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Electron-Transfer Quenching of Ruthenium(II) Photosensitizers by Mercury(II) Chlorides. 1. Reactions in Aqueous Solution

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Excited-state interactions of tris(α-diimine)ruthenium(II) photosensitizers with $HgCl_x^{2-x}$ (x = 2, 3, 4) were studied in aqueous media with use of luminescence quenching and flash photolysis methods. $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{2-}$ exhibit sufficiently different quenching constants to permit luminescence determination of the equilibrium constants for their formation. Quenching proceeds via oxidative electron transfer to yield Ru(III) and a $HgCl_x^{1-x}\cdot$ free radical. The quenching data are interpreted with use of Marcus electron-transfer theory. The experimental order of reactivity ($HgCl_4^{2-} << HgCl_2 < HgCl_3^-$) differs from that expected on purely electrostatic grounds. The low reactivity of $HgCl_4^{2-}$ arises from a larger inherent barrier to electron transfer ($\Delta G^*(0)$). From the quenching data the redox potentials for the otherwise unmeasurable Hg(II) + $e^- \rightarrow$ Hg(I)· reactions are determined to be ~−0.80 V vs. NHE. Back electron transfer between Ru(III) and Hg(I) in the encounter pair proceeds very rapidly, precluding detection of the Hg(I) free radical. The 2,2′-bipyridine and 1,10-phenanthroline derivatives appear to behave differently, and this may cloud the interpretation of photochemical and photophysical studies that mix the two types of complexes.

Introduction

The recent surge of interest in the photochemistry of transition-metal complexes has been increasingly directed toward solar energy conversion schemes.[1-6] Approaches include photochemical production of fuels such as hydrogen from water, development of silicon solar cells, storage of thermal energy through reversible photochemical reactions, and energy conversion with photogalvanic cells. Research efforts in the area of photogalvanic cells have focused on systems exhibiting reversible excited-state electron-transfer reactions. For useful storage of chemical energy, the production efficiency of redox products should be as high as possible and the thermal back-reaction as slow as possible. Achievement of this latter requirement and prevention of photodegradation have proven to be major problems. Storage of energy via photogalvanic means has typically been limited to seconds due to the rapidity of the back-reaction.[7]

Recently, we reported an energy-trapping system based on quenching by Hg^{2+} (eq 1–6),[8] where D = $[Ru(bpy)_3]^{2+}$ and

$$D + h\nu \rightarrow {}^*D \tag{1}$$

$$ {}^*D \rightarrow D + h\nu \tag{2}$$

$$ {}^*D + Hg^{2+} \xrightarrow{k_q} D^+ + Hg^{+}\cdot \text{ or } D + Hg^{2+} \tag{3}$$

$$D^+ + Hg^{+}\cdot \xrightarrow{k_b} D + Hg^{2+} \tag{4}$$

$$Hg^+ + Hg^+ \xrightarrow{k_d} Hg_2^{2+} \tag{5}$$

$$D^+ + {}^1/_2Hg_2^{2+} \xrightarrow{k_{th}} D + Hg^{2+} \tag{6}$$

bpy = 2,2′-bipyridine. The Hg_2^{2+} trap species was formed with high overall efficiency. k_{th} for the back-reaction between Ru(III) and the trap species (eq 6) is ~4 M^{-1} s^{-1}, which is ~10^9 times slower than the free-radical back-reaction (eq 4) and 10^5 times slower than the analogous photogalvanic reaction based on the Fe^{3+}/Fe^{2+} system.[7] Thus, this photochemical system meets the two requirements for efficient energy storage outlined above. In fact, a photogalvanic cell based on this system produced potentials in the 200–300-mV range and could be recycled repeatedly for several days with no deterioration in performance.[8a] To understand this system, we continued our studies of Hg(II) quenching and the photochemical and photophysical processes involving the photosensitizers and the mercury species.

In further studies using Hg(II) as a quencher, we chose to work with $HgCl_2$. Our choice of this Hg(II) species was influenced by the possibility of generating Hg_2Cl_2 as the trap species. Initial studies using $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ indicated that while $HgCl_2$ was a good quencher, there were no observable photoproducts even in flash photolysis experiments monitored on a microsecond time scale. This lack of net photochemical reactivity makes the $HgCl_2$ system simpler to work with than the highly photoreactive Hg^{2+} system. Since $HgCl_2$ should also quench by excited-state electron transfer, information derived from the $HgCl_2$ studies should be transferable to the Hg^{2+} system. Also, it seemed that use of neutral $HgCl_2$ should minimize ionic-strength problems.

We report here on the rich photochemical behavior of $HgCl_2$ with a variety of $[RuL_3]^{2+}$ photosensitizers (L = substituted 2,2′-bipyridine or 1,10-phenanthroline) in aqueous solutions. In the following paper, we report a similar study on the photophysics of $HgCl_2$ in sodium lauryl sulfate micelles.[2d]

Experimental Section

The ligands, and our abbreviations, are as follows: 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy), 1,10-phenanthroline (phen), 5-chloro-1,10-phenanthroline (Cl-phen), 5-bromo-1,10-phenanthroline (Br-phen), 5-methyl-1,10-phenanthroline (Me-phen), 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2phen), 5,6-dimethyl-1,10-phenanthroline (5,6-Me_2phen), and 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen). All ligands were from G. Frederick Smith Chemical Co. and were used without further purification.

$[Ru(bpy)_3]Cl_2\cdot 6H_2O$ from G. Frederick Smith Chemical Co. was recrystallized from water. The remaining ruthenium complexes were

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(1) (a) Grätzel, M. *Acc. Chem. Res.* **1981**, *14*, 376. (b) Grätzel, M.; Kalyanasundaram, K.; Kiwi, J. *Struct. Bonding* (*Berlin*) **1982**, *49*, 37. (c) Grätzel, M. *ACS Symp. Ser.* **1982**, *No. 177*, 113.

(2) (a) Heller, A. *Acc. Chem. Res.* **1981**, *14*, 154. (b) Heller, A.; Miller, B. *Adv. Chem. Ser.* **1980**, *No. 184*, 215. (c) Creutz, C.; Keller, A. D.; Sutin, N.; Zipp, A. P. *J. Am. Chem. Soc.* **1982**, *104*, 3618. (d) Dressick, W. J.; Hauenstein, B. L.; Demas, J. N.; DeGraff, B. A., *Inorg. Chem.*, following paper in this issue.

(3) Tributsch, H. *Struct. Bonding* (*Berlin*) **1982**, *49*, 127.

(4) Hautala, R. R.; King, R. B.; Kutal, C. *Sol. Energy: Chem. Convers. Storage*, [*Symp.*] **1979**, 333.

(5) Hoffman, M. Z.; Lichtin, N. N. *Sol. Energy: Chem. Convers. Storage*, [*Symp.*] **1979**, 153.

(6) DeGraff, B. A.; Demas, J. N.; Taylor, D. G. *Sol. Energy: Chem. Convers. Storage* [*Symp.*] **1979**, 189.

(7) Lin, C.-T.; Sutin, N. *J. Phys. Chem.* **1976**, *80*, 97.

(8) (a) DeGraff, B. A.; Demas, J. N. *J. Am. Chem. Soc.* **1980**, *102*, 6169. (b) Hauenstein, B. L.; Dressick, W. J.; Demas, J. N.; DeGraff, B. A. *J. Phys. Chem.*, in press.

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Table I. $^*E°$'s, K_{SV}'s and k_q's for $HgCl_2$ Quenching of RuL_3^{2+}

			0.09 M $NaNO_3$		0.99 M $NaNO_3$	
ligand, L	τ_0, µs	$^*E°$, V[a]	K_{SV},[b] M^{-1}	$10^{-9} \times k_q$, M^{-1} s^{-1}	K_{SV},[b] M^{-1}	$10^{-9} \times k_q$, M^{-1} s^{-1}
Me_4phen	2.28	−1.11	6730	2.95	*c*	*c*
4,7-Me_2phen	1.87	−1.01	5290	2.82	5330	2.82
Me_2bpy	0.34	−0.94	515	1.51	638	1.91
5,6-Me_2phen	1.91	−0.93	5510	2.88	5070	2.57
Me-phen	1.35	−0.90	2590	1.91	3620	2.63
phen	1.11	−0.87	1470	1.32	2040	1.86
bpy	0.63	−0.84	107	0.170	144	0.229
Cl-phen	1.23	−0.77	477	0.389	706	0.575
Br-phen	1.25	−0.76	587	0.468	719	0.575

[a] Excited-state reduction potentials were taken from ref 9.
[b] Experiments were performed at constant ionic strength in 0.01 M HNO_3, 0.09 M $NaNO_3$ and in 0.01 M HNO_3, 0.99 M $NaNO_3$.
[c] Not determined because of precipitation of the Ru(II) complex.

prepared by modifying the literature methods[9] as follows: $RuCl_3 \cdot (1-3)H_2O$ (Alfa, typically 0.2 g) was dissolved in 25 mL of refluxing absolute ethanol. A 3.2–3.3-mol amount of the appropriate ligand per mole of ruthenium was added, and a 4–5-fold excess of hydroxylamine hydrochloride was added as a reducing agent. After the solution was refluxed for 1 h, the solvent was removed with gentle heating. The complexes were recrystallized from ethanol–water (4:1 v/v). With some of the more soluble complexes, small amounts of HCl or $HClO_4$ were added to initiate precipitation. The complexes were shown to be pure on the basis of TLC on silica. Excited-state lifetimes, absorption and emission spectra, and redox potentials in acetonitrile agreed with the literature values.[9,10] Table I includes our observed luminescent lifetimes for deaerated aqueous solutions at 25 °C.

UV–visible spectra were obtained on a Cary 14 spectrophotometer. Emission spectra and emission intensity quenching data were obtained on an SLM 8000 spectrofluorimeter. The lifetime apparatus used a Molectron UV-14 pulsed nitrogen laser excitation source, trigger (RCA 931) and signal detection (RCA C7164R) photomultiplier tubes (PMT), and a Jobin-Yvon H10-V emission monochromator. The PMT signal was smoothed by a fast-buffer amplifier and passed to a Tektronix R7912 transient digitizer equipped with 7B92A dual time base and 7A19 vertical amplifier plug-ins. From the digitizer the data could be transferred to, and manipulated by, a microcomputer.[11] Lifetimes were determined from the slope of the semilogarithmic plot of intensity vs. time; the plots were linear over at least 2 half-lives. All samples were deaerated with water-saturated N_2.

Flash photolysis experiments were performed on nitrogen-purged samples with use of a modification of an instrument described previously.[12] The modified system included a Physical Data transient digitizer for data acquisition. Data could be displayed on an X-Y plotter or transferred to a Hewlett-Packard HP-85A computer for data processing.

Both intensity and lifetime quenching were used to measure $HgCl_2$ reactivity with $[Ru(phen)_3]^{2+}$ and $[Ru(Cl\text{-}phen)_3]^{2+}$. All other quenching results were determined with use of lifetime measurements. Stern–Volmer quenching constants, K_{SV}, for $HgCl_2$ were determined from the slope of the $\tau_0/\tau - 1$ vs. $[HgCl_2]$ plot with use of a linear least-squares fit to the experimental data. The plots were linear within experimental error.

Quenching measurements were made at both 0.10 and 1.0 M ionic strength with use of $NaNO_3$ and HNO_3 (0.01 M) as the supporting electrolytes. If NO_3^- was replaced with Cl^-, the apparent K_{SV}'s varied dramatically with $[Cl^-]$. To quantitate this phenomenon, we carried out a series of titrations at fixed ionic strength (1.0 M) and fixed total Hg(II) concentration with the mercury introduced as $HgCl_2$. The concentration of Cl^- was varied, and the apparent K_{SV} was calculated on the basis of the total Hg(II) concentration. In a typical experiment, solutions were prepared with fixed concentrations of the ruthenium complex and $HgCl_2$; conditions were selected to give a τ_0/τ of ~3 for the solution prepared without added Cl^-. Acid concentration was maintained at 0.01 M HNO_3, and the ionic strength was maintained at 1.0 M with $NaNO_3$. Titrations beginning at either extreme overlapped well.

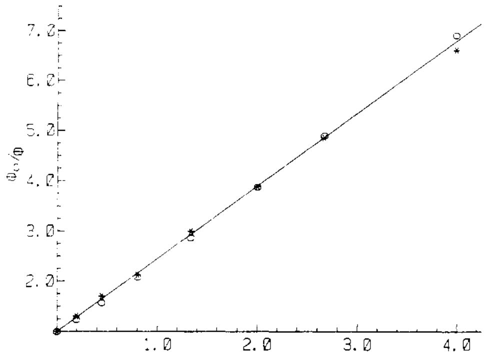

Figure 1. Stern–Volmer plot of lifetime (*) and intensity (O) quenching of $^*[Ru(phen)_3]^{2+}$ by $HgCl_2$. Intensity data are blank corrected. Experiments were carried out at 0.09 M $NaNO_3$ and 0.01 M HNO_3.

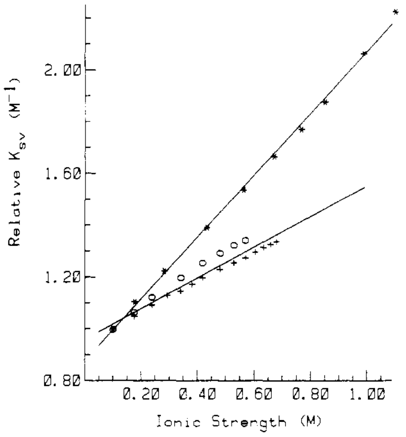

Figure 2. Relative K_{SV} for $HgCl_2$ quenching of $^*[Ru(bpy)_3]^{2+}$ as a function of ionic strength: (*) 0.10 M $HClO_4$ plus $NaClO_4$ to control ionic strength; (O) 0.10 M HNO_3 plus $NaNO_3$; (+) 0.10 M HNO_3 plus Na_2SO_4. Concentrations of the Ru(II) complex and $HgCl_2$ were fixed in all cases at 1×10^{-5} M and 8.0 mM, respectively. The solid lines represent linear least-squares fits to the data.

All nonlinear least-squares simplex fitting employed a BASIC version of the FORTRAN program of Daniels.[13] Calculations were performed on a Hewlett-Packard HP-85A microcomputer.

Results

Figure 1 shows a typical intensity and lifetime quenching plot for $[Ru(phen)_3]^{2+}$ quenched by $HgCl_2$. The two plots agree within experimental error, showing that quenching is essentially all diffusional with no detectable static or associational quenching.[14] Similar results were obtained for $[Ru(Cl\text{-}phen)_3]^{2+}$. Table I shows the Stern–Volmer and quenching rate constants for $HgCl_2$ and each of the complexes studied. There are slight increases in the quenching rate constant as the ionic strength is increased from 0.10 to 1.0 M.

Figure 2 demonstrates more clearly the effect of ionic strenth on K_{SV} for $HgCl_2$ in the absence of extra Cl^-. On the basis of charge, variations of ionic strength should not greatly affect

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[9] Lin, C.-T.; Bottcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536.
[10] Hauenstein, B. L., Jr.; Mandal, K.; Saunders, D. E.; Dallara, J.; Demas, J. N., unpublished results.
[11] Complete details of the lifetime system may be found in: Turley, T. J. M.S. Thesis, University of Virginia, 1980.
[12] DeGraff, B. A.; Lang, K. J. *J. Phys. Chem.* **1970**, *74*, 4181.
[13] Daniels, R. W. "An Introduction to Numerical Methods and Optimization Techniques"; North-Holland: New York, 1978; Chapter 8.
[14] Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. S. *Coord. Chem. Rev.* **1975**, *15*, 321.

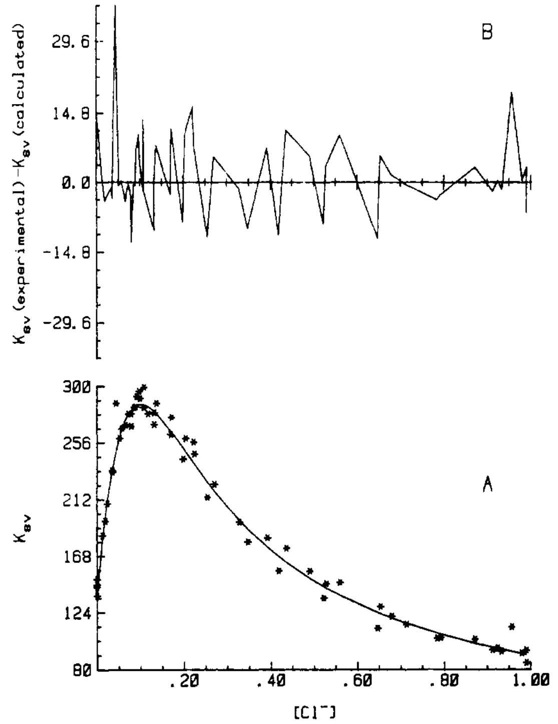

Figure 3. (A) K_{SV} vs. [Cl⁻] for $[Ru(bpy)_3]^{2+}$ at 1 M ionic strength. The total Hg(II) concentration was 8.0 mM and was established by adding $HgCl_2$. Fitting parameters used to draw the solid line are in Tables I and II. (B) Residuals plot of the best-fit K_{SV}'s.

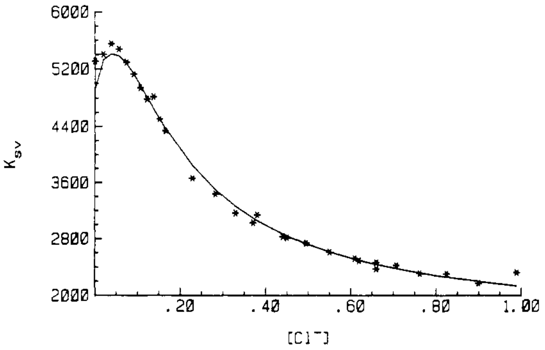

Figure 4. K_{SV} vs. [Cl⁻] for $[Ru(5,6\text{-}Me_2phen)_3]^{2+}$ at 1 M ionic strength. [Hg(II)] = 0.32 mM. Fitting parameters used to draw the solid line are in Tables I and II.

the rate of reaction between neutral $HgCl_2$ and the dipositive photosensitizers. Perchlorate, however, greatly enhances $HgCl_2$ quenching of $^*[Ru(bpy)_3]^{2+}$ while nitrate and sulfate have much smaller effects. The exact systems of the ClO_4^- effect is unclear, but it appears to be complicated. Gaines[15] has observed anomalously large enhancements of paraquat quenching rate constants in the presence of ClO_4^-. We have observed similar increases of $HgCl_2$ quenching rate constants with increasing $[ClO_4^-]$ when the donor molecule was the anionic $[Ru((SO_3Ph)_2phen)_3]^{4-}$.[16] That perchlorate should cause an increase in $HgCl_2$ quenching for both cationic and anionic Ru(II) photosensitizers is very anomalous.

We have no explanation for the enhanced quenching in the presence of perchlorate. Since 1 M $HClO_4$ or $NaClO_4$ did not affect the viscosity of water by more than 5%, we rule out a viscosity effect. Therefore, we feel that perchlorate should be used with caution as an "inert" counterion in photochemical studies. Because perchlorate-containing systems behave anomalously and because many of our photosensitizers are insoluble in perchlorate-containing media, we have carried out all of our remaining studies using HNO_3 and $NaNO_3$ as the supporting electrolytes. Figure 3 shows the variation in the Stern–Volmer constant for $^*[Ru(bpy)_3]^{2+}$ quenched by $HgCl_2$ as the [Cl⁻] is varied at a constant 1 M ionic strength. The titration curve is very atypical for a simple change in the nature of the supporting electrolyte and clearly arises from chemical changes in the system. Another typical titration curve is shown in Figure 4. We attribute the shapes of these curves to the equilibria of Hg(II) and Cl⁻ (eq 7 and 8).[17]

$$HgCl_2 + Cl^- \rightleftharpoons HgCl_3^- \quad K_3 \tag{7}$$

$$HgCl_3^- + Cl^- \rightleftharpoons HgCl_4^{2-} \quad K_4 \tag{8}$$

Under our conditions, the concentrations of Hg^{2+} and $HgCl^+$ can be ignored. Further, we postulate that each complex has a different K_{SV}. The maximum apparent K_{SV} occurs at [Cl⁻] = ~0.1 M, which is near the maximum concentration of $HgCl_3^-$. At higher [Cl⁻] the Hg(II) distribution becomes increasingly dominated by $HgCl_4^{2-}$, and K_{SV} falls well below the K_{SV} for pure $HgCl_2$. The order of reactivity is then $HgCl_3^- > HgCl_2 > HgCl_4^{2-}$.

To test this description of quenching by the chloro–mercury(II) species, we modeled the titration curves as follows: The solution composition was assumed to be controlled by eq 7 and 8 with equilibrium constants K_3 and K_4. $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{2-}$ were each assumed to quench with quenching constants $K_{SV}(HgCl_2)$, $K_{SV}(HgCl_3^-)$, and $K_{SV}(HgCl_4^{2-})$. The K's and K_{SV}'s were all assumed to be constant. Simplex optimization was then used to fit the observed K_{SV}'s to

$$K_{SV} = \sum f_x[K_{SV}(HgCl_x^{2-x})] \tag{9a}$$

$$K_{SV}(HgCl_x^{2-x}) = \tau_0[k_q(HgCl_x^{2-x})] \tag{9b}$$

where the summation is from x = 2–4. The f's represent the fractions of Hg(II) present as $HgCl_x^{2-x}$ (x = 2–4), and the k_q's are the bimolecular quenching rate constants for the indicated mercury species. τ_0 is the unquenched donor lifetime.

Initially, simplex fits were made to the chloride titration data obtained for each complex. Four parameters, $K_{SV}(HgCl_3^-)$, $K_{SV}(HgCl_4^{2-})$, K_3, and K_4, were varied to obtain the best fits. To minimize the number of adjustable parameters, $K_{SV}(HgCl_2)$ was determined from a separate experiment carried out in a nitrate medium (Table I). Because of experimental errors, the K_3's and K_4's differed somewhat for the different complexes. To refine these parameters, the following procedure was used: A best K_3 was obtained by averaging all the K_3's (excluding two outlying values) calculated from the four-parameter fits. K_3 was then fixed at this value, 3.7 ± 1.5 M^{-1} (indicated error is the standard deviation), and a three-parameter fit was carried out on all complexes varying K_4, $K_{SV}(HgCl_3^-)$, and $K_{SV}(HgCl_4^{2-})$. A best K_4 (14.5 ± 6.5 M^{-1}) was then obtained by averaging all the K_4's (excluding the outlying values) from the three-parameter fits. Finally, with use of the averaged global K_3 and K_4 values, a two-parameter fit was carried out on all the complexes to obtain $K_{SV}(HgCl_3^-)$'s and $K_{SV}(HgCl_4^{2-})$'s. These K_3 and K_4 values agree reasonably well with the values of 4.88 and 14.4 M^{-1} obtained for $[Ru(bpy)_3]^{2+}$, where we had the most extensive data set. In all cases the titration curves were fit within experimental error with use of the average K_3 and K_4. Literature values for a perchlorate media are K_3 = 7.09 M^{-1} and K_4 = 10.0 M^{-1}.[17] Given the differences in media, the agreement in equilibrium constants is satisfactory.

Typical examples of the quality of the simplex fits are shown in Figures 3 and 4, where the global K_3 and K_4 values were used to generate the calculated curves. The residual plots are

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(15) Gaines, G. L., Jr. *J. Phys. Chem.* **1979**, *83*, 3088.

(16) Mandal, K.; Hauenstein, B. L., Jr.; Demas, J. N., unpublished observations.

(17) (a) Sillen, L. G. *Acta Chem. Scand.* **1947**, *1*, 473. (b) Lindgren, B.; Jonsson, A.; Sillen, L. G. *Ibid.* **1947**, *1*, 479.

Table II. $^*E^\circ$'s, K_{SV}'s, and k_q's for $HgCl_3^-$ and $HgCl_4^{2-}$ Quenching of RuL_3^{2+}

		$HgCl_3^-$		$HgCl_4^{2-}$	
ligand, L	$^*E^\circ$,[a] V	K_{SV},[b] M^{-1}	$10^{-9} \times k_q$, M^{-1} s^{-1}	K_{SV},[b] M^{-1}	$10^{-9} \times k_q$, M^{-1} s^{-1}
4,7-Me_2phen	−1.01	16000	8.51	1950	1.02
Me_2bpy	−0.94	1730	5.13	237	0.724
5,6-Me_2phen	−0.93	10000	5.01	1530	0.776
Me-phen	−0.90	8540	6.31	1110	0.813
phen	−0.87	6120	5.50	362	0.324
bpy	−0.84	1060	1.66	23	0.0372
Cl-phen	−0.77	3070	2.51	137	0.112
Br-phen	−0.76	2290	1.82	314	0.251

[a] Excited-state reduction potentials taken from ref 9. [b] Experiments were carried out at constant ionic strength in 0.01 M HNO_3 and $[NaNO_3 + NaCl] = 0.99$ M. Values determined from simplex fits to chloride titration data at fixed $[Hg(II)]_{tot}$ and fixed ionic strength. See text for details of fitting procedure.

suitably random with respect to sign and magnitude, and the deviations fall within the estimated accuracy of our instrument. The K_{SV}'s and k_q's for the various ruthenium and mercury complexes are summarized in Tables I and II. The excellent agreement between the calculated and observed fits supports our contention that chloride and nitrate are not anomalous counterions. If there were differences in specific ion effects between nitrate and chloride, one would not expect such good agreement with the model of eq 7 and 8.

Figure 5 shows Weller plots of log k_q vs. the excited-state reduction potential of the photosensitizers with $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{2-}$ (1.0 M ionic strength). We exclude the Br-phen complex for all but the $HgCl_2$ plots. We had originally not recognized the photosensitivity of this complex, and the long exposure times in the Cl^- titration curves yielded less accurate rate constants. The Weller plots of Figure 5 are characteristic of electron-transfer quenching reactions.[18] For strongly reducing excited states, k_q reaches the diffusion-controlled limit in the plateau region, but for reducing powers below a threshold level, k_q falls rapidly. The threshold level corresponds to the one-electron potential of the Hg(II) species to give a Hg(I) radical.

The shapes of the Weller plots leave little doubt that all three Hg(II) species react via electron transfer. A similar plot was obtained for $HgCl_2$ at 0.1 M ionic strength except that we were able to include the less soluble $[Ru(Me_4phen)_3]^{2+}$, which has an even more reducing exciting state (Table I). There was, however, no further increase in the k_q's on going from the 4,7-Me_2phen complex to the Me_4phen complex, which shows that we have reached the diffusion-controlled rate.

Simple electrostatic considerations predict that the relative order of reactivity should be $HgCl_2 < HgCl_3^- < HgCl_4^{2-}$, which differs from the experimental reactivities. Also, the curvature of the $HgCl_4^{2-}$ plot is much greater than the curvature of the other two plots. Another anomaly of the data is the relative k_q's for $[Ru(bpy)_3]^{2+}$ and for $[Ru(Cl\text{-}phen)_3]^{2+}$ and $[Ru(Br\text{-}phen)_3]^{2+}$. On the basis of their excited-state reduction potentials, the halogen-substituted phen complexes should be less reactive than the bpy complex. Experimentally, the opposite is true.

Flash photolysis studies with $[RuL_3]^{2+}$ (L = bpy, phen, Br-phen, Cl-phen, Me_2bpy, and Me_4phen) photosensitizers and $HgCl_2$ yielded negligible photochemistry. Any back-reaction, if present, was essentially complete before the termination of the flash (~30 μs). This result sets a lower limit of 2×10^{10} M^{-1} s^{-1} for k_b between any separated Ru(III) and Hg(I). This rate constant seems too high for any possible products, and we conclude that the back electron transfer occurs before the initial photoproducts diffuse apart.

On two occasions, evidence of a fine white precipitate was seen under constant illumination. We suspected the formation of Hg_2Cl_2 (formed by dimerization of HgCl· after expulsion of Cl^- from $HgCl_2^-$),[19] but these experiments could not be repeated.

Discussion

The equilibrium model of eq 7 and 8 explains all our quenching data in the presence of added Cl^-. The observed and calculated titration curves agree within experimental error for all of the Ru(II) complexes studied (excluding the photosensitive Br-phen complex) even though the same K_3 and K_4 values were used in all fits. Thus, we conclude that this quenching arises from equilibrium amounts of $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{2-}$.

We next show that all of the observed Hg(II) quenching is by electron transfer. Since the spectra of the $HgCl_x^{2-x}$ (x = 2, 3, and 4) complexes show no low-lying states,[20] energy-transfer quenching is precluded. Ru(II) photosensitizers have been shown to be immune to heavy-atom quenching.[21] Ground-state associational quenching is ruled out by the agreement between the intensity and lifetime quenching data for $[Ru(Cl\text{-}phen)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ with $HgCl_2$.

We cannot rule out the presence of some ion pairing in the $HgCl_3^-$ and $HgCl_4^{2-}$ cases. However, we have shown that for systems similar to the present ones dynamic quenching accounts for >80% of the quenching even when ion pairs have high stability.[21] Further, all of the remaining quenching data used lifetime measurements that are immune to associational phenomena. Dynamic electron-transfer quenching is, thus, left as the sole bimolecular deactivational pathway. This is supported by the observed variation of k_q with reducing power of the excited states (Figure 5 and Table I); the data follow classic Weller behavior expected for oxidative electron-transfer quenching. Also, as we shall show, the quenching data can be explained quantitatively with use of theories for electron-transfer reactions.

Flash photolysis studies have shown that, with Hg^{2+} as the quencher, the initial ruthenium photoproduct is ruthenium(III) with no evidence of ruthenium(I).[8a] In the analogous osmium(II) systems, however, we have seen successful separation of redox products.[8b] By analogy we assert that in the current study the initial mercury photoproducts are $HgCl_x^{1-x}\cdot$ free radicals.

Marcus theory has been used to correlate data for a large number of electron-transfer reactions.[22] Recently, Scandola, Balzani, and Schuster have described a particularly convenient set of equations of reversible and irreversible reactions based on a Marcus approach.[23] They use the generalized electron-transfer scheme

$$^*D + A \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} {}^*D\cdots A \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} D^+\cdots A^- \xrightarrow{k_{30}} D\cdots A \qquad (10a)$$

$$D\cdots A \rightarrow D + A \qquad (10b)$$

We have omitted any formation of separated redox products due to our failure to observe any transient photochemistry in

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(18) (a) Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834. (b) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(19) Nazhat, N. B.; Asmus, K. D. *J. Phys. Chem.* **1973**, *77*, 614.

(20) Spectra of $HgCl_2$ solutions with varying amounts of added Cl^- revealed no absorbance features above 290 nm.

(21) Demas, J. N.; Addington, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 5800.

(22) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Sutin, N. In "Inorganic Biochemistry"; Eichorn, G., Ed.; Elsevier: Amsterdam, 1973; p 611. (c) Marcus, R. A. In "Tunneling in Biological Systems"; Chanece, B., et al., Eds.; Academic Press: New York, 1979; p 109 and references therein.

(23) Scandola, F.; Balzani, V.; Schuster, G. *J. Am. Chem. Soc.* **1981**, *103*, 2519

these systems. An equation describing the overall forward rate constant, k_p, was developed

$$k_p = k_{12}/[1 + (k_{21}/k_{30})e^{\Delta G_{23}/RT} + (k_{21}/k°_{23})e^{\Delta G^{\ddagger}/RT}] \tag{11}$$

where $k°_{23}$, $\Delta G^{\ddagger}$, and ΔG_{23} are the frequency factor, the standard free activation energy, and the standard free energy for the electron transfer. For our quenching studies k_p corresponds to k_q.

For an electron-transfer reaction involving an excited state, ΔG_{23} is

$$\Delta G_{23} = E°(D^+/{*D}) - E°(A/A^-) + W_p - W_r \tag{12}$$

where, in our systems, $E°(D^+/{*D})$ is the reduction potential for the Ru(III)/*Ru(II) couple, $E°(A/A^-)$ is the one-electron reduction potential for $HgCl_x^{2-x}$ to the corresponding Hg(I) free radical, W_p is the work necessary to bring the reactants together prior to reaction, and W_r is the corresponding term for the products. $W_p - W_r$ is negligible (< 0.02 V) in this study; the method of calculation is outlined in the following paper.[2d]

The $\Delta G^{\ddagger}$ term can be expressed with use of the hyperbolic equation (13) developed by Marcus[22a] and Agmon and Levine.[24]

$$\Delta G^{\ddagger} = \Delta G_{23} + \frac{\Delta G^{\ddagger}(0)}{\ln 2} \ln \left[1 + \exp \frac{-\Delta G_{23} \ln 2}{\Delta G^{\ddagger}(0)} \right] \tag{13}$$

$\Delta G^{\ddagger}(0)$ is an "intrinsic barrier" to the electron transfer that is related to the energy of the atomic rearrangements which occur prior to the electron transfer.[23]

A key problem in using this method is obtaining good approximations of k_{12}, k_{21}, $k°_{23}$, and k_{30}. Inspection of the data shows that the phenanthroline complexes show a smooth reasonable curve. $[Ru(bpy)_3]^{2+}$ is anomalously low in all cases. To a lesser extent the Me_2bpy complex also appears too low. We conclude that the phenanthroline and bipyridine complexes are too dissimilar to be treated as a common family. In all subsequent data fitting, we restrict ourselves to the phenanthroline complexes.

For each set of phenanthroline quenching results, we assumed that the values of k_{12}, k_{21}, $k°_{23}$, and k_{30} were constant since a single quencher and a series of structurally and electronically similar ruthenium(II) photosensitizers were involved. As we will show, this assumption is reasonable for the phenanthroline complexes but less so for the bipyridine complexes.

k_{12} could be approximated from the Debye–Smoluchowski equation[25] or a version by Meares, Yeh, and Stryer,[26] which explicitly takes ionic strength into account

$$k_{ex} = k_0 \exp[-Z_A Z_B e^2/(\epsilon R_{AB} \times 10^7(1 + \kappa R_{AB})kT)] \tag{14a}$$

$$\kappa = 3.3 I^{1/2} \tag{14b}$$

where k_0 is the maximum rate of reaction in the absence of charge effects, Z_A and Z_B are the charges on the two reactants, e is the charge on the electron, ϵ is the dielectric constant, R_{AB} is the distance of closest approach of the reactants, I is the ionic strength, k is the Boltzmann constant, and T is the absolute temperature. From eq. 14 we obtain k_q at 1 M ionic strength of (8–10) × 10^9 M^{-1} s^{-1} for $HgCl_2$, (9–11) × 10^9 M^{-1} s^{-1} for $HgCl_3^-$, and (8–12) × 10^9 M^{-1} s^{-1} for $HgCl_4^{2-}$. The ranges correspond to differences in the ionic radii of the different mercury species. Theoretical calculations of diffusion-limited rate constants are frequently in error and should be treated only as first approximations.

The molecular radii required for the calculation of k_{12} were determined from the geometric mean of three orthogonal radii. The latter values were the sum of the appropriate bond distances and the radius of the pendant atom; one of the radii was chosen to correspond to the largest dimension of the molecule. The individual molecular radii for the unhydrated species are 0.25, 0.33, and 0.47 nm for $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{2-}$ and 0.84 nm for a typical RuL_3^{2+} species. Hydrated species had radii ~0.2 nm larger and account for the range of k_{12}'s above.

Using these theoretical values of k_{12} gave fits to the Weller plots that were unsatisfactory. The plateau levels for k_q were below the theoretical calculation of k_{12}. Because of the inherent assumptions in the calculated values of k_{12} we chose values of k_{12} for our final Weller plot as the largest k_q for a system. Clearly a plateau region was obtained for $HgCl_2$ and $HgCl_3^-$, and this procedure should give good estimates for k_{12}. It is less clear that a plateau was achieved for $HgCl_4^{2-}$, but as we shall show, k_{12} estimated in this fashion yields satisfactory fits to the data.

k_{21} was determined as follows: For each combination of donor and quencher the equilibrium constant for the formation of the precursor complex (*D···Q) was calculated from the Fuoss equation.[27,28] k_{21} was then calculated from these values of the equilibrium constants, and the k_{12} values were determined as described above.

$k°_{23}$ is the frequency factor[23] and was determined by using the relationship developed by Dogondaze[29]

$$k°_{23} = \nu/2\pi \tag{15}$$

where ν is the solvent vibrational frequency. Recent measurements[30] indicate that ν for water is 10^{13} s^{-1}, so $k°_{23}$ becomes 1.6 × 10^{12} s^{-1}, which we use in subsequent calculations. Similar calculations based on the theory of liquids[31] give values near 10^{12}.

The evaluation of k_{30} presented some difficulty, since in the absence of photochemistry it could not be directly determined. The Hg^{2+} system is, however, photosensitive, and for the photosensitizers used here, $k_{30} = (2.0 \pm 0.5) \times 10^{10}$ s^{-1}. This value is similar to the (2–4) × 10^{10} s^{-1} for $[Ru(bpy)_3]^{2+}$ with paraquats,[2c] which is also a highly driven back-electron-transfer reaction. Therefore, we approximated k_{30} for all the mercury chloride systems at 2 × 10^{10} s^{-1}.

$E°(A/A^-)$ is also necessary for the application of eq 11. From the Weller plots for $HgCl_2$, $E°(A/A^-)$ is ~0.8 V. This parameter was varied in the fitting procedure.

The final fits to the data were established by varying only $E°(A/A^-)$ and $\Delta G^{\ddagger}(0)$. k_{21}/k_{30} and $k_{21}/k°_{23}$ were evaluated with use of the estimates of the parameters given above. We evaluated $E°(A/A^-)$ only for $HgCl_2$, where the data were of the highest quality. For both the 0.1 and the 1.0 M ionic strengths the best fits were for −0.80 ± 0.05 V. To minimize the adjustable parameters, we assumed that $E°(A/A^-)$ would not vary greatly for $HgCl_3^-$ and $HgCl_4^{2-}$ and fixed this value at −0.80 V. The parameters used in the final fits of Figure 5 are given in Table III. The calculated fits to the data for the phenanthroline complexes are excellent for both the 1.0 M ionic strength (Figure 5) and the 0.1 M ionic strength data. In particular, we consider the rate constants only approximate. $E°(A/A^-)$ and $\Delta G^{\ddagger}(0)$, however, were not very sensitive to variations in the different rate constants. For example, a factor of 2 change in k_{12} affected these parameters by the indicated

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(24) Agmon, A.; Levine, R. D. *Chem. Phys. Lett.* **1977**, *52*, 197.

(25) Debye, P. *Trans. Electrochem. Soc.* **1942**, *82*, 265.

(26) Meares, C. F.; Yeh, S. M.; Stryer, L. *J. Am. Chem. Soc.* **1981**, *103*, 1607.

(27) (a) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059. (b) Hemmes, P. *Ibid.* **1972**, *94*, 75.

(28) Eigen, M. *Z. Phys. Chem.* (*Wiesbaden*) **1954**, *1*, 176.

(29) Dogondaze, R. R. *Dokl. Phys. Chem.* (*Engl. Transl.*) **1962**, *142*, 156.

(30) Giverdtsiteli, M. I. *Sov. Electrochem.* (*Engl. Transl.*) **1976**, 1073.

(31) North, A. M. "The Collision Theory of Chemical Reactions in Liquids"; Metheun: London, 1964.

Table III. Parameters Used in Fits to Weller Plots

	quencher			
	$HgCl_2$ [a]	$HgCl_2$ [b]	$HgCl_3^-$ [c]	$HgCl_4^{2-}$ [c]
k_{12}, $M^{-1}\ s^{-1}$	2.87×10^9	2.86×10^9	8.51×10^9	2.00×10^9
k_{21}, s^{-1}	8.89×10^8	8.85×10^8	1.33×10^9	2.9×10^8
k_{30}, s^{-1}	2.00×10^{10}	2.00×10^{10}	2.00×10^{10}	2.00×10^{10}
k^0_{23}, s^{-1}	1.60×10^{12}	1.60×10^{12}	1.60×10^{12}	1.60×10^{12}
$E°[Hg(II/I)]$, V	−0.80 ± 0.04	−0.80 ± 0.04	−0.80	−0.80
$\Delta G^‡(0)$, cal	5000 ± 500	4700 ± 500	4300 ± 800	6600 ± 400

[a] Conditions: 0.01 M HNO_3, 0.09 M $NaNO_3$. [b] Conditions: 0.01 M HNO_3, 0.99 M $NaNO_3$. [c] Conditions: 0.01 M HNO_3, [NaCl] + [$NaNO_3$] = 0.99 M.

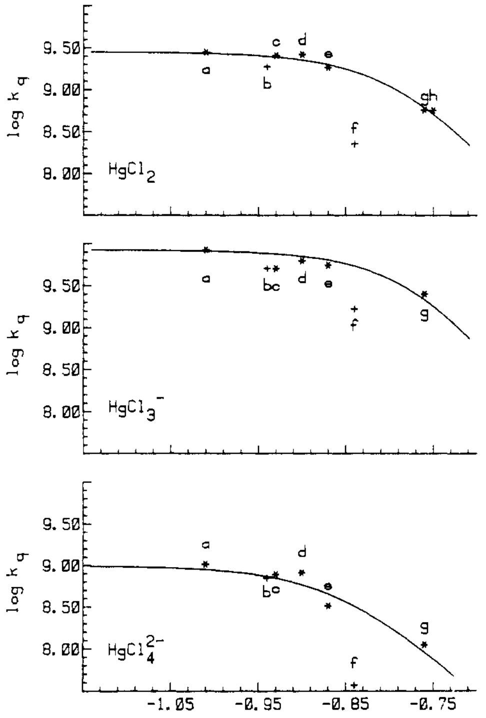

Figure 5. Weller plots for $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{2-}$ at 1.0 M ionic strength. The solid lines represent fits using the values of Table III in eq 11. Letters identify experimental points for the following complexes: (a) $[Ru(4,7\text{-}Me_2phen)_3]^{2+}$; (b) $[Ru(Me_2bpy)_3]^{2+}$; (c) $[Ru(5,6\text{-}Me_2phen)_3]^{2+}$; (d) $[Ru(Me\text{-}phen)_3]^{2+}$; (e) $[Ru(phen)_3]^{2+}$; (f) $[Ru(bpy)_3]^{2+}$; (g) $[Ru(Cl\text{-}phen)_3]^{2+}$; (h) $[Ru(Br\text{-}phen)_3]^{2+}$. Phenanthroline and bipyridine complexes are denoted by *'s and +'s, respectively.

errors in Table III. We consider $E°(A/A^-)$ and $\Delta G^*(0)$ probably accurate to better than 0.1 V and 1000 cal, respectively. The excellent quality of the fit gives further convincing evidence for the electron-transfer nature of the quenching.

With $HgCl_2$ and $HgCl_3^-$ the $\Delta G^*(0)$'s are 4–5 kcal/mol. This indicates that the intrinsic barriers and reorganizational energies in these cases are relatively small. For $HgCl_4^{2-}$, however, $\Delta G^*(0)$ is noticeably larger, which, in part, accounts for its reduced quenching rate compared to those for the other species.

One factor contributing to the larger value of $\Delta G^*(0)$ for $HgCl_4^{2-}$ may be a steric effect. The large tetrahedral $HgCl_4^{2-}$ [32] may prevent the encounter complex from forming at an optimum distance for electron transfer. Thus, the transfer must occur over a longer distance, decreasing the orbital overlap and lowering k_q.[33] Alternatively, a larger conformational change may be required to form the Hg(I) free-radical product. In both cases, $\Delta G^*(0)$ would be larger.

A striking feature of Figure 5 is the widely different reactivities of $[Ru(bpy)_3]^{2+}$ and both $[Ru(Cl\text{-}phen)_3]^{2+}$ and $[Ru(Br\text{-}phen)_3]^{2+}$. Two possible explanations exist for these differences in reactivity: either the halogenated derivatives exhibit enhanced reactivity or the bipyridine complex exhibits decreased reactivity.

A specific interaction between the halogen in the 5-position of the phenanthroline ring and Hg(II) would stabilize the encounter complex and enhance the electron-transfer rate. Several experimental observations run counter to this hypothesis. Similar enhancement is observed with $HgCl_4^{2-}$, which is unlikely to coordinate to the halogen on the phenanthrolines. Further, there is no experimental evidence for static quenching of $[Ru(Cl\text{-}phen)_3]^{2+}$ by $HgCl_2$, which would be the most likely species to exhibit binding. Also, we have observed no spectral evidence for ground-state or excited-state complexes between the halogenated derivatives and any Hg(II) species.

Closer inspection of the data plots indicates that $[Ru(Me_2bpy)_3]^{2+}$ also reacts somewhat below its expected rate. The major difference between the bipyridine and phenanthroline derivatives is the presence of a central aromatic ring in the phenanthroline cases. $HgCl_2$ forms π complexes with aromatic molecules.[34] A similar interaction between the Hg(II) chloride species and the central aromatic ring of the phenanthroline ligands may stabilize the encounter complex and enhance k_q's for the phenanthroline derivatives relative to the bipyridine complexes. The quenching data, however, preclude the possibility of ground-state complex formation. We have also observed similar differences in behavior between bipyridine and phenanthroline complexes in other systems.[35] Thus, the structural differences between bipyridine and phenanthroline complexes may be too great for quantitative comparisons.

In conclusion, we have used luminescence quenching to probe the reactivity of tris(α-diimine)ruthenium(II) photosensitizers with $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{2-}$. The reactions proceed via electron transfer from the Ru(II) excited states to yield Ru(III) and Hg(I) radical species. The Weller–Marcus theory of electron transfer was used to correlate k_q and $E(D^+/^*D)$ values. The order of reactivity is $HgCl_3^-$ > $HgCl_2$ >> $HgCl_4^{2-}$. Following electron transfer the encounter pair is electrostatically stabilized and fast back electron transfer prevents separation of redox products.

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[32] Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Clarendon Press: Oxford, 1975; p 921.

[33] Marcus, R. A.; Siders, P. *J. Phys. Chem.* **1982**, *86*, 622.

[34] (a) Eliezer, I. *J. Chem. Phys.* **1965**, *42*, 3625. (b) Eliezer, I.; Avinur, P. *Ibid.* **1971**, *55*, 2300. (c) Vezzosi, I. M.; Peyronal, G.; Zanoli, A. F. *Inorg. Chim. Acta* **1974**, *8*, 229.

[35] Mandal, K.; Hauenstein, B. L., Jr.; Demas, J. N.; DeGraff, B. A. *J. Phys. Chem.* **1983**, *87*, 328.

Inorg. Chem. **1984**, *23*, 1107–1113

carried out on the University of Virginia laser facility purchased in part through National Science Foundation Grant No. CHE 77-09296.

Registry No. $Ru(Me_4phen)_3^{2+}$, 64894-64-0; $Ru(4,7\text{-}Me_2phen)_3^{2+}$, 24414-00-4; $Ru(Me_2bpy)_3^{2+}$, 32881-03-1; $Ru(5,6\text{-}Me_2phen)_3^{2+}$, 14975-40-7; $Ru(Me\text{-}phen)_3^{2+}$, 14975-39-4; $Ru(phen)_3^{2+}$, 22873-66-1; $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(Cl\text{-}phen)_3^{2+}$, 47860-47-9; $Ru(Br\text{-}phen)_3^{2+}$, 66908-45-0; $HgCl_2$, 7487-94-7; $HgCl_3^-$, 14988-07-9; $HgCl_4^{2-}$, 14024-34-1.

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Electron-Transfer Quenching of Ruthenium(II) Photosensitizers by Mercury(II) Chlorides. 2. Reactions in Aqueous Sodium Lauryl Sulfate Micellar Solutions

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Excited-state interactions of tris(α-diimine)ruthenium(II) photosensitizers with $HgCl_x^{2-x}$ (x = 2, 3, 4) were studied in the presence of sodium lauryl sulfate micelles. The results are compared with those of our previous study on the surfactant-free systems. The photosensitizers are tightly bound to the micelles, and the quenchers appear to be entirely in the aqueous phase, which radically modifies the quenching behavior. Equilibrium constants for formation of $HgCl_3^-$ and $HgCl_4^{2-}$ were evaluated by luminescence methods. Quenching proceeds via oxidative electron transfer to yield Ru(III) and Hg(I) free radicals. The failure to detect efficient ejection of anionic Hg(I) radicals from the anionic micelles is attributed to very fast reactions of the type $HgCl_2^-\cdot \rightarrow HgCl\cdot + Cl^-$. Marcus electron-transfer theory is modified to account for the differences between the micellar and homogeneous cases. $HgCl_2$ and $HgCl_3^-$ exhibit large inherent barriers to electron transfer ($\Delta G^*(0)$). Marcus theory permits evaluation of the otherwise unmeasurable redox potentials for the reaction Hg(II) + $e^- \rightarrow$ Hg(I); the values are estimated to be $\sim$−0.80 V, which agree with the values in surfactant-free media.

Introduction

We recently began investigating the excited-state reactivity of tris(α-diimine)ruthenium(II) complexes and mercury(II) species. We have described the quenching of a series of structurally and electronically similar $^*[RuL_3]^{2+}$ complexes (L = 2,2′-bipyridine, 1,10-phenanthroline, and their substituted derivatives) by Hg^{2+}[1] and by $HgCl_x^{2-x}$ (x = 2, 3, 4) in aqueous solution.[2] Quenching occurs by electron transfer. With Hg^{2+} the redox products, Hg_2^{2+} and the Ru(III) complex, are formed with high efficiency. The back-reaction between the Ru(III) species and Hg_2^{2+} is relatively slow (<10 M^{-1} s^{-1}) and provides an energy trap which forms the basis of a photogalvanic cell.[1]

We expected $HgCl_2$ to be superior to Hg^{2+} for solar energy storage because one of the anticipated final products, Hg_2Cl_2, should be insoluble and therefore slow the thermal back-reaction even further. For the $HgCl_x^{2-x}$ quenchers in fluid solution, however, no redox products have been observed even under flash photolysis conditions.[2] The main problem appears to be one of separation of the initial photoproducts

$$^*D + HgCl_2 \rightarrow {}^*D|HgCl_2 \rightarrow D^+|HgCl_2^- \qquad (1a)$$

$$D^+|HgCl_2^- \rightarrow D|HgCl_2 \rightarrow D + HgCl_2 \qquad (1b)$$

$$D^+|HgCl_2^- \rightarrow D^+ + HgCl_2^-\cdot \qquad (1c)$$

where D denotes the Ru(II) photosensitizer and the encounter pairs are denoted by "|". Apparently, the dissociation step for the electrostatically stabilized pair $D^+|HgCl_2^-$ (eq 1c) is much slower than the energetically favorable back electron-transfer reaction (eq 1b). Any modifications that accelerate the separation of the redox partners in eq 1c would improve the yield of energetically valuable products.

One approach for assisting separation of the initial photoproducts is the use of charged micelles.[3,4] In our current system, an anionic micelle binds the Ru(II) photosensitizer, but the charge does not impede the approach of neutral $HgCl_2$. Following electron transfer, however, the negatively charged $HgCl_2^-$ should be ejected from the micelle, and the back-reaction should then be impeded by the electrostatic barrier. In addition to the possibility of enhancement of product separation, fundamental photochemical studies in micellar systems are inherently interesting because surfactants can enormously influence the nature and rates of reactions.[3,4]

We present here our study of the photochemical interactions of $HgCl_x^{2-x}$ (x = 2, 3, 4) and $[RuL_3]^{2+}$ photosensitizers in aqueous micellar NaLS solutions. We chose the relatively well-understood anionic surfactant sodium lauryl sulfate (NaLS) for study. The results are compared with those of our preceding study of the same systems in surfactant-free media,[2] and a model is developed to describe the effects introduced by the micelles. The model is also used in conjunction with Marcus electron-transfer theory to explain the quenching behavior for different Hg(II) species. Finally, the feasibility of the aqueous and micellar systems as solar energy converters is examined.

Experimental Section

The ruthenium(II) complexes used in this study and their preparation, purification, and characterization were described in the pre-

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[†] University of Virginia.

[‡] James Madison University.

(1) DeGraff, B. A.; Demas, J. N. *J. Am. Chem. Soc.* **1980**, *102*, 6169.

(2) Hauenstein, B. L., Jr.; Mandal, K.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.*, preceding paper in this issue.

(3) (a) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975. (b) Holt, S. L., Ed. "Inorganic Reactions in Organized Media"; American Chemical Society: Washington, DC, 1982; ACS Symp. Ser. No. 177.

(4) (a) Grätzel, M. *Acc. Chem. Res.* **1981**, *14*, 376. (b) Grätzel, M.; Kalyanasundaram, K.; Kiwi, J. *Struct. Bonding* (*Berlin*) **1982**, *49*, 37. (c) Grätzel, M. *ACS Symp. Ser.* **1982**, *No. 177*, 113. (d) Yekta, A.; Aikawa, M.; Turro, N. *J. Chem. Phys. Lett.* **1979**, *63*, 543. (e) Ziemiecki, H.; Cherry, W. R. *J. Am. Chem. Soc.* **1981**, *103*, 4479. (f) Turro, N. J.; Grätzel, M.; Braun, A. M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 675. (g) Infelta, P. P.; Grätzel, M.; Thomas, J. K. *J. Phys. Chem.* **1974**, *78*, 191.

0020-1669/84/1323-1107$01.50/0