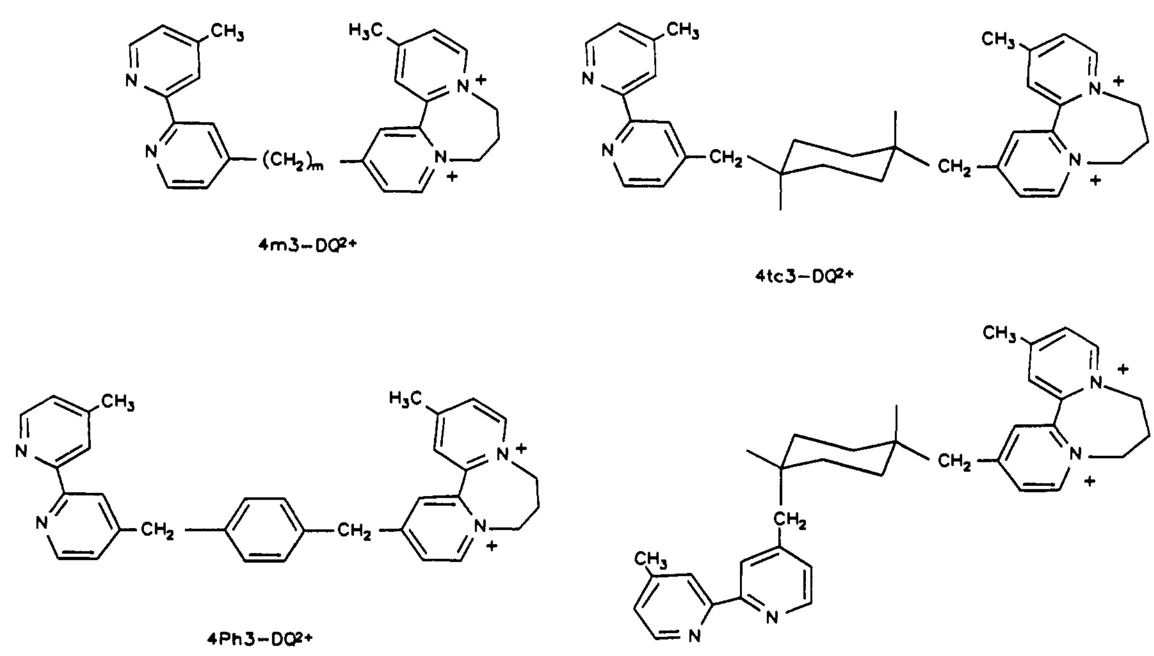

$4m3-DQ^{2+}$

$4tc3-DQ^{2+}$

$4Ph3-DQ^{2+}$

$4cc3-DQ^{2+}$

Figure 1. Ligands used in preparation of $[(L)_2Ru(4x3-DQ^{2+})]^{4+}$ complexes.

lutions of these systems was found to be faster than the quenching process. Recent studies by Mallouk and co-workers have showed that when complexes having Ru(II) chromophores and viologen acceptors are bound to zeolites, the viologen resides in the channel of the zeolite and the Ru(II) center is bound to the surface. In such systems electron-transfer quenching of the Ru(II) complex is still observed and the transient ions (Ru(III) and reduced viologen) can be observed by flash photolysis to have a lifetime much longer than the excited complex.[34] The results suggest that conformational effects for forward and back electron transfer differ.

In this work studies of Ru(II)–diquat systems are expanded to include variation of the moiety bridging the complex and the diquat including (a) varying the length of the hydrocarbon chain linking the adjacent bipyridine and diquat and (b) introduction of some steric constraints in the bridging ligand. The ligands examined in this work are shown in Figure 1 along with the abbreviations to be used here. Of particular interest are results from examination of the dependence of the forward electron transfer rate on increasing chain length in systems having MLCT excited states localized principally on either the adjacent or the remote ligand of the complex. A preliminary account of these results has been published.[22]

Experimental Section

Materials and Supplies. All reagents were used without further purification unless specified otherwise. 4,4′-dimethyl-2,2′-bipyridine was obtained from Reilly Tar and Chemical Co. and was recrystallized from ethyl acetate prior to use. Diisopropylamine was distilled from KOH under a N_2 atmosphere and stored over molecular sieves (Linde, 4 A). Acetonitrile (Burdick and Jackson) was distilled from CaH_2 immediately prior to use. Tetraethylammonium perchlorate (TEAP) was prepared according to the method of Sawyer.[36] Preparation of diquat-containing complexes of the type $[(bpy)_2Ru(4m3-DQ^{2+})]^{4+}$ and $[(tmb)_2Ru(4m3-DQ^{2+}]^{4+}$ is described in an earlier paper.[8a] All ruthenium complexes were purified by medium-pressure chromatography on silica gel using 5:4:1 acetonitrile–water–saturated KNO_3 (aq) as the eluent. The complexes were isolated as the PF_6^- salts and were determined to be pure by cyclic voltammetry and TLC. ^1H NMR data are available for selected ligands and complexes as supplemental material.

Syntheses. 1,4-Bis[(4′-methyl-2,2′-bipyridyl-4-yl)methyl]cyclohexane-1,4-diol, I. A solution containing 31.4 g (0.31 mol) (43.6 mL) of i-Pr_2NH in 80 mL of THF and 208 mL (0.32 mol, 1.54 M in hexane) of n-BuLi were combined under N_2, and the mixture was stirred for 1 h at −78 °C. A solution containing 55.3 g (0.3 mol) of 4,4′-dimethyl-2,2′-bipyridine in 1500 mL of THF was added (poor solubility!) in one portion, and the mixture was stirred for 1 h in an ice bath. A solution containing 11.2 g (0.1 mol) of 1,4-cyclohexanedione in 200 mL of THF was then added. The mixture changed from red-brown to green. Stirring under N_2 was continued for 16 h, after which 5 mL of MeOH and 200 mL of H_2O were added to quench any remaining carbanion. About 50% of the solvent was removed by rotary evaporation. CH_2Cl_2 was added to the solution. The mixture was extracted with water, and the organic fraction was separated and dried over $MgSO_4$. After further evaporation ~50% of the initial unreacted bipyridine precipitated and was filtered off. The remaining solvent was removed, and the residue (32.6 g) was separated by silica gel column chromatography (eluent 2% Et_3N in EtOAc, increased to 10% Et_3N in EtOAC). A 0.2-g sample of pure *trans*-diol (mp 241 °C, mass spectrometry, NMR) and 8.1 g of mixed *cis*- and *trans*-diol (18%) were obtained. *cis*-Diol has mp 195–196 °C (NMR, mass spectrometry, IR). This reaction was run several times; the yields of diol product varied from 15 to 30%.

1,4-Bis[(4′-methyl-2,2′-bipyridyl-4-yl)methyl]cyclohexa-1,4-diene, II. The mixture of diols I (9.8 g, 0.0204 mol) was dissolved in 700 mL of glacial HOAc and cooled in an ice–water bath. To this solution was added 175 mL of H_2SO_4 dropwise with stirring. After the addition of a few drops, the salt of bipyridine and H_2SO_4 was formed, and stirring became difficult. The addition of H_2SO_4 was continued slowly, keeping the temperature in the range of 15–25 °C; finally, the salt redissolved. Stirring at room temperature was continued for 24 h. The reaction mixture was then diluted with cold water, neutralized to pH ~7 with NaOH solution (in an ice–water bath), and extracted with CH_2Cl_2, and the CH_2Cl_2 was dried over $MgSO_4$. After removal of the solvent under reduced pressure, an oily residue was obtained (~9 g crude) which was

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chromatographed on a silica gel column (eluent EtOAc–hexane–Et_3N (10:10:2 (vol)); yield 8.1 g, 89.2%). ^1H NMR spectrum showed the mixture of different dienes, and a very small amount of aromatic compound. This reaction was run several times; yields were from 60 to 90%.

α,α′-Bis(4′-methyl-2,2′-bipyridyl-4-yl)-*p*-xylene, III. To a solution of 8 g (0.018 mol) of the mixed dienes II in 200 mL of dry mesitylene was added 2 g of 5% Pd/C. Heating and stirring under N_2 was continued for 41 h (monitored by NMR every ~8 h). Initially no change in the ratio of aromatic compound to diene was observed. A second portion of catalyst was added (~1.5 g), and heating and stirring were continued for 48 h. The catalyst was then removed by filtering through Celite which was washed with toluene several times. The combined solvents were evaporated under reduced pressure to yield an oily residue, 7.9 g, which contained the aromatic compound III, dienes, and unidentified byproducts. Separation by silica gel column chromatography (eluent hexane–EtOAc–Et_3N (10:2:1 (vol))) yielded III nearly pure (4.2 g, 52%), but small amounts of unidentified products were present which coelute with III. Recrystallization several times from EtOAc, however, yielded pure III, mp 160.5–162 °C (NMR, mass spectrometry). As with the previous preparations, this reaction was run several times, with varying yields.

1,4-Bis[(4′-methyl-2,2′-bipyridyl-4-yl)methyl]cyclohexane, *cis*-IVa and *trans*-IVb. To the mixture of dienes II (7.8 g, 0.0175 mol) dissolved in 35 mL of HOAc was added 0.2 g of PtO_2 in a Fisher-Porter bottle; the bottle was purged with hydrogen, and the mixture was stirred under 42 psi (3 atm) of H_2 for 46 h. The catalyst was filtered off through Celite, and the majority of HOAc was evaporated. The residue was dissolved in CH_2Cl_2, washed with 5% NaOH solution, and dried over $MgSO_4$, and the solvent was evaporated, yielding ~7 g of crude product (NMR of crude mixture showed that IV was contaminated with small amounts of III, II, and other olefin products; yields of IV were typically ~25–30%).

The crude mixture was dissolved in HOAc (~150 mL), and a solution containing 0.455 mL of bromine in 3 mL of HOAc was added dropwise. Initially some yellow solid precipitated which redissolved immediately. Stirring was continued for 18 h at room temperature. At this point the NMR of the sample shows no olefinic protons. Most of the HOAc was evaporated, and the residue was mixed with water, extracted with CH_2Cl_2, and then washed with H_2O and Na_2CO_3 solution. The CH_2Cl_2 was removed to yield an oily residue (~7 g).

To convert the brominated contaminants to more polar (and thus more easily separated) alcohols, the crude mixture after bromination was dissolved in 250 mL of dioxane and 50 mL of water. The solution was stirred for 11 h at 80–90 °C (monitored by TLC). Then the solvent was evaporated and the residue mixed with water. This mixture was extracted with CH_2Cl_2; the organic layer was washed with Na_2CO_3 solution and dried over $MgSO_4$. After solvent evaporation, the crude mixture was separated by chromatography on a silica gel column (EtOAc eluent), yielding a mixture of the two isomers of the cyclohexyl compound IV (3.8 g, 48.2% yield).

The mixture of cis and trans isomers were separated by repeated fractional recrystallization from EtOAc (IVb) and EtOH (IVa) (IVb, mp 239–241 °C (mass spectrometry, X-ray structural determination); IVa, mp 133–135 °C). The purity of the trans and cis isomers could be easily determined by NMR spectra, which show characteristic doublets of the methylene group between the pyridine ring and cyclohexyl ring at 2.55 and 2.7 ppm, respectively.

α,ω-Bis[4′-methyl[2,2′-bipyridyl]-4-yl]alkanes. Straight chain linked bipyridines were synthesized as reported previously.[8a,c,22]

Formation of *n* = 3 "Diquats" from III, IVa, and IVb. One of the two bipyridines in each of the compounds III, IVa, IVb and bis(bipyridylyl)alkanes could be converted to the respective diquaternary salt (diquat) having three methylene units linking the two bipyridine nitrogens ($4Ph3DQ^{2+}$, $4cc3DQ^{2+}$, $4tc3DQ^{2+}$, and $4m3\text{-}DQ^{2+}$, respectively) by reaction with 1,3-dibromopropane via procedures previously reported.[8a,c] Purification and yields were similar to those reported previously.[8a,c] After purification by chromatography on silica gel [eluent H_2O–KNO_3(aq satd)–acetonitrile (4:1:5 (vol)), the acetonitrile was removed at reduced pressure and the respective compounds were each isolated by precipitation as their PF_6^- salts.

Luminescence lifetimes of the complexes were obtained in room temperature acetonitrile solutions freeze–pump–thaw degassed (FPT) to a final pressure of $<10^{-5}$ Torr. Samples were prepared and degassed in the dark and were sealed under vacuum in 3-mm-diameter Pyrex tubes. Luminescence decays were measured by time-correlated single photon counting when the lifetime was less than 20 ns and by capture of transient decays following pulsed N_2 laser photolysis for longer lifetimes. Both the photon counting and N_2 laser systems have been described elsewhere.[36,37] Decays were fit as either single or double exponential using a modified Marquardt algorithm.[39]

Scheme I

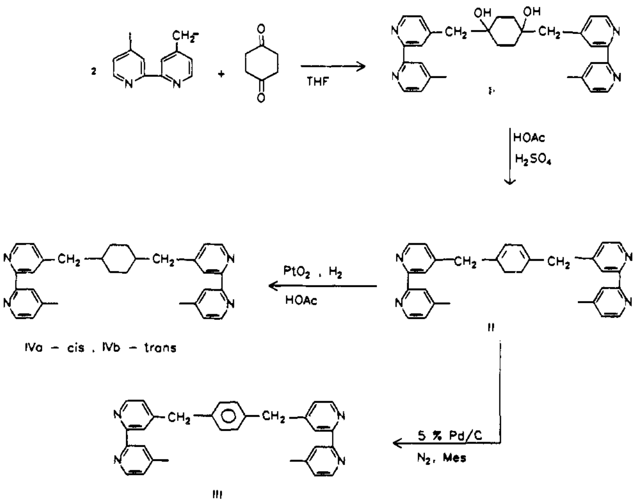

Table I. Representative Reduction Potentials[a] and Luminescence Maxima for $[(L)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ Complexes in CH_3CN at Room Temperature

L	Ru(III/II)	$DQ^{2+/+}$	$DQ^{+/0}$	Ru(II/I)	E_{em}, cm^{-1}
bpy	1.24	–0.64	–0.92	–1.36	16000
dmb	1.13	–0.65	–0.93	–1.45	16000
tmb	1.06	–0.65	–0.93	–1.51	15800

[a] Potentials are given as volts vs the SSCE reference with tetraethylammonium perchlorate as supporting electrolyte.

Variable-temperature lifetimes were obtained on FPT degassed samples in 4:1 ethanol–methanol. Sealed samples were mounted in a home-built cylindrical Cu holder and mounted in an Air Products Displex helium refrigerator. Luminescence decays were obtained between 150 K and room temperature following N_2 laser excitation as described above. Luminescence decays obtained at temperatures below approximately 250 K were multiexponential for all the complexes studied. A variety of explanations exist for the observation of inhomogeneous kinetics associated with intramolecular electron transfer. These include (a) impurity emission, (b) conformational effects,[42,47] and (c) the appearance of an inhomogeneous distribution of solvent relaxation times.[4f] Since the data were obtained using a digitizer having only 10-bit vertical resolution, detailed analysis of multiple exponential decays did not yield quantitatively reproducible results. As a result, only the observation of the appearance of multiexponentiality is reported here.

Luminescence quantum yields were determined from integrated corrected emission spectra of the diquat complexes relative to $[(bpy)_3Ru]^{2+}$ as reference. The diquat complexes, dissolved in CH_3CN and absorbance matched to the $[(bpy)_3Ru]^{2+}$ solution, were freeze–pump–thaw degassed prior to measurement of the emission spectra. Quantum yields were determined from the ratio of integrated emission spectra, assuming $\phi_{em} = 0.028$ for $[(bpy)_3Ru]^{2+}$ in aerated water.[38] Quantum yields were corrected for refractive index differences between the solvent of the sample and reference.[36]

Results

The preparation of the ligands and Ru(II) complexes follows methods similar to those outlined in an earlier paper describing the photophysical behavior of $[(L)_2Ru(42n\text{-}DQ^{2+})]^{4+}$ complexes.[8a] Preparation of the *cis*- and *trans*-cyclohexyl-containing ligands ($4cc3\text{-}DQ^{2+}$ and $4tc3\text{-}DQ^{2+}$) and the *p*-xylyl-bridged ligand ($4Ph3\text{-}DQ^{2+}$) follows Scheme I. Reaction of 1,4-cyclohexanedione with 2 equiv of the monoanion of 4,4′-dimethyl-2,2′-bipyridine yields the diol I. Dehydration of the diol was achieved with H_2SO_4 in acetic acid to yield the diene II. The diene was converted to III by aromatization with 5% Pd/C in mesitylene. Reduction of II with H_2/PtO_2 yielded a mixture of the *cis*- and *trans*-me-

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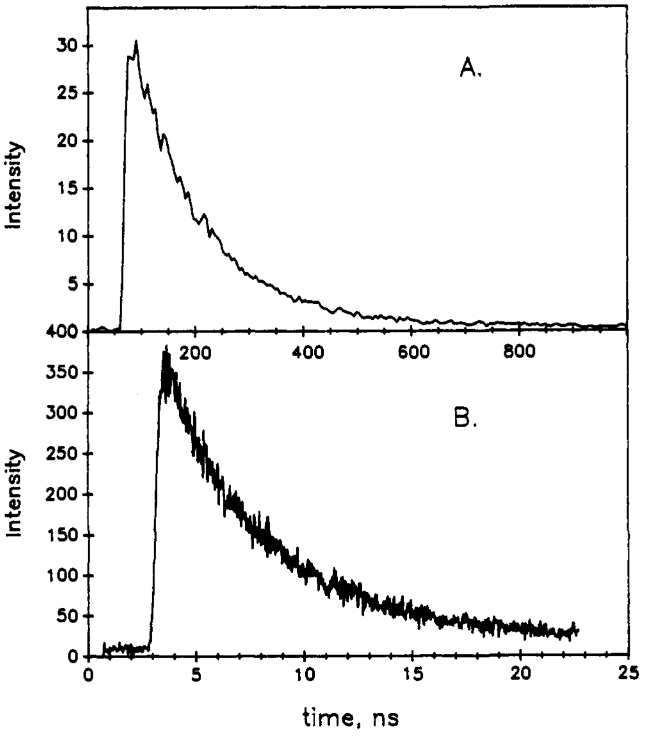

Figure 2. Room temperature luminescence decays in CH_3CN observed for $[(bpy)_2Ru(453\text{-}DQ^{2+})]^{4+}$ (A) obtained by direct digitization of the decay and $[(tmb)_2Ru(443\text{-}DQ^{2+})]^{4+}$ (B) obtained by time-correlated single photon counting.

thylcyclohexane derivatives IVa and b. Ligands III and IV were quaternarized to the $4m3\text{-}DQ^{2+}$ derivatives using 1,3-dibromopropane, as described earlier.[8a] Structural data for the *trans*-methylcyclohexyl ligand IVb is reported elsewhere.[48]

The redox potentials of complexes of the type $[(L)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ vary with L, but are independent of the bridge between the diquat and the metal center (m in the $4m3\text{-}DQ^{2+}$). Table I gives reduction potentials for complexes having L = bpy, dmb, and tmb. Potentials were determined by cyclic voltammetry in CH_3CN using sweep rates between 50 and 200 mV/s. All of the waves observed were chemically reversible on this time scale ($i_{p,c}/i_{p,a} \approx 1$). The metal-centered Ru(III/II) reduction potential (eq 2) becomes more negative with increasing alkylation of the bipyridine while both the first (eq 3) and second reduction of the diquat ($DQ^{2+/+}$ and $DQ^{+/0}$) are unaffected by variation of the ligand L on the metal center.[8a] Of particular importance is the observation that the one-electron reduction of the coordinated $423\text{-}DQ^{2+}$ is identical to that of the longer chain diquats.

$$[(L)_2Ru(III)(4m3\text{-}DQ^{2+})]^{5+} \xrightleftharpoons{e^-} [(L)_2Ru(II)(4m3\text{-}DQ^{2+})]^{4+} \quad (2)$$

$$[(L)_2Ru(II)(4m3\text{-}DQ^{2+})]^{4+} \xrightleftharpoons{e^-} [(L)_2Ru(II)(4m3\text{-}DQ^{+})]^{3+} \quad (3)$$

Room temperature luminescence maxima of the Ru(II) complexes in CH_3CN are also given in Table I. Only a slight variation in the emission maximum is observed as L is changed from bpy to tmb. Luminescence quantum yields of $[(tmb)_2Ru(463\text{-}DQ^{2+})]^{4+}$ and $[(bpy)_2Ru(463\text{-}DQ^{2+})]^{4+}$ were determined in CH_3CN relative to $[(bpy)_3Ru]Cl_2$ in H_2O.[38] Values of 0.003 and 0.008 were obtained for freeze–pump–thaw degassed samples of the tmb and bpy complexes, respectively.

Luminescence lifetimes of $[(L)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ (L = tmb or bpy) complexes having straight chain alkyl bridges ($(CH_2)_m$, m = 2–7, 12) were measured in CH_3CN. Complexes having lifetimes longer than 30 ns were measured by direct transient digitization of emission from samples excited by a N_2 laser or N_2-pumped dye laser (coumarin 460 at 460 nm). Shorter lifetimes were measured by time-correlated single photon counting using a mode-locked, cavity-dumped Ar^+ laser for excitation.[38] In most cases observed decays could be fit as single exponentials. Some samples required two exponentials to adequately fit the data; the long lifetime component in these cases was long enough that it could be ascribed to luminescence from Ru(II) complexes not covalently linked to an intact diquat quencher. Representative luminescence decays are shown in Figure 2. Room temperature luminescence decays of diquat complexes were assumed to consist of only radiative (k_r) and nonradiative (k_n) decay from the ^3MLCT state of the Ru complex and electron transfer to the diquat (k_f, eq 4).

$$1/\tau_{obs} = k_r + k_n + k_f \qquad k_f = 1/\tau_{obs} - 1/\tau_0 \quad (4)$$

Table II. Rate Constants for Intramolecular Electron Transfer in $[(L)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ Complexes[a]

$4m3\text{-}DQ^{2+}$ complex	distance[b]	L = tmb k_{et}, $\times 10^{-7}$ s^{-1}	L = bpy k_{et}, $\times 10^{-7}$ s^{-1}	tmb/bpy
423	8.5	1110	59	19
433	9.7	20	2.4	8.3
443	11.0	33	5.4	6.1
453	12.2	4.6	0.76	6.0
463	13.5	3.6	0.87	4.1
473	14.7	1.7	0.62	2.7
4123	21.0		0.13	

[a] Rate constants given are ±10%. [b] Distance (Å) estimated from molecular models for separation of 2-carbons of the bridging bipyridine ligands (see Figure 3).

Table III. Intramolecular Photoinduced Electron-Transfer Rate Constants for $[(L)_2Ru(4x3\text{-}DQ^{2+})]^{4+}$ Complexes Having Six Carbons between the Ru(II) Complex and Diquat

L	$4x3\text{-}DQ^{2+}$	Distance, Å[a]	k_{et}, $\times 10^{7}$ s^{-1}
tmb	463	13.5	3.6
tmb	4ph3	11.9	3.2
tmb	4cc3	11.0	2.3
tmb	4tc3	12.3	2.0
dmb	4tc3	12.3	1.3
bpy	4ph3	11.9	0.68

[a] Separation distance obtained for fully extended conformers (see text).

The observed electron transfer rate, k_f, was obtained from the difference between the decay rate of the diquat complex and the decay rate, $1/\tau_0$, of the parent Ru(II) complex having no attached diquat (eq 4). The parent complexes for both the $[(bpy)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ and $[(tmb)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ series, $[(bpy)_2Ru(dmb)]^{2+}$ and $[(tmb)_2Ru(dmb)]^{2+}$, respectively, both have decay rate constants of 1.4×10^6 s^{-1} in FPT degassed room temperature acetonitrile. It is assumed that k_r and k_n are the same for both the parent complex and the complex having the covalently attached diquat. This is supported by the observation that radiative decay rates of $[(tmb)_2Ru(463\text{-}DQ^{2+})]^{4+}$ and $[(bpy)_2Ru(463\text{-}DQ^{2+})]^{4+}$, calculated from the measured luminescence quantum yields (above) and luminescence lifetimes, are close to those of the parent complexes. Observed electron-transfer rate constants determined by eq 4 are reported in Table II. Rate constants for several complexes having six carbons as the shortest through-bond path between the bipyridine of the complex and the diquat are given in Table III.

For purposes of comparison, distances separating the 2-pyridyl carbons of the coordinated bipyridine and the diquat were determined as shown in Figure 3. The distances were determined for fully extended conformations from molecular models constructed using the program QUANTA. In all cases a torsion angle of 90° was assumed between the bipyridine plane and the first two carbon atoms of the bridge (Figure 3). Distances determined in this manner are reported in Tables II and III.

Figure 4 shows the ionic strength dependence of the luminescence lifetime of $[(bpy)_2Ru(453\text{-}DQ^{2+})]^{4+}$ and $[(bpy)_2Ru(4123\text{-}DQ^{2+})]^{4+}$ in CH_3CN using tetraethylammonium perchlorate as the added electrolyte. In both complexes the lifetime decreases with increasing ionic strength, but a larger effect is

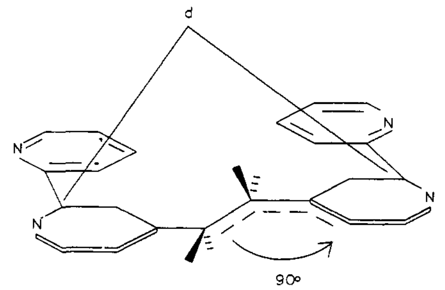

Figure 3. Representation of 423-DQ^{2+} showing 90° torsion between the pyridine rings and the bridging methylenes and the sites chosen for determination of the average separation distance of the donor Ru(II) complex and the diquat acceptor.

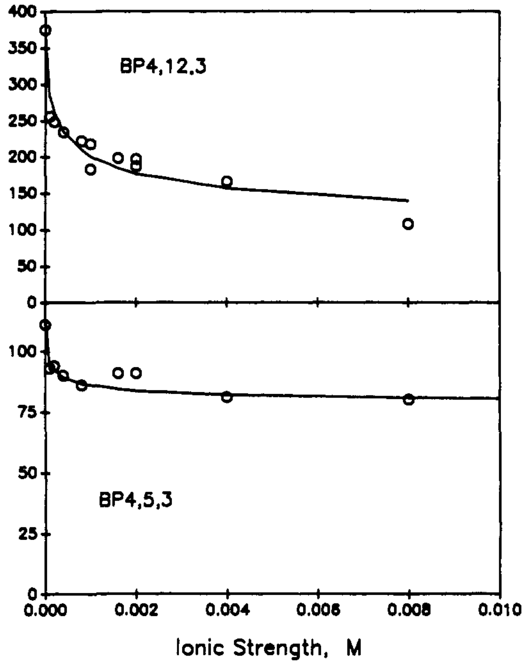

Figure 4. Luminescence lifetimes of $[(bpy)_2Ru(4123\text{-}DQ^{2+})]^{4+}$ and $[(bpy)_2Ru(453\text{-}DQ^{2+})]^{4+}$ as a function of ionic strength (tetraethylammonium perchlorate) in CH_3CN. Solid lines represent fits of the data (see text).

observed for the 4123-DQ^{2+} complex. The luminescence decay rate constant of the 453-DQ^{2+} complex increased by a factor of 1.4 upon increasing the ionic strength from 0 to 0.008 while that of the 4123-DQ^{2+} increased by a factor of 2.5 over the same range. The solid lines of Figure 4 represent fits of the data to an expression commonly used for intermolecular electron-transfer reactions:[41]

$$\ln (1/\tau) \approx \ln k_{\mathrm{et}} = \ln k_{\mathrm{et}_0} + \frac{w_0 \beta \sigma \sqrt{\mu}}{(1 + \beta \sigma \sqrt{\mu}) RT}$$

where w_0 is the work required to bring the reactants together at infinite dilution ($z_{\mathrm{Ru}} z_{\mathrm{DQ}} e^2 / D_s \sigma$), β is the ion interaction parameter ($(8\pi N e^2/1000 D_s RT)^{1/2}$), σ is the separation distance of the ions in the precursor complex, k_{et_0} is the zero ionic strength rate constant, and μ is the ionic strength. The only variable parameter in the fits was σ; the value obtained has no physical meaning, however, since the calculated value for w_0 is inappropriate for an intramolecular reaction.

Discussion

Linkage Dependence of Intramolecular Electron Transfer. The luminescence of both $[(tmb)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ and $[(bpy)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ series is strongly quenched relative to the parent chromophores lacking the covalently attached diquat. In an earlier report on these complexes, Cooley and co-workers concluded that, for a series of 42m-DQ^{2+}-containing complexes ($m = 2$–4), photoinduced electron transfer occurs from the charge-transfer state localized on the bridging ligand to the attached diquat (Scheme II).[8a] The rate of the electron transfer is influenced by both the driving force for the process as determined from electrochemical and spectroscopic data and the position of the intramolecular equilibrium of the charge-transfer excited states (eq 6). Intramolecular equilibration of the charge-transfer states localized on remote and adjacent ligands (eq 6) was found to be rapid relative to electron transfer (eq 7). In every case examined, back electron transfer (eq 8) was faster than excited-state electron transfer.

Scheme II

$$[(L)_2Ru(II)(bpy\text{-}4m3\text{-}DQ^{2+})]^{4+} \xrightarrow{h\nu} [(L)(L^-)Ru(III)(bpy\text{-}4m3\text{-}DQ^{2+})]^{4+*} \quad (5)$$

$$[(L)(L^-)Ru(III)(bpy\text{-}4m3\text{-}DQ^{2+})]^{4+*} \rightleftharpoons [(L)_2Ru(III)(bpy^-\text{-}4m3\text{-}DQ^{2+})]^{4+*} \quad (6)$$

$$[(L)_2Ru(III)(bpy^-\text{-}4m3\text{-}DQ^{2+})]^{4+*} \xrightarrow{k_\alpha} [(L)_2Ru(III)(bpy\text{-}4m3\text{-}DQ^{+})]^{4+} \quad (7)$$

$$[(L)_2Ru(III)(bpy\text{-}4m3\text{-}DQ^{+})]^{4+} \xrightarrow{k_b} [(L)_2Ru(II)(bpy\text{-}4m3\text{-}DQ^{2+})]^{4+} \quad (8)$$

The observed electron-transfer rate constant, k_f, can be expressed as the product of the fraction of the MLCT state population localized on the adjacent ligand, α, and the rate constant for electron transfer from the adjacent ligand, k_{et}, to the diquat (eq 9).[8a] In the series $[(L)_2Ru(42n\text{-}DQ^{2+})]^{4+}$ it was found that

$$k_f = \alpha k_{\mathrm{et}} \qquad k_{\mathrm{et}} = \nu_n \kappa_{\mathrm{el}} \exp(-\Delta G^\ddagger / RT)$$
$$\Delta G^\ddagger = (\lambda/4)(1 + \Delta G/\lambda)^2 \qquad (9)$$

reasonably good agreement between k_f and the product of calculated values of α and k_{et} (using classical electron-transfer theory) is obtained for all complexes except $[(tmb)_2Ru(423\text{-}DQ^{2+})]^{4+}$, where the rate of electron transfer is fast enough (Table III) that the assumption of equilibration of the charge-transfer states may no longer hold. Values of k_{et} were calculated by assuming that the nuclear frequency factor, ν_n, electronic transmission coefficient, κ_{el}, and reorganizational energy, λ, were invariant from complex to complex in the series.

In a series of complexes having identical ΔG, but varying in the length of the alkyl chain bridging the metal complex and the diquat, both the reorganizational energy and the electronic transmission coefficient are expected to change.[5b,10b,40] Semiclassical descriptions of electron-transfer reactions predict that the electronic transmission coefficient, and thus the electron transfer rate, will decrease exponentially with increasing separation of the donor and acceptor (eq 10).[1f,2k,40,41] This has been elegantly demonstrated for rigidly bridged, conformationally identical organic donor–acceptor complexes[1] and, with a smaller degree of certainty, in other systems exhibiting intramolecular electron transfer.[2,3,10,13] Values of β range from 0.8 to 1.4 $Å^{-1}$.

$$k_{\mathrm{et}}(r) = k_{\mathrm{et}}(R_0) \exp[-\beta(r - R_0)]$$
$$R_0 = \text{distance of closest approach} \qquad (10)$$

In the series of Ru(II)–diquat complexes examined here, luminescence decays are single exponential at room temperature. The implication of the observation is that either (a) electron transfer occurs from a single conformation or (b) conformational motion is fast relative to electron transfer.[17c,42] Since measured electron-transfer rates are relatively slow ($\sim 10^7\ s^{-1}$) in most cases, the latter explanation is more likely; however, because the donor Ru(II) complex and the diquat are both dications, it is also likely that the distribution of conformations in solution heavily favors

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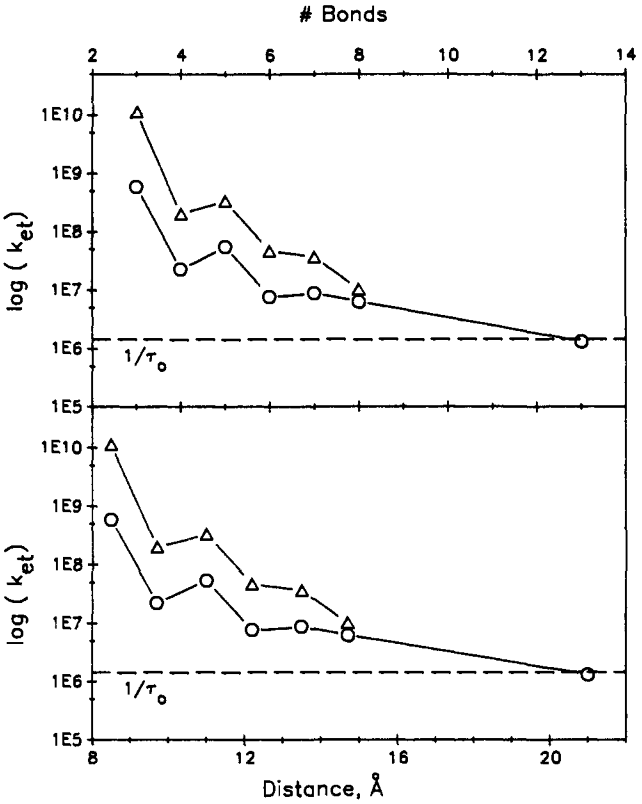

Figure 5. Dependence of log k_f on the number of bonds and distance of the bridge between the Ru complex and diquat for $[(tmb)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ (△) and $[(bpy)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ (○).

conformers similar to that having a fully extended alkyl chain (Figure 3). If coulombic factors are important in influencing the conformational distribution in solution and if conformational change is rapid relative to electron transfer, increasing the ionic strength of the solution should result in an increase in observed electron-transfer rates and luminescence decays should remain single exponential. This proved to be the case for $[(bpy)_2Ru(453\text{-}DQ^{2+})]^{4+}$ and $[(bpy)_2Ru(4123\text{-}DQ^{2+})]^{4+}$ in CH_3CN using tetraethylammonium perchlorate as the added electrolyte (Figure 4). The complex bridged by 12 methylenes exhibits a factor of 2.5 increase in the luminescence decay rate upon increasing the ionic strength to 0.01 M while the complex having 5 methylenes increases by only a factor of 1.5. The result suggests that the relative effect of ionic strength on the distribution of conformers increases with increasing chain length of the bridge (decreasing coulombic interaction of the Ru(II) complex and diquat). This observation is also consistent with trends found in the quenching of a series of $[L_2Ru(42m\text{-}DQ^{2+})]^{4+}$ complexes as a function of solvent dielectric; namely, the quenching rate constant decreases in going from CH_3CN to 1,2-dichloroethane solvent.[8d]

Figure 5 shows the dependence of log k_f on both the number of bonds of the bridging ligand spacer and the donor–acceptor distance (as defined in Figure 3) for the series $[(tmb)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ and $[(bpy)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$. The figure clearly shows that rate constants for complexes having an odd number of bonds, $2n + 1$, in the chain are generally faster than those of complexes having $2n$ bonds in the chain and that the odd–even chain length alternation in the observed rate constant remains when log k_{et} is plotted vs the *distance* (as defined in Figure 3). This odd–even alternation has been observed in organic donor–acceptor complexes which form intramolecular excimers and exciplexes[43] and others which exhibit intramolecular electron transfer.[44]

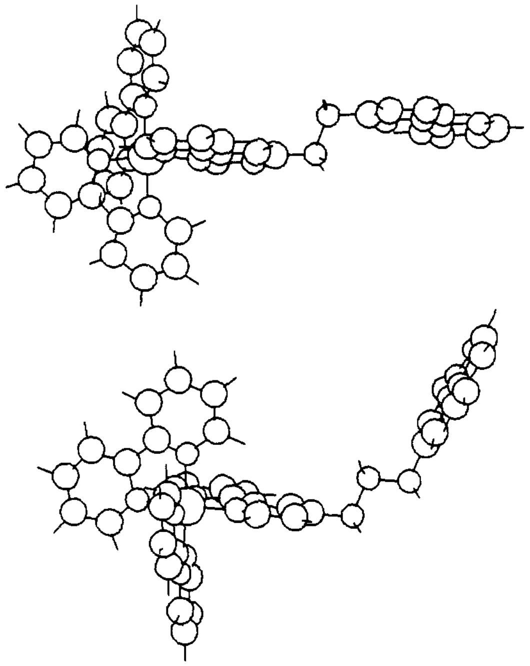

Figure 6. Ball and stick representations of fully extended conformers (as in Figure 3) for $[(bpy)_2Ru(420\text{-}DQ^{2+})]^{2+}$ and $[(bpy)_2Ru(430\text{-}DQ^{2+})]^{2+}$.

Several explanations can account for the observed odd–even alternation. For reactions occurring over long distances, electronic coupling is influenced by both through-space and through-bond interactions. Extended Huckel calculations by Hoffman and co-workers showed the importance of orbital interactions through σ-bonding networks and clearly showed that, for a given conformation, the magnitude of the interaction is stronger for bridges having an odd number of σ bonds between a donor and an acceptor.[45] More recent theoretical work has elaborated on the simple extended Huckel model, but the qualitative results are similar.[12b,46] Although the data is limited, rate constants for complexes having bridges with $2n + 1$ bonds are faster than those having $2n$ bonds for both the bpy and tmb series (with one exception), consistent with the predicted behavior. However, results of others indicate that relative through-bond interactions are strongly dependent upon conformation[13,45,46] and, given the conformational flexibility of the complexes studied, the observed correlation with theory may be fortuitous. A second explanation for the observed effect is that, for most of the complexes, electron transfer occurs predominantly via a through-space interaction from one of a limited number of rapidly equilibrating conformers, and that the predominant conformers of the complexes bridging by odd numbers of bonds have greater donor–acceptor overlap than those bridged by even numbers of carbons. Figure 6 shows ball and stick model representations of the fully extended conformers (with torsion angles defined as in Figure 3) of the two- and three-carbon-bridged complexes. It is clear that significant differences exist for a given set of torsion angles in the bridged complexes. Thus, the relative importance of through-bond and through-space interactions in these complexes cannot be inferred from the observation of an odd–even rate alternation alone.

One means of assessing the relative importance of through-space and through-bond interactions in these systems is to examine the magnitude of the decrease in log k_{et} with increasing bridge length since through-space interactions have a much stronger distance dependence.[40,46] Examination of Figure 5 reveals that the decrease

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in log k_f with the number of bonds is nearly linear for both the even and odd series (with fewer than 10 bonds in the bridge). For the complexes having an even number of bonds in the bridge, the slope of the logarithmic (base 10) dependence is 0.62 (correlation coefficient (cc) 0.992) per bond for the $[(tmb)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ series and 0.46 (cc = 0.997) for $[(bpy)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$. Much smaller slopes are observed for the bridges having even numbers of bonds (0.22 per bond for $[(tmb)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ and 0.14 for $[(bpy)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$. Paddon-Row and Jordan calculated the dependence of intramolecular self-exchange electron-transfer rates of a series of norbornyl-type dienes as a function of the number of bonds separating the sites of unsaturation assuming either pure through-bond or pure through-space interactions.[46] The slopes of plots of log k_{et} vs the number of bonds in the bridge were 0.40 per bond for pure through-bond coupling and 1.56 per bond for pure through-space coupling. The relatively weak "distance" dependence observed here suggests, by comparison with the results of Paddon-Row, that through-bond interactions could explain the observed behavior.

Alternatively, the weak distance dependence of the electron-transfer rate on carbon number could reflect a predominantly through-space mechanism which occurs in conformations that are less than fully extended. A simple electrostatic calculation assuming two-point charges of +2 in a dielectric continuum equal to that of acetonitrile gives some insight into the degree of conformational energetics. If the fully extended distance is assumed to be 5, 10, and 20 Å, the decrease in distance that corresponds to a k_bT increase in electrostatic repulsion of two dications is respectively 0.4, 1.5, and 5.2 Å at room temperature. Thus, all other factors being equal, the importance of less than fully extended conformations to the electron-transfer quenching would be expected to increase as the chain length increases. This would produce a trend such that the dependence of the log k_{et} on carbon number would be strongest for short chains which is qualitatively what is observed. The odd–even dependence of the electron-transfer rate on carbon number (Table II and Figure 5) would have to reflect a phenomenon other than superexchange through the σ framework of the linkage. This is not unreasonable given the conformational difference illustrated in Figure 6 for the $423\text{-}DQ^{2+}$ and $433\text{-}DQ^{2+}$ in fully extended form and the possibility of entropic contributions from restricted chain motion in partially "collapsed" conformations.

The variation in the relative electron-transfer rate of $[(bpy)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ and $[(tmb)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ as a function of chain length also can be used to examine the nature of the electron transfer. Due to the electron-rich nature of the tmb ligands the MLCT state of $[(tmb)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ is a slightly stronger reducing agent than is that of $[(bpy)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$. Ignoring any difference between populations of the MLCT states localized on remote and adjacent bipyridines, the rate of electron-transfer quenching is predicted to be ca. 2.5 times faster for $[(tmb)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ than for $[(bpy)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ given the difference in the excited-state potentials. The last column of Table II gives the ratio of the experimentally determined quenching rates of these two complexes as a function of chain length. For the $423\text{-}DQ^{2+}$-containing complexes the relative rate difference is almost 20. As the chain length increases the ratio decreases to a value of 2.7 for the $473\text{-}DQ^{2+}$ complexes, a value close to the ratio predicted on energetic grounds. The model developed to explain the excited-state electron-transfer quenching for the $[L_2Ru(42n\text{-}DQ^{2+})]^{4+}$ series of complexes assumes that only electron transfer from the adjacent bipyridine is important (ca. 6% localized for L = bpy and 96% for L = tmb). This assumption was considered reasonable because the relative shortest through-space distances between the diquat moiety and the remote and adjacent bipyridines, respectively, differed by a factor of ca. 3 for the fully extended conformation. However, as the chain length linking the diquat to the adjacent bipyridine increases, the relative through-space distance decreases to a factor of ca. 1.3 for the $473\text{-}DQ^{2+}$ complexes, thus increasing the relative likelihood of significant contribution of electron transfer from the remote bipyridine to the overall quenching rate. A purely superexchange mechanism, on the other hand, could not easily accommodate these results.

Another approach to assessing the relative magnitude of through-bond interactions in flexible chain bridged complexes such as the $[(L)_2Ru(4m3\text{-}DQ^{2+})]^{4+}$ series is to examine the effect of introducing some degree of conformational rigidity into the complexes. Table III shows rate constants for photoinduced electron transfer for a series of complexes of the type $[(L)_2Ru(4x3\text{-}DQ^{2+})]^{4+}$ having seven bonds in the bridge. For L = tmb the measured electron-transfer rate constant varies by less than a factor of 2 for complexes having *cis*-cyclohexyl, *trans*-cyclohexyl, or phenyl moieties in the bridge. In such complexes the range of conformations possible varies considerably and electron transfer via purely through-space interactions should exhibit a larger range of rates. A surprising observation is that the complexes having an aromatic portion in the bridge ($4x3\text{-}DQ^{2+} = 4Ph3\text{-}DQ^{2+}$ with L = tmb or bpy) have electron-transfer rate constants which are nearly the same as the straight chain alkyl bridged complexes. In a related study, Heitele and Michel-Beyerle examined intramolecular photoinduced electron transfer in $A\text{–}CH_2\text{–}(Ph)_{1,2}\text{–}CH_2\text{–}D$ complexes where A is either anthracene or pyrene and D is *p*-dimethylaniline.[4h] The decrease in k_{et} between the complex with one and two phenyl groups, expressed as $\Delta(\log k_{et})/\Delta n$, is 0.36 per bond for the pyrenyl derivative and 0.34 for the anthryl derivative. Thus, insertion of an additional phenyl group in these complexes results in nearly as large a per bond diminution in the electron-transfer rate as addition of methylene groups in the series of complexes examined here. Results of Joran and co-workers on zinc octamethylporphyrin complex donors linked to benzoquinone via either phenyl (Ph), phenylbicyclooctyl (Ph-BCO), or phenylbis(bicyclooctyl) (Ph-BCO-BCO) bridges suggest that a single aliphatic link can diminish the effect of an aromatic portion of the bridge.[17c] In these complexes the decrease in k_{et} with increasing number of bonds in the bridge, expressed as $\Delta(\log k_{et})/\Delta n$, is 0.52 per bond between the Ph and Ph-BCO complexes and 0.49 between the Ph-BCO and Ph-BCO-BCO complexes. The implication of this observation is that, in this series, electronic coupling through the phenyl bridge is no more effective than coupling through the bicyclooctyl moiety. The relatively weak coupling of the phenyl bridge in this case may also be the result of orientation effects, as shown by Cave, Seiders, and Marcus in calculations[11c] and as demonstrated experimentally by Helms, Heiler, and McLendon for porphyrin dimers bridged by aromatic spacers.[21] Their results indicate that, in systems having aromatic spacers, electronic coupling through the bridge depends on the π-orbital symmetries of the donor, bridge, and acceptor. The three experimental results given above, obtained with widely varying donors and acceptors, clearly show that incorporating unsaturation into the bridge does not necessarily impart stronger electronic coupling.

The relatively small variation in the observed rate constants for the complexes bridged by the phenyl- and cyclohexyl-containing ligands is not consistent with electron transfer via purely through-space interactions. Similar through-space electron-transfer rates for these complexes are expected only if the electron-transfer distances and orbital overlap are nearly the same. Given the differences in relative orientation and flexibility of the central portion of the linkages, it is difficult to imagine how these complexes could yield such similar quenching rates unless electron-transfer quenching occurs from nearly fully extended conformations; even then, likely orientational differences between, for example, the cis and trans isomers of the methylcyclohexyl-linked system are problematic.

As noted earlier, back electron transfer from the reduced diquat to the Ru(III) of the photoproduct (eq 8) was found to be faster than the quenching step (eq 7) in all cases examined.[49] The reorganizational barrier for forward electron transfer has been found to be approximately 0.8 V.[8a,33] The back electron transfer is exergonic by greater than 1.5 V in all cases studied,[8a] and it is surprising that the back transfer rate is faster than the excit-

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[49] J. Connolly, Solar Energy Research Labs, personal communication.

ed-state electron-transfer rate, k_f, since it is expected that the reorganizational barrier for forward and back electron transfer should be similar and back electron transfer should occur in the Marcus "inverted" region. If both forward and back electron transfer occur via a through-bond (i.e., superexchange) mechanism, an explanation for the observed behavior may be that the forward electron transfer occurs via a superexchange path involving unoccupied orbitals of the bridge (electron transfer) while the back electron transfer occurs via hole transfer from occupied σ-bonding levels of the framework. Recently Waiselewski and co-workers used spectroscopic and electrochemical data to show that, for porphyrin-pentacene-quinone systems, forward electron transfer occurs via electron transfer while back electron transfer occurs via hole transfer and is faster than the forward electron transfer.[3h] Without further information it is not possible to distinguish which of the superexchange paths predominates in this case, but back electron transfer via hole transfer is not unreasonable since the requirement is that the energy gap between the metal $d\pi$ levels and the σ-bonding levels of the bridge be smaller than the gap between the diquat π^* levels and the σ^* levels of the bridge.

Summary. Intramolecular, photoinduced electron transfer from two ruthenium(II) diimine complex chromophores to a given diquat occurs with a variety of aliphatic tethers linking the chromophore and the diquat. The rate constant decreases sharply as the number of methylenes separating the donor and acceptor increases in straight chain alkyl bridged complexes. An odd-even alternation in the electron-transfer rate constant was observed in the straight chain series. Rate constants for electron transfer in a series of complexes bridged by a series of spacers having a fixed number of bonds but differing steric environments varied by only a factor of 2. On the basis of the data presented here, it is not possible to establish unambiguously whether or not there exists a significant superexchange contribution to the electron-transfer quenching process in these systems. Given the much weaker distance dependence expected for superexchange relative to through space coupling, superexchange would be expected to be most important for the longest linkages. The weight of the data presented here as well as data previously reported for similar systems tend to support a significant contribution of through-space electron transfer for the shortest chain linkages. For the longer linkages results are less clear; however, based on the results for the series of seven-bond-bridged complexes, through-bond interactions appear to contribute to the electron transfer.

Acknowledgment. R.H.S. thanks the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. C.M.E. acknowledges the National Science Foundation (Grant CHE 8821752) for support of this work. We thank Dr. Mark Sulkes for time-correlated single photon counting lifetime measurements and Professors David Kelley and George McLendon and the reviewers for valuable advice.

Registry No. *cis*-I, 137648-26-1; *trans*-I, 137648-27-2; II, 137648-28-3; III, 137648-29-4; *cis*-IVa, 137648-30-7; *trans*-IVa, 137648-31-8; $[(tmb)_2Ru(423\text{-}DQ^{2+})]^{4+}$, 96897-22-2; $[(tmb)_2Ru(433\text{-}DQ^{2+})]^{4+}$, 137648-32-9; $[(tmb)_2Ru(443\text{-}DQ^{2+})]^{4+}$, 137648-33-0; $[(tmb)_2Ru(453\text{-}DQ^{2+})]^{4+}$, 137648-34-1; $[(tmb)_2Ru(463\text{-}DQ^{2+})]^{4+}$, 137648-35-2; $[(tmb)_2Ru(473\text{-}DQ^{2+})]^{4+}$, 137648-36-3; $[(tmb)_2Ru(4123\text{-}DQ^{2+})]^{4+}$, 137648-37-4; $[(bpy)_2Ru(423\text{-}DQ^{2+})]^{4+}$, 96410-77-4; $[(bpy)_2Ru(433\text{-}DQ^{2+})]^{4+}$, 137648-38-5; $[(bpy)_2Ru(443\text{-}DQ^{2+})]^{4+}$, 137648-39-6; $[(bpy)_2Ru(453\text{-}DQ^{2+})]^{4+}$, 116595-54-1; $[(bpy)_2Ru(463\text{-}DQ^{2+})]^{4+}$, 137648-40-9; $[(bpy)_2Ru(473\text{-}DQ^{2+})]^{4+}$, 137648-41-0; $[(bpy)_2Ru(4123\text{-}DQ^{2+})]^{4+}$, 137648-42-1; $[(tmb)_2Ru(4ph3\text{-}DQ^{2+})]^{4+}$, 137648-43-2; $[(tmb)_2Ru(4cc3\text{-}DQ^{2+})]^{4+}$, 137648-44-3; $[(tmb)_2Ru(4tc3\text{-}DQ^{2+})]^{4+}$, 137764-34-2; $[(dmb)_2Ru(4tc3\text{-}DQ^{2+})]^{4+}$, 137648-45-4; $[(bpy)_2Ru(4ph3\text{-}DQ^{2+})]^{4+}$, 137648-46-5; $[(dmb)_2Ru(423\text{-}DQ^{2+})]^{4+}$, 96897-20-0; 4,4'-dimethyl-2,2'-bipyridine, 1134-35-6; 1,4-cyclohexanedione, 637-88-7.

Supplementary Material Available: Selected ^1H NMR spectral data (15 pages). Ordering information is given on any current masthead page.

Spironaphthopyran Photochromism: Picosecond Time-Resolved Spectroscopy

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Received July 1, 1991. Revised Manuscript Received September 13, 1991

Abstract: Photochromism of a spironaphthopyran (1'-(methoxyethyl)-3',3',5'-trimethyl-spiro[2*H*-1-naphthopyran-2,2'-indoline]) is studied with picosecond transient absorption and picosecond time-resolved resonance Raman spectroscopies. A photochromic reaction occurring within 50 ps after ultraviolet (287 nm) irradiation produces merocyanine species which absorb at 574 nm in both polar and nonpolar solvents. For as long as 1.5 ns, neither absorption nor resonance Raman spectroscopy reveals any changes in the merocyanine isomer(s) initially formed. In polar solvents, a second transient absorption (400-460 nm) appears both before the merocyanine isomer(s) is formed and whenever the merocyanine isomer(s) is excited at 574 nm. No back-reaction from the merocyanine isomer(s) to the spiro form is observed when the sample is irradiated at either 574 or 425 nm with delays of 100 ps to 1 ns after 287-nm excitation. A reaction mechanism describing spiropyran photochromism is suggested from these results.

Introduction

Photochromism describes photolytic intramolecular reactions which proceed through the excited state(s) of the parent molecule and are characterized by a dramatic color change in the sample associated with the formation of products. Photochromism involving changes in the visible absorption spectrum, and thereby changes in the associated π-electron conjugation system, have drawn considerable attention.[1] For example, the photochromism observed in fulgides is derived from ring closure induced by the ultraviolet (UV) irradiation while spiro compounds undergo color

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