

# Photolytic and Radiolytic Studies of $Ru(bpy)_3^{2+}$ in Micellar Solutions<sup>1</sup>

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**Abstract:**  $Ru(bpy)_3^{2+}$  is shown to form a water-insoluble salt with dodecyl sulfate ions (DS) which is solubilized by sodium dodecyl sulfate (SDS) micelles. In the micelles the rate of the reaction of  $Ru(bpy)_3^{2+}$  with  $e_{aq}^-$  is reduced while its rate of reaction with various metal cations in their reduced form ( $Zn^+$ ,  $Cd^+$ ,  $Co^+$ ) is enhanced. This, as well as the ionic strength effect on these rates, clearly indicates that  $Ru(bpy)_3^{2+}$  resides in a negatively charged ionic atmosphere. In the presence of SDS micelles the luminescence from the charge transfer excited state of  $Ru(bpy)_3^{2+}$  is red shifted as compared to its spectrum in the absence of SDS. Since long-chain alcohols have a similar effect it is concluded that  $Ru(bpy)_3^{2+}$  must strongly interact with the hydrocarbon chain of the surfactant. Our kinetic results indicate that essentially all of the  $Ru(bpy)_3^{2+}$  is bound to the micelles under our experimental conditions. The rates of reaction of the lowest charge transfer excited state of  $Ru(bpy)_3^{2+}$  in micellar solutions are shown to be faster with  $Cu^{2+}$  ions and slower with  $Fe(CN)_6^{3-}$  ions as compared to the rates of the same reactions in simple aqueous solutions. However, the yield of the redox products of the reaction with  $Cu^{2+}$  that can escape to the bulk of the solution is greatly reduced by the micelles.

The catalytic or inhibitory effect of micelles on the kinetics of a large variety of reactions is well documented in the literature.<sup>3</sup> Introduction of the pulse-radiolysis and laser flash photolysis techniques in the study of micellar effects on reaction kinetics of highly reactive radicals and excited states<sup>4</sup> revealed that such effects might occur at various stages of the reaction (e.g., diffusion to the micelle, intra- and intermicellar processes).<sup>4,5</sup> Moreover, solubilization in micelles was shown to alter the quantum yields of primary products.<sup>6</sup> From phenothiazine,<sup>6a</sup> for example, the yields of hydrated electrons and the counterions were increased by incorporation of the phenothiazine in negative micelles, while the yields of excited states were correspondingly reduced. However, the question of whether this effect is a kinetic effect of the negative field of the micelle in inhibiting the back reaction of the electrons or an energetic thermodynamic effect is still to be answered.

$Ru(bpy)_3^{2+}$  (where  $bpy = 2,2'$ -bipyridine) is the subject of many intensive studies currently underway. While these studies are focusing on its spectroscopic and photochemical redox properties,<sup>7,8</sup> its possible use in solar energy conversion systems is often suggested.<sup>9,10</sup> Pertinent to this subject is a recent report in which  $Ru(bpy)_3^{2+}$  derivatives, spread in monolayers, are claimed to photolytically decompose water into hydrogen and oxygen.<sup>11</sup>

When simple ions are added to micellar solutions their effect on the properties of the micelles ( $cmc =$  critical micelle concentration, fraction of charge, number of monomers per micelle, etc.) are well known.<sup>12</sup> The location of the ions in the micelle is also reasonably predictable and a Poisson-Boltzmann distribution of the gegenion normal to the micelle is usually assumed. On the other hand, when organic additives are solubilized in micelles, it is usually assumed that they would reside in the lipoidic core of the micelle at different distances from its surface. Very little is known about the effects of micelles on the kinetics of complex ions and even the site of residence of an ion like  $Ru(bpy)_3^{2+}$  in negative micelles is hard to predict. In view of the widespread interest in  $Ru(bpy)_3^{2+}$  as a possible participant in solar energy conversion systems we initiated this study on the kinetic effects of micelles on  $Ru(bpy)_3^{2+}$  reactions. In this report we will mainly be concerned with the effects of micellar SDS solutions on the kinetics of electron transfer to  $Ru(bpy)_3^{2+}$  and from its lowest charge transfer triplet excited state.

## Experimental Section

$Ru(bpy)_3Cl_2$  was recrystallized three times by standard procedures.

Sodium dodecyl sulfate was recrystallized several times from ethanol and dried in vacuo. No difference between the recrystallized surfactant and the nonrecrystallized SDS could be observed in the pulse radiolysis, flash photolysis, or emission experiments, except for the lowering of the background rate of reaction of  $e_{aq}^-$  with the micellar solutions in the absence of any other additive. Nonetheless, all results to be reported here were obtained with the recrystallized surfactant. All other materials were reagent grade and were used as received. Solutions without surfactant were deaerated by bubbling prepurified argon (Matheson) through the solution using the syringe technique. Stock solutions of sodium dodecyl sulfate were passed through a large number of evacuations and intensive agitations. The desired quantity of surfactant solutions was then transferred to syringes which contained the other components of the final solutions and which had been prepurged with argon as described above. Solutions were used immediately after preparation or stored in the dark overnight and irradiated on the next day. No difference in results could be observed between solutions which were used 1 h after preparation or on the next day. All solutions were checked for changes in absorption with no changes observed except for those to be reported. Concentrations of  $Ru(bpy)_3^{2+}$  were determined spectrophotometrically using  $\epsilon_{453} 1.4 \times 10^4 M^{-1} cm^{-1}$ . Unless otherwise stated, solutions were buffered at  $pH 7.0 \pm 0.1$  (3 mM of each of the phosphate components) measured on a Radiometer pH meter 4. Triply distilled water was used for all solutions.

The pulse-radiolysis setup has already been described previously.<sup>13</sup> Electron pulses of 4-ns width produced  $\sim 2 \times 10^{-6} M$  total concentration of radicals in 5-cm length cells. Only about 50% of these, i.e., less than  $10^{-6} M$  of  $e_{aq}^-$  are believed to be of interest in our study as will be shown later. The rise time of the electronic setup was less than 10 ns and cannot affect any of our results.

Emission spectra were taken in 1-cm square cells on an Hitachi Perkin-Elmer spectrofluorimeter with excitation at 450 nm. However, several check experiments were done with excitation at 470 nm to ensure that there was no effect of absorbed light intensity on the results. Cutoff filters were used to minimize scattered light effects. Emission spectra were not corrected for sensitivity dependence of the detecting photomultiplier on wavelength. Conductivity measurements were done on a General Radio Co. conductivity bridge at a frequency of 1 kHz.

Flash photolysis experiments were done with a Xenon Corp. Model 720 instrument. Cylindrical Pyrex cells, 10 cm long and 1 cm diameter, were protected from light of  $\lambda < 400$  nm using appropriate short wavelength cutoff filters. The energy delivered to the flash lamp was 200 J with a flash duration of 20  $\mu s$  (90%). All experiments were performed at  $24 \pm 1^\circ C$ .

## Results and Discussion

**Solubilization by Negative Micelles.** When  $Ru(bpy)_3^{2+}$  is added to solutions containing increasing concentrations of SDS

**Table I.** Solubility Product for the Precipitate of Ru(bpy)<sub>3</sub><sup>2+</sup> with SDS<sup>a</sup>

[Ru(II)] <sub>0</sub>	[SDS] <sub>0</sub>	[Ru(II)] <sub>S</sub>	[Ru(II)] <sub>P</sub>	[SDS] <sub>P</sub>	[SDS] <sub>S</sub>	K <sub>SP</sub> <sup>b</sup>
2 × 10 <sup>-4</sup>	5 × 10 <sup>-4</sup>	5.36 × 10 <sup>-5</sup>	1.46 × 10 <sup>-4</sup>	2.93 × 10 <sup>-4</sup>	2.1 × 10 <sup>-4</sup>	2.30 × 10 <sup>-12</sup>
2 × 10 <sup>-4</sup>	1 × 10 <sup>-3</sup>	6.36 × 10 <sup>-6</sup>	1.94 × 10 <sup>-4</sup>	3.87 × 10 <sup>-4</sup>	6.13 × 10 <sup>-4</sup>	2.39 × 10 <sup>-12</sup>
4 × 10 <sup>-4</sup>	5 × 10 <sup>-4</sup>	2.07 × 10 <sup>-4</sup>	1.93 × 10 <sup>-4</sup>	3.86 × 10 <sup>-4</sup>	1.14 × 10 <sup>-4</sup>	2.69 × 10 <sup>-12</sup>
4 × 10 <sup>-4</sup>	1 × 10 <sup>-3</sup>	4.31 × 10 <sup>-5</sup>	3.57 × 10 <sup>-4</sup>	7.14 × 10 <sup>-4</sup>	2.86 × 10 <sup>-4</sup>	3.53 × 10 <sup>-12</sup>

<sup>a</sup> The indices 0, S, P represent initial concentration, concentration remaining in solution after separation of the precipitate, and the concentrations precipitated, respectively. Ru(II) stands for Ru(bpy)<sub>3</sub><sup>2+</sup>. Concentrations are in M. <sup>b</sup> Solubility product defined as [Ru(II)]<sub>S</sub>[SDS]<sub>S</sub><sup>2</sup>.

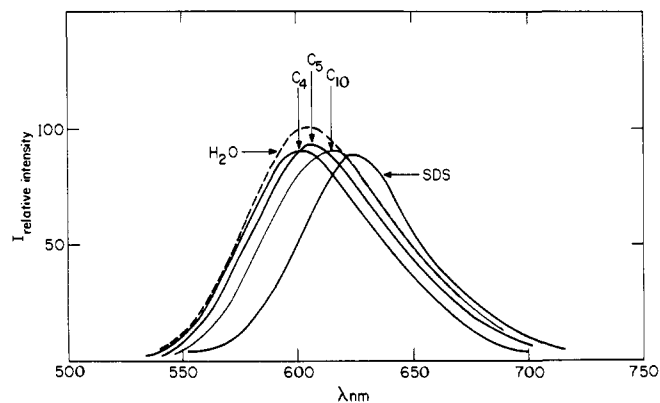
precipitation can be seen when an equivalent concentration of SDS to Ru(bpy)<sub>3</sub><sup>2+</sup> is present in the solution. However, this precipitate disappears when the region of the cmc of SDS is reached. Once the precipitate is solubilized by the micelles the absorption spectrum of Ru(bpy)<sub>3</sub><sup>2+</sup> is nearly the same as its spectrum in the absence of the surfactant. Minor changes could be observed in this spectrum (~5% reduction in the absorbance at 455 nm and an increase of ~5 nm in the width of this band). The nearly identical spectra are considered as an indication that the Ru(II) central cation retains its ligand bipyridines in the micelles. The precipitation is probably due to formation of the insoluble Ru(bpy)<sub>3</sub>(DS)<sub>2</sub> (reaction 1), which is then solubilized in the micelles.



Indication that this is indeed the case is given in Table I where the results on the amount of precipitated Ru(bpy)<sub>3</sub><sup>2+</sup> and the amount remaining in solution are presented. The precipitates were centrifuged and filtered several times until no change in the absorption spectra was observed on further filtration. The clear solutions were then analyzed spectrophotometrically for Ru(bpy)<sub>3</sub><sup>2+</sup>. From the results in Table I the solubility product, defined as K<sub>SP</sub> = [Ru(bpy)<sub>3</sub><sup>2+</sup>][SDS]<sup>2</sup>, is seen to be fairly constant in the range studied. A rather small range of concentrations was examined since at lower concentrations difficulties were encountered in separation of the precipitate by conventional techniques. Higher concentrations were avoided since solubilization by low molecular weight aggregates might occur. However, the amount of Ru(bpy)<sub>3</sub><sup>2+</sup> remaining in solution is seen in Table I to change by a factor of 30. Any other "solubility product" would either yield much higher fluctuations or be chemically incompatible. Further experiments in the range where precipitation occurs were avoided and in all experiments reported below [SDS] ≥ 10<sup>-2</sup> M was employed. It should be noted that the precipitation and the solubilization can be reversed by addition of SDS or water. At [SDS] > cmc, no precipitation could be observed even at 1 mM of Ru(bpy)<sub>3</sub><sup>2+</sup>.

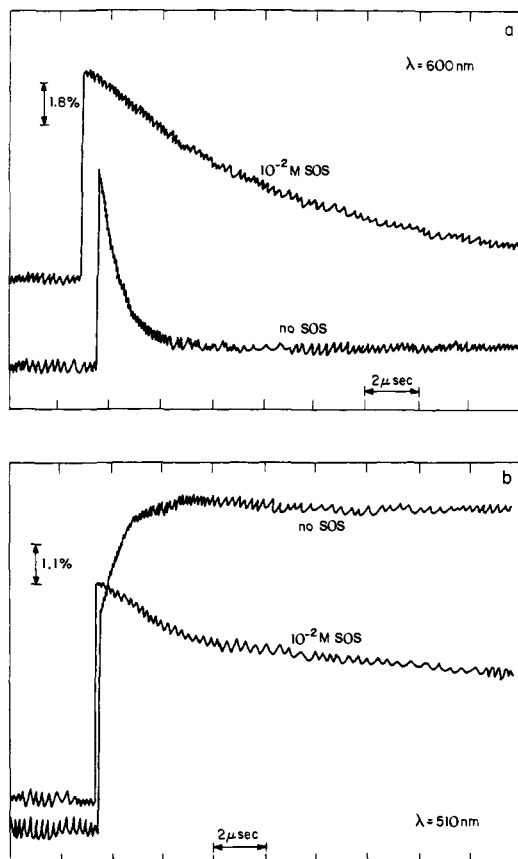
Since changes of the cmc might be suspected when the Ru(bpy)<sub>3</sub><sup>2+</sup> complex is added to the micellar solution, several conductivity measurements were made. In the absence of any additive the cmc that we obtain is 7.8 × 10<sup>-3</sup> M and the addition of 2 × 10<sup>-5</sup> M Ru(bpy)<sub>3</sub>Cl<sub>2</sub>, which is the concentration used in most of the photolysis and radiolysis experiments, had a negligible effect on the cmc. This result may be compared with 8.1 × 10<sup>-3</sup> M obtained by the highly accurate experiments of Williams et al.<sup>14a</sup> On addition of 2 × 10<sup>-4</sup> M Ru(bpy)<sub>3</sub>Cl<sub>2</sub> the cmc drops to 7.0 × 10<sup>-3</sup> M while the addition of the same amount of MgCl<sub>2</sub> yields a cmc of 6.8 × 10<sup>-3</sup> M. We therefore conclude that the effect of Ru(bpy)<sub>3</sub><sup>2+</sup> on the cmc is similar to the effect of other divalent ions.<sup>12</sup> Several attempts to characterize the size of the micelles by light scattering in the presence of Ru(bpy)<sub>3</sub><sup>2+</sup> were fruitless owing to difficulties arising from the combination of light absorption and emission in the green and red regions (546 and 578 nm) by the complex.

Solubilization in the micelles restored the absorption spectrum but permanent changes were observed in the emission



**Figure 1.** Effect of various alcohols on the emission spectrum of (CT)-Ru(bpy)<sub>3</sub><sup>2+</sup>. C<sub>4</sub> = *n*-butyl alcohol, C<sub>5</sub> = amyl alcohol, C<sub>10</sub> = *n*-decyl alcohol, SDS = 10<sup>-2</sup> M SDS, dotted spectrum is in water. [Ru(bpy)<sub>3</sub><sup>2+</sup>] ≈ 2 × 10<sup>-5</sup> in all cases.

spectrum. The maximum of the emission spectrum was shifted from 605 nm in water to 625 nm in the micellar solutions, and the half-width of this spectrum correspondingly decreased from 75 to 60 nm, respectively. The emission intensity at λ<sub>max</sub>, however, was nearly the same in both environments. It seems, therefore, that the dodecyl sulfate chains in the near vicinity of Ru(bpy)<sub>3</sub><sup>2+</sup> affect both the position and the half-width of the fluorescence spectrum. In order to check the effect of the hydrocarbon chain portion, we measured the emission spectra of Ru(bpy)<sub>3</sub><sup>2+</sup> in several alcohols with increasingly longer hydrocarbon chains. These spectra are shown in Figure 1. It is clear that the longer the alcohol hydrocarbon chain, the larger the red shift in the emission spectrum. Yet even in the longest alcohol used, the magnitude of the shift is not as great as in the SDS solutions. The half-width of the spectrum, even in the lowest alcohol, is 15 nm smaller than in water. We thus may conclude that the close environment of Ru(bpy)<sub>3</sub><sup>2+</sup> alters both the position of the emission peak and its half-width. This conclusion is in line with the CTTS nature of the CT transition of Ru(bpy)<sub>3</sub><sup>2+</sup> as suggested previously.<sup>15</sup> While the hydrocarbon chains have a pronounced effect on the emission spectrum of the lowest charge transfer excited state, (CT)-Ru(bpy)<sub>3</sub><sup>2+</sup>, addition of 0.5 M Na<sub>2</sub>SO<sub>4</sub> or 5 × 10<sup>-2</sup> M polyvinyl sulfate had no effect on this spectrum. Since there can be little doubt that in the latter case Ru(bpy)<sub>3</sub><sup>2+</sup> cannot escape the potential field of the polyelectrolyte we conclude that the spectral shifts by the micelles stem from the interaction of Ru(bpy)<sub>3</sub><sup>2+</sup> with the hydrocarbon chains rather than with the polar head groups. This, however, does not necessarily mean that the site of residence of Ru(bpy)<sub>3</sub><sup>2+</sup> is in the inner core of the micelle. Since water molecules can penetrate into the outer core of the micelles which occupies ~70% of the micellar volume<sup>14b</sup> so may the Ru(bpy)<sub>3</sub><sup>2+</sup>. The large magnitude of the salt effect on the rate of electron transfer reactions, to be described later, may indicate that Ru(bpy)<sub>3</sub><sup>2+</sup> is located in the vicinity of the Stern layer. The differences between the emission spectra in the presence and absence of SDS micelles will be used later as an analytical tool to determine



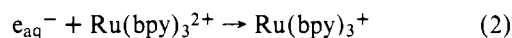
**Figure 2.** Oscillograms showing the rate of the reaction of  $e_{aq}^-$  with  $Ru(bpy)_3^{2+}$ : (a) at  $\lambda$  600 nm, (b)  $\lambda$  510 nm. With and without  $10^{-2}$  M SDS.  $[Ru(bpy)_3^{2+}] = 2.0 \times 10^{-5}$  M, deaerated solutions at pH 7. When SDS is absent 0.017 M *tert*-butyl alcohol was added.

whether  $Ru(bpy)_3^{2+}$  stays in the micellar environment or is released to the bulk of the solution.

**Micellar Effects on Reactions with  $e_{aq}^-$ ,  $Zn^{2+}$ ,  $Co^+$ , and  $Cd^+$ .** In order to gain some insight into the kinetic effects on  $Ru(bpy)_3^{2+}$  in the micelles we performed some experiments in which the rate constants of several species highly reactive with  $Ru(bpy)_3^{2+}$  were measured. When aqueous solutions are irradiated with a pulse of high-energy electrons the reactive radicals  $e_{aq}^-$ , H, and OH are produced during the pulse. In SDS containing solutions both OH and H are efficiently scavenged by the surfactant to produce radicals which are nonreactive toward  $Ru(bpy)_3^{2+}$ . This was checked by irradiating  $N_2O$ -saturated solution containing  $10^{-2}$  M SDS and  $4 \times 10^{-5}$  M  $Ru(bpy)_3^{2+}$ . Since the rate of  $e_{aq}^-$  with SDS is relatively slow<sup>4a</sup> all of the  $e_{aq}^-$  would react with  $N_2O$  to pro-

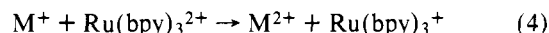
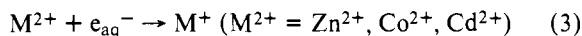
duce OH radicals in a time comparable with the pulse width. These radicals, as well as the hydrogen atoms, will then react with the hydrocarbon chains of the surfactant, probably by hydrogen abstraction. If these radicals would in turn react with  $Ru(bpy)_3^{2+}$ , changes in the absorbance of the above-mentioned solution are expected to occur. However, no such changes were observed in the spectral region we have investigated and we therefore conclude that the radicals derived from SDS do not interfere with the reactions we studied. Whenever solutions without SDS were studied, 0.017 M *tert*-butyl alcohol was added as an efficient scavenger for OH radicals, resulting in replacement of the reactive OH by the unreactive  $(CH_3)_2C(OH)CH_2$  radical.

The  $e_{aq}^-$  is known to react very rapidly with  $Ru(bpy)_3^{2+}$ .



We have recently measured<sup>16</sup> and confirmed again in this study  $k_2 = 6.0 \times 10^{10} M^{-1} s^{-1}$  in aqueous solutions, close to the value previously measured by Baxendale and Fiti<sup>17</sup> of  $8.0 \times 10^{10} M^{-1} s^{-1}$ . However, when  $Ru(bpy)_3^{2+}$  is incorporated in SDS micelles a strong inhibition of the rate of reaction 2 is observed. This striking effect is shown in the computer-processed oscillograms of Figure 2. At  $\lambda$  600 nm where  $e_{aq}^-$  has a much higher extinction coefficient than  $Ru(bpy)_3^{2+}$ , the absorbance is seen to decay much more slowly in the presence of SDS than in its absence. From the results at  $\lambda$  510 nm, where  $\epsilon_{e_{aq}^-}$  is only  $6000 M^{-1} cm^{-1}$ , as compared to  $\epsilon_{Ru(II)} - \epsilon_{Ru(I)}$   $9600 M^{-1} cm^{-1}$ ,<sup>16</sup> it is clear that only a fraction of the solvated electrons react with  $Ru(bpy)_3^{2+}$  in the presence of the surfactant under these conditions; otherwise, the absorption would increase with time rather than decrease. The rate constant for reaction 2 could thus be measured either by following the decay at 600 nm, or by measuring the yields of  $Ru(bpy)_3^+$  at 510 nm. Both methods gave essentially the same results. However, since following the decay of  $e_{aq}^-$  is more straightforward and probably more accurate only these results will be presented here.

In Table II we present results of the second-order rate constants for reaction 2 under a large variety of conditions. Each experiment was done with and without SDS. Also shown in Table II are rate constants of several unusual monovalent cations. In these experiments the concentration of the divalent parent cation was chosen such that most of the  $e_{aq}^-$  will react with it in the bulk of the solution rather than with  $Ru(bpy)_3^{2+}$  (reaction 3).

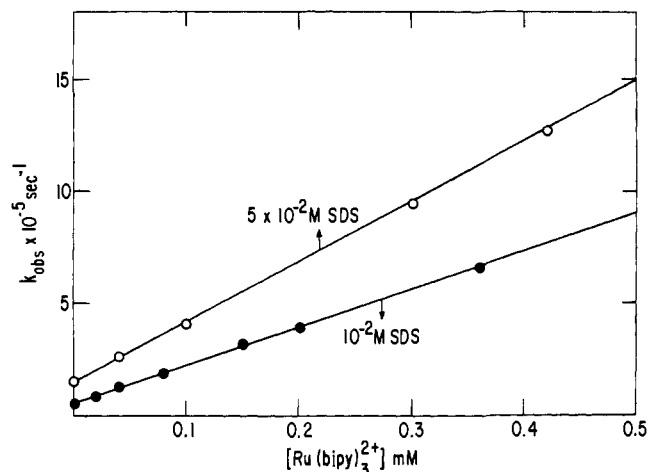


The formation of  $Ru(bpy)_3^+$  in reaction 4 was then followed by the increase in absorbance at 510 nm. From the yield at this

**Table II.** Micellar Effects on Specific Rates with  $Ru(bpy)_3^{2+}$  <sup>a</sup>

Reaction	[SDS], M	[NaCl], M	[Ru(II)], M	[Additive], M	pH	$k$ , $M^{-1} s^{-1}$
$e_{aq}^- + SDS$	$10^{-2}$				7	$6.5 \times 10^6$
$e_{aq}^- + SDS$	$10^{-2}$	0.5			7	$1.0 \times 10^7$
$e_{aq}^- + Ru(II)$			$(2-8) \times 10^{-5}$		7	$5.9 \times 10^{10}$
$e_{aq}^- + Ru(II)$		0.1-0.5	$2 \times 10^{-5}$		7	$(6.0-4.5) \times 10^{10}$
$e_{aq}^- + Ru(II)$	$10^{-2}$		$(2-50) \times 10^{-5}$		7	$1.7 \times 10^9$
$e_{aq}^- + Ru(II)$	$10^{-2}$	0.1-0.5	$2 \times 10^{-5}$		7	$(6.8-12) \times 10^9$
$e_{aq}^- + Ru(II)$	$5 \times 10^{-2}$		$(2-50) \times 10^{-5}$		7	$2.7 \times 10^9$
$Zn^{2+} + Ru(II)$	$10^{-2}$		$4 \times 10^{-5}$	$ZnSO_4, 5 \times 10^{-2}$	5.19	$2.9 \times 10^9$
$Zn^{2+} + Ru(II)$			$4 \times 10^{-5}$	$ZnSO_4, 5 \times 10^{-2}$	5.19	$1.6 \times 10^9$
$Co^{2+} + Ru(II)$	$10^{-2}$		$4 \times 10^{-5}$	$CoSO_4, 10^{-2}$	6.9	$6.3 \times 10^9$
$Co^{2+} + Ru(II)$			$(1.6-4) \times 10^{-5}$	$CoSO_4, 2.5 \times 10^{-3}$	6.9	$1.75 \times 10^9$
$Cd^{2+} + Ru(II)$	$10^{-2}$		$4 \times 10^{-5}$	$CdSO_4, 10^{-2}$	5.9	$4.1 \times 10^9$
$Cd^{2+} + Ru(II)$			$4 \times 10^{-5}$	$CdSO_4, 3 \times 10^{-2}$	5.9	$6.1 \times 10^8$

<sup>a</sup> When SDS is present no *t*-BuOH added, when absent 0.017 M *t*-BuOH added. All were deaerated.



**Figure 3.** Dependence of the pseudo-first-order rate constant for  $e_{aq}^- + Ru(bpy)_3^{2+}$  on the concentration of  $Ru(bpy)_3^{2+}$ : ●, in  $10^{-2}$  M SDS solutions; ○, in  $5 \times 10^{-2}$  M SDS solutions. Deaerated solutions at pH 7.

wavelength it was concluded that practically all  $M^+$  ions were scavenged by  $Ru(bpy)_3^{2+}$ . It is clear from the results in Table II that rates of negatively charged species ( $e_{aq}^-$ ) are retarded by the negative micelles while rates of positively charged species ( $M^+$ ) are accelerated.

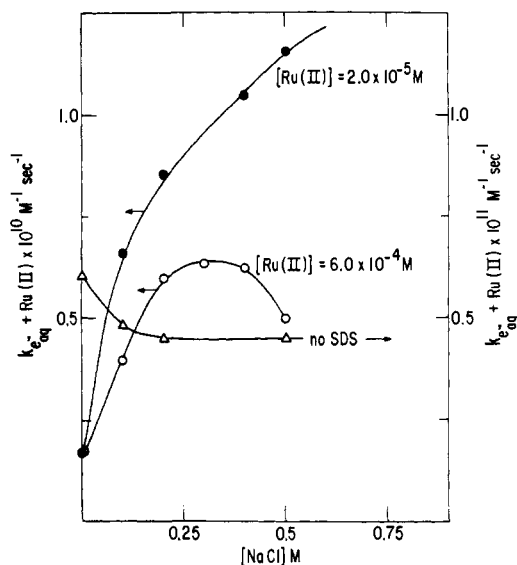
The rate of reaction 2 deserves some more detailed analysis. In Figure 3 we show the dependence of the pseudo-first-order rate constant  $k_{obsd}$  for reaction 2 on  $[Ru(bpy)_3^{2+}]$  at two different concentrations of surfactant. For both concentrations SDS  $k_{obsd}$  is linearly dependent on  $[Ru(bpy)_3^{2+}]$ . The small positive intercepts for these lines, which are actual experimentally measured points obtained in the absence of  $Ru(bpy)_3^{2+}$ , are attributed mainly to reactions of  $e_{aq}^-$  with impurities in the solutions and with the surfactant itself. From the slopes we obtain  $k_2 = 1.7 \times 10^9$  and  $2.7 \times 10^9 M^{-1} s^{-1}$  at  $10^{-2}$  and  $5 \times 10^{-2}$  M SDS, respectively. The 50% increase in the rate in the higher concentration of SDS can be attributed to the kinetic salt effect which will be shown to be very pronounced.

Two conclusions are to be drawn from the complete constancy of  $k_2$  as observed in Figure 3. The first point concerns the amount of  $Ru(bpy)_3^{2+}$  which remains free in the bulk of the solution. Since the specific rate of reaction 2 in the absence of SDS is 30 times faster than its rate in the micellar solutions, it can be concluded that the ratio of free  $Ru(bpy)_3^{2+}$  to  $Ru(bpy)_3^{2+}$  which is bound to micelles, i.e.,  $[Ru(bpy)_3^{2+}]_{free}/[Ru(bpy)_3^{2+}]_{micelles}$ , is  $\leq 3\%$  even at the highest  $[Ru(bpy)_3^{2+}]$  and lowest [SDS] used. In fact this ratio must be much smaller than 3% since it seems unlikely that  $Ru(bpy)_3^{2+}$  which is bound to the micelle would not react at all with  $e_{aq}^-$ . Moreover, if only the free  $Ru(bpy)_3^{2+}$  was the reactive species toward  $e_{aq}^-$ , then the salt effect that we observe in the presence of SDS (see below) would be in the reverse direction to the one that we actually find.

The second point to be raised here concerns the number of  $Ru(bpy)_3^{2+}$  molecules per one micelle. The concentration of micellar aggregates  $[m]$  can be calculated using

$$[m] = \frac{C_0 - cmc}{N} \quad (I)$$

where  $C_0$  is the total concentration of surfactant and  $N$  is the number of DS monomers in one micelle. The concentration of micelles in  $10^{-2}$  M SDS and in the absence of  $Ru(bpy)_3^{2+}$  is thus  $3.0 \times 10^{-5}$  ( $cmc = 8.1 \times 10^{-3}$  M,  $N = 62$ ).<sup>20</sup> Assuming that small amounts of  $Ru(bpy)_3^{2+}$  do not significantly change both  $N$  and the  $cmc$ , then the number of  $Ru(bpy)_3^{2+}$  ions per micelle,  $n_{Ru} = [Ru(bpy)_3^{2+}]/[m]$ , can be calculated. Since practically all the  $Ru(bpy)_3^{2+}$  that was added is bound to the

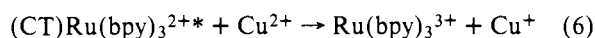
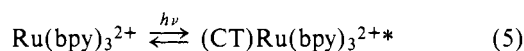


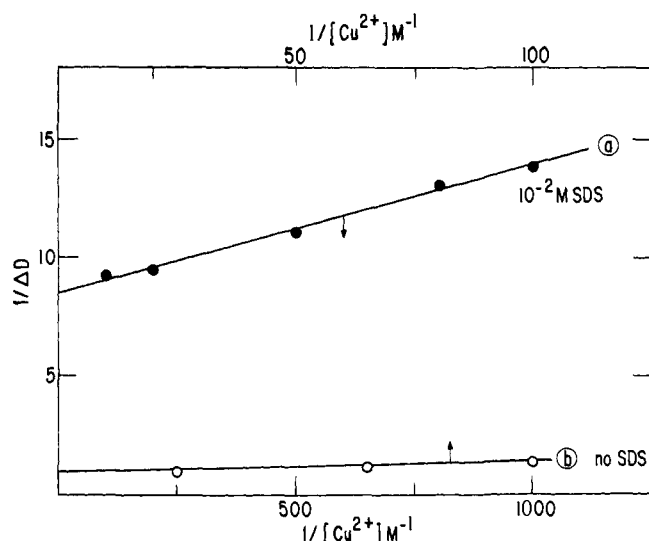
**Figure 4.** Ionic strength effect on the rate constant of  $e_{aq}^- + Ru(bpy)_3^{2+}$ : Δ,  $2.0 \times 10^{-5}$  M  $Ru(bpy)_3^{2+}$ , no SDS; ●,  $2.0 \times 10^{-5}$  M  $Ru(bpy)_3^{2+}$  in  $10^{-2}$  M SDS; ○,  $6.0 \times 10^{-4}$  M  $Ru(bpy)_3^{2+}$  in  $10^{-2}$  M SDS. All solutions deaerated and buffered at pH 7.

micelles, as shown above, one gets  $n_{Ru} = 0.67$  at  $2 \times 10^{-5}$  M  $Ru(bpy)_3^{2+}$ . At the higher concentrations of  $Ru(bpy)_3^{2+}$  the  $cmc$  drops to somewhat lower values. In  $2 \times 10^{-4}$  M  $Ru(bpy)_3^{2+}$  we obtain  $cmc$  of  $7 \times 10^{-3}$  M which yields  $n_{Ru} = 4.1$   $Ru(bpy)_3^{2+}$  per micelle. Even if a value of  $cmc = 2.0 \times 10^{-3}$  M, which is a typical value for dodecyl sulfate-bivalent ion micellar solutions,<sup>18</sup> is assumed,  $n_{Ru} = 3.9$  is obtained at the higher  $[Ru(bpy)_3^{2+}]$ . The linear dependence of the pseudo-first-order rate constant on  $[Ru(bpy)_3^{2+}]$ , as seen in Figure 3, would therefore indicate that the shielding by the micelle changes very little in this concentration range.

Further demonstration that the  $Ru(bpy)_3^{2+}$  is imbedded in a highly negatively charged microenvironment is revealed by the ionic strength effect on the rate of reaction 2. In Figure 4 we show the change in  $k_2$  on addition of variable NaCl concentrations. In the absence of SDS we find a decrease in  $k_2$  as expected and this amounts to about 30% on addition of 0.2 M or more NaCl. In contradistinction with this relatively small inhibitory salt effect a large accelerating effect of the NaCl can be seen in Figure 4 for SDS-containing solutions. Two sets of experiments were conducted, one at low  $n_{Ru}$  ( $[Ru(bpy)_3^{2+}] = 2.0 \times 10^{-5}$  M), the other at high  $n_{Ru}$  ( $[Ru(bpy)_3^{2+}] = 6.0 \times 10^{-4}$  M). In both sets of experiments the kinetics are seen to be accelerated by NaCl. One might argue that the increased rate obtained on addition of NaCl results from replacement of  $Ru(bpy)_3^{2+}$  by  $Na^+$  ions on the micellar surface. However, since the fluorescence spectra remains unchanged by 0.5 M NaCl (both in aqueous or micellar solutions) we conclude that this does not take place. Clearly these results indicate that a reaction between two similarly charged entities (the  $e_{aq}^-$  and  $Ru(bpy)_3^{2+}$  in a negative micelle) takes place. The smaller salt effect in the case of higher  $n_{Ru}$  and the drop in the efficiency of the salt accelerating effect can be rationalized by the decreased effective negative charge of the micelles under these conditions.

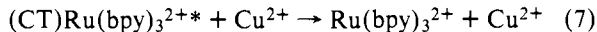
**Micellar Effects on Electron Transfer from (CT) $Ru(bpy)_3^{2+*}$ .** Intensive studies have shown that excitation of  $Ru(bpy)_3^{2+}$  at  $\lambda \leq 550$  nm results in a charge transfer state, capable of reducing various acceptors, with a quantum yield often approaching unity.<sup>8-10</sup>





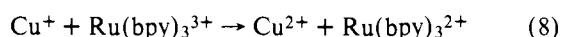
**Figure 5.** The effect of SDS on the rate of electron transfer from (CT)-Ru(bpy)<sub>3</sub><sup>2+\*</sup> to Cu<sup>2+</sup>: (a) 10<sup>-2</sup> M SDS and different concentrations of Cu(ClO<sub>4</sub>)<sub>2</sub> and Mg(ClO<sub>4</sub>)<sub>2</sub> at constant ionic strength  $\mu = 0.04$  M; (b) no SDS, with different concentrations of Cu(ClO<sub>4</sub>)<sub>2</sub> and Ca(ClO<sub>4</sub>)<sub>2</sub> at constant  $\mu = 1.9$  M.

One such an electron acceptor is the Cu<sup>2+</sup> ion, which was recently shown to react with (CT)Ru(bpy)<sub>3</sub><sup>2+\*</sup> with a rate constant of  $7.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  via reaction 6.<sup>16</sup> Using the flash photolysis technique we have studied the effect of micellar SDS on reaction 6. The bleaching of Ru(bpy)<sub>3</sub><sup>2+</sup> at  $\lambda$  480 nm was followed at several [Cu<sup>2+</sup>]. Assuming that this bleaching depends upon reactions -5, 6, and 7, the data were treated in terms of eq II.

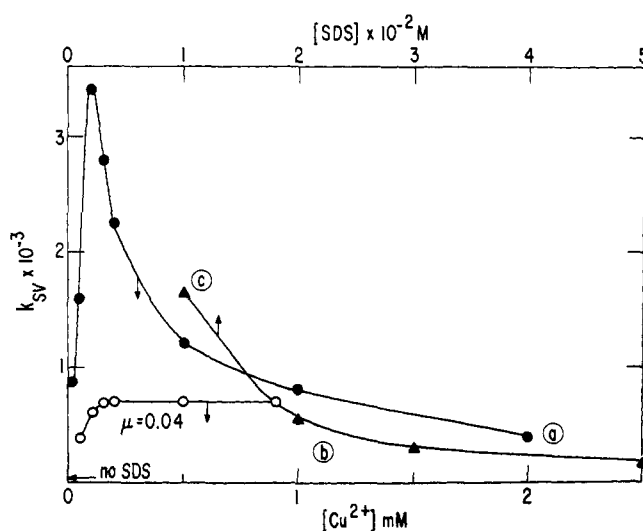


$$\frac{1}{-\Delta[\text{Ru II}]} = \frac{1}{I\phi} \left( \frac{k_6 + k_7}{k_6} + \frac{k_{-5}}{k_6[\text{Cu}^{2+}]} \right) \quad (\text{II})$$

In eq II,  $-\Delta[\text{Ru II}]$  is the change in [Ru(bpy)<sub>3</sub><sup>2+</sup>] produced by the photoflash and  $I$  and  $\phi$  are the absorbed light in einstein/L and the quantum yield of the charge transfer excited state (assumed to be unity), respectively. Figure 5 shows the fit to eq II in the absence of SDS and in 10<sup>-2</sup> M SDS solutions. Experiments with SDS were done at constant ionic strength of  $\mu = 0.04$  M using Mg(ClO<sub>4</sub>)<sub>2</sub> as an inert salt. In the absence of SDS Ca(ClO<sub>4</sub>)<sub>2</sub> provided the constant  $\mu = 1.9$  M. The difference in the ionic strengths used was necessary owing to the differences in [Cu(ClO<sub>4</sub>)<sub>2</sub>] required for effective competition in the two sets of experiments. The ratio between the slope and the intercept for each line in Figure 5 gives  $k_{-5}/(k_6 + k_7)$ . However, since in the absence of SDS  $k_6 \gg k_7$  and the only reaction between Cu<sup>2+</sup> and (CT)Ru(bpy)<sub>3</sub><sup>2+\*</sup> is an electron transfer reaction,<sup>16</sup> the ratio of the slope of the line in the presence of SDS to the intercept in its absence yields  $k_{-5}/k_6$  in the presence of SDS. Assuming that  $k_{-5}$  is not significantly changed by the micelles, an assumption which is substantiated by the fact that only minor changes are observed in the intensity of the emission in the presence of the micelles,  $k_6 = 1.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_7 = 1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  are obtained for our micellar solutions. Although the rate of the electron transfer reaction is faster by at least a factor of 2 in the presence of the micelles, the yield of the electron transfer is only 11% compared to the yield in the absence of SDS. The other mode which might contribute to this decrease in the yield of the redox reaction other than the energy transfer reaction 7 is an electron transfer (reaction 6) followed by the back reaction



at times faster than the resolution of our flash apparatus ( $<$



**Figure 6.** Stern-Volmer constants for quenching of the emission by Cu(ClO<sub>4</sub>)<sub>2</sub>.  $2.0 \times 10^{-5}$  M Ru(bpy)<sub>3</sub><sup>2+</sup> excited at 450 nm and monitored at 625 nm: (a) ●, 10<sup>-2</sup> M SDS; (b) ○, 10<sup>-2</sup> M SDS and Mg(ClO<sub>4</sub>)<sub>2</sub> added to keep the ionic strength constant at  $\mu = 0.04$  M; (c) ▲,  $7.5 \times 10^{-4}$  M Cu(ClO<sub>4</sub>)<sub>2</sub> at various [SDS] (upper scale). Arrow indicates  $K_{SV}$  in the absence of SDS and concentration of Cu(ClO<sub>4</sub>)<sub>2</sub> between 20 and 100 mM at constant ionic strength of 1.9 M obtained with Ca(ClO<sub>4</sub>)<sub>2</sub>.

20  $\mu\text{s}$ ). However, if reaction 8 is responsible for the decreased yield, this cannot be a bulk reaction of Cu<sup>+</sup> with bound Ru(bpy)<sub>3</sub><sup>3+</sup> since the rate of the bulk part of reaction 8 could be followed with our instrument and occurred on the same time scale in the presence and absence of SDS. This would mean that reaction 8 should be separable into the two-dimensional component of a reaction between Cu<sup>+</sup> and Ru(bpy)<sub>3</sub><sup>3+</sup> in an intramicellar reaction and the three-dimensional component of intermicellar reaction or bulk-micellar reaction as was recently observed in micellar systems.<sup>21</sup> Whether these modes proceed by a "dynamic" or "static" effects cannot be resolved by these experiments. Further studies are underway to elucidate this point;<sup>22</sup> nonetheless, emission quenching experiments to be described below substantiate the findings that the negative micelles drastically reduce the lifetime of the excited triplet in the presence of reactive positively charged ions.

**Micellar Effects on Emission Quenching.** The effects of SDS on the quenching of the fluorescence of Ru(bpy)<sub>3</sub><sup>2+</sup> by Cu(ClO<sub>4</sub>)<sub>2</sub> was checked under various conditions. The Stern-Volmer constant was calculated for each concentration of added Cu(ClO<sub>4</sub>)<sub>2</sub> using

$$K_{SV} = \left( \frac{f_0 - f}{f} \right) / [\text{Cu}^{2+}] \quad (\text{III})$$

where  $f_0$  and  $f$  are the intensity of emission in the absence and at the particular concentration of Cu<sup>2+</sup>, respectively. Results on the dependence of  $K_{SV}$  on [Cu<sup>2+</sup>] are shown in Figure 6. Large enhancement, reaching up to a factor of 50 over  $K_{SV}$  in the absence of SDS, can be seen. However, the quenching process is totally a non-Stern-Volmer type, the efficiency of the quenching increasing to a maximum, then dropping back (curve a, Figure 6). The decreasing part can be accounted for by the ionic strength effects on both the kinetics and the cmc. Through its effect on the cmc an increase in the ionic strength is expected to increase the number of micelles, so that the number of Cu<sup>2+</sup> ions per micelle increases more slowly than [Cu<sup>2+</sup>]. Indeed, when the ionic strength was kept constant by addition of Mg(ClO<sub>4</sub>)<sub>2</sub> the  $K_{SV}$  remained constant over a wide range of [Cu(ClO<sub>4</sub>)<sub>2</sub>] (curve b, Figure 6). Under these conditions, an equilibrium between the similar ions Mg<sup>2+</sup> and Cu<sup>2+</sup> in the Gouy-Chapman double layer exists and a well-defined  $K_{SV}$  is expected. Furthermore, in the absence of

$\text{Mg}(\text{ClO}_4)_2$ , saturation of the micelles by  $\text{Cu}^{2+}$  ions is expected when  $[\text{Cu}^{2+}]$  approaches the concentration of available sites on the micelle, thus leading to a decrease in the efficiency of  $\text{Cu}^{2+}$  as an emission quencher of the (CT) $\text{Ru}(\text{bpy})_3^{2+*}$  in the micelle. This effect would also be masked by the added  $\text{Mg}^{2+}$  ions since under these conditions most of the available sites in the micelles would be occupied anyway either by  $\text{Mg}^{2+}$  or  $\text{Cu}^{2+}$  ions and the ratio between them on the micelles would be determined by their relative concentrations and the equilibrium constant. In line with this interpretation are also our results of the effect of  $[\text{m}]$  at constant  $[\text{Cu}^{2+}]$  on the efficiency of the quenching (curve c, Figure 6). It can be seen that on increasing  $[\text{SDS}]$ , thus increasing  $[\text{m}]$  and reducing the number of  $\text{Cu}^{2+}$  ions per micelle,  $K_{\text{SV}}$  drops very rapidly. The average number of  $\text{Cu}^{2+}$  ions per micelle can be calculated as described above. Such calculations reveal the following points: (a) At the lowest  $[\text{Cu}^{2+}]$  and  $[\text{SDS}]$  used ( $1.9 \times 10^{-4}$  and  $10^{-2}$  M, respectively) the average number of  $\text{Cu}^{2+}$  ions on a micelle is about 4.0 while the intensity of the emission is 87% that of the fluorescence in the absence of  $\text{Cu}^{2+}$ . Assuming a Poisson distribution of  $\text{Cu}^{2+}$  ions among the micelles, the probability that a micelle will contain no  $\text{Cu}^{2+}$  ions on its surface is only 1.8%. Clearly this indicates that there is a high probability for (CT) $\text{Ru}(\text{bpy})_3^{2+*}$  to emit light even when it is attached to a micelle that contains at least one  $\text{Cu}^{2+}$  ion. (b) At highest  $[\text{Cu}^{2+}]$  and lowest  $[\text{SDS}]$  ( $2.0 \times 10^{-3}$  and  $10^{-2}$  M, respectively), the average number of  $\text{Cu}^{2+}$  per micelle is 25 and there still is about 12% emission compared to the emission in the absence of  $\text{Cu}^{2+}$ . This means that even under such extreme conditions there still is a finite probability for (CT) $\text{Ru}(\text{bpy})_3^{2+*}$  to emit light and that total scavenging is hard to achieve. The mechanism of quenching might be the static effect. This effect may result from the time-dependent term in the Smoluchowski equation,<sup>23</sup> or from the finite probability that a quencher happens to be in the "sphere of action" surrounding the fluorophore,<sup>24</sup> or from the formation of a ground state  $\text{Cu}^{2+}$ - $\text{Ru}(\text{bpy})_3^{2+}$  ion pair.<sup>25</sup> However, recent results indicate that the mechanism is a dynamic electron transfer (reactions 6 and 8 as discussed above) which is completed on a time scale shorter than the time resolution of our flash apparatus.<sup>22</sup>

Another example of the dramatic effect of micellar environment on the emission quenching is the quenching by  $\text{Fe}(\text{CN})_6^{3-}$ . In a solution containing  $2 \times 10^{-5}$  M  $\text{Ru}(\text{bpy})_3^{2+}$  and  $4.5 \times 10^{-3}$  M  $\text{K}_3\text{Fe}(\text{CN})_6$  in  $10^{-2}$  M SDS excited at 467 nm (where 60% of the light is absorbed by  $\text{Ru}(\text{bpy})_3^{2+}$ ), we find  $K_{\text{SV}} \leq 20$ , which is to be compared with  $K_{\text{SV}} = 3.9 \times 10^3$  obtained in the absence of SDS at  $\mu = 0.5$ .<sup>7</sup> This lowering in the quenching efficiency clearly results from the Coulombic interaction as the high negatively charged quencher approaches the negatively charged micelle.

## Conclusions

We have shown in this study that  $\text{Ru}(\text{bpy})_3^{2+}$ , which forms an insoluble salt with SDS, can be solubilized by SDS micelles. Practically all of the  $\text{Ru}(\text{bpy})_3^{2+}$  is incorporated in the micelles

even at relatively high concentrations of  $\text{Ru}(\text{bpy})_3^{2+}$  and low micelle concentrations. Rates of reaction of  $\text{Ru}(\text{bpy})_3^{2+}$  either in the ground or the excited state are significantly altered as well as are the redox yields of reactions of the excited state. Hopefully, redox yields or photoionization yields would be increased through the choice of the appropriate scavengers.

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