

Comparative Study of Emission Quenching of Tris(α,α' -diimine)-Ruthenium(II) Complexes in Homogeneous and Sodium Dodecyl Sulfate Micellar Solutions

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Received August 3, 1991

Emission quenching of photoexcited tris(α,α' -diimine)ruthenium(II) complex cations, RuL_3^{2+} (L: 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine; 4,4'-diphenyl-2,2'-bipyridine; 1,10-phenanthroline; 5-methyl-1,10-phenanthroline; 5,6-dimethyl-1,10-phenanthroline or 4,7-diphenyl-1,10-phenanthroline) by Cu^{2+} , dimethylviologen (MV^{2+}), nitrobenzene (NB), and oxygen was studied in aqueous homogeneous and sodium dodecyl sulfate (SDS) micellar solutions. The apparent bimolecular quenching rate constants k_q were determined from the quenching data and life-times of $^*\text{RuL}_3^{2+}$. In homogeneous media, the quenching rate was considerably slower than that for the diffusion-controlled reaction. The decreasing order of quenching activity of quenchers was $\text{NB} > \text{O}_2 > \text{MV}^{2+} > \text{Cu}^{2+}$. The rate with Cu^{2+} was faster as the reducing power of $^*\text{RuL}_3^{2+}$ is greater. On the other hand, the rates with NB and O_2 were faster as the ligand is more hydrophobic. This was attributed to the stabilization of encounter pair by van der Waals force. The presence of SDS enhanced the rate of quenching reactions with Cu^{2+} and MV^{2+} , whereas it attenuated the quenching activity of NB and O_2 toward RuL_3^{2+} . The binding affinity of quenchers to SDS micelle and binding sites of the quenchers and RuL_3^{2+} in micelle appear to be important factors controlling the micellar effect on the quenching reactions.

Introduction

The photophysics and photochemistry of tris(α,α' -diimine)-ruthenium(II) complexes have been extensively investigated in recent years.¹ This is primarily due to their ability as photosensitizers in solar energy conversion into hydrogen. Microheterogeneous systems such as surfactant micelles, vesicles, and polyelectrolytes have been employed to improve the efficiency of the conversion.^{2,3} More recently, the Ru(II) photosensitizers have been used as probes for microenvironment of the microheterogeneous systems.⁴ Much of the works have been carried out with tris(2,2'-bipyridine)ruthenium(II) ($\text{Ru}(\text{bpy})_3^{2+}$). The series of Ru(II) complexes RuL_3^{2+} , where L is 2,2'-bipyridine or 1,10-phenanthroline derivatives, exhibit nearly identical absorption and emission spectra, whereas the redox potentials and life-times of the complexes depend highly on the nature of the ligand.⁵⁻⁸ Thus the rates of electron or energy-transfer quenching with a given quencher may be varied by the ligand as demonstrated with inorganic ions.^{5,8} Both electrostatic and hydrophobic interactions are important in the binding of the Ru(II) complexes to micelles^{7,9-11} and polyelectrolytes.¹² These interactions are also possible between RuL_3^{2+} and quenchers in homogeneous media and influence the quenching rate. Because of the hydrophobic interaction between RuL_3^{2+} and a micelle, RuL_3^{2+} binds at different region of a micelle depending on ligand hydrophobicity.^{7,9-11} This may influence the rates of emission quenching of RuL_3^{2+} by a quencher in a micellar solution. Also the micellar effect is expected to depend critically on the binding affinity of the quencher to micelle and solubilization site of the quencher in micelle.

In the present work, the influence of ligand hydrophobicity on the luminescence properties of RuL_3^{2+} is investigated in aqueous homogeneous and sodium dodecyl sulfate (SDS) micellar solutions. The rates of quenching reactions with Cu^{2+} , dimethylviologen (MV^{2+}), nitrobenzene, and molecular oxy-

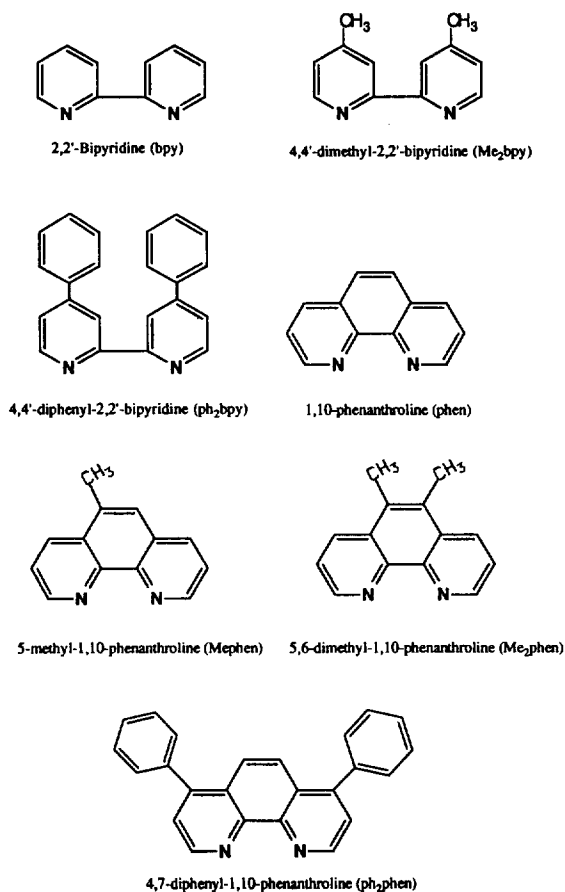


Figure 1. Ligands and abbreviations for Ru(II) complexes studied.

gen (O_2) are determined in both media and compared. The ligands of RuL_3^{2+} employed in this investigation are shown in Figure 1.

Table 1. Life-time Data of Photo-excited RuL_3^{2+} at 25 °C

<i>L</i>	In the absence of SDS			[SDS]=10.0 mM		
	τ_{air} (ns)	$I_{\text{de aer}}/I_{\text{air}}$	$\tau_{\text{de aer}}$ (ns)	τ_{air} (ns)	$I_{\text{de aer}}/I_{\text{air}}$	$\tau_{\text{de aer}}$ (ns)
bpy	382	1.53	584(608) ^a	488	1.56	761(821) ^a
Me_2bpy	243	1.31	318(340) ^b	377	1.33	501
phen	470(429) ^a	1.90	893(890) ^a	778(756) ^a	2.47	1920(1930) ^a
Mephen	530	2.48	1310(1350) ^b	845	2.97	2510
Me_2phen	551	3.10	1710(1870) ^b	892	3.48	3100
ph_2bpy	376	— ^d	(670) ^c	546	1.55	846
ph_2phen	756(801) ^a	— ^d	(4680) ^c	1030	4.41	4550

^aTaken from ref 17. ^bTaken from ref 8. ^cTaken from ref 3. ^dNot determined due to complication arising from adsorption of the complex.

Experimental

Materials. The complexes of Ru(II) were prepared by modification of the literature methods⁵⁻⁸ as follows: $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Aldrich, 0.2 g), 330 mol % amount of the appropriate ligand (Aldrich), and 0.3 g of hydroxylamine hydrochloride were dissolved in 25 ml of absolute ethanol and the reaction mixture was refluxed for 24-48 hr. After evaporating off the solvent, the complexes were recrystallized 2-3 times from ethanol-water (4:1). To initiate precipitation, small amounts of HCl (for $L=\text{Me}_2\text{bpy}$; ph_2bpy ; ph_2phen) or HClO_4 (for other complexes) were added. Each product showed a single spot on tlc and absorption and emission spectra of the complexes agreed well with those in the literature.⁵ SDS (Aldrich) was recrystallized three times after washing with ether. Dimethylviologen dichloride was made by reacting 4,4'-bipyridine with methyl iodide followed by counter ion exchange by stirring with AgCl .¹² Solutions were prepared with glass distilled deionized water and contained 0.1 M NaCl.

Spectral Measurements. Steady state luminescence spectra were recorded with a Hitachi F-3010 fluorescence spectrometer. Experiments were carried out under air-saturated or deoxygenated conditions at 25.0 ± 0.2 °C. For deoxygenation of solutions, solvent-saturated nitrogen gas was purged until no change in emission intensity is observed (normally it takes 30 min). The relative sensitivity of the photo-multiplier to light of different wavelengths was corrected by the quantum-counter method with Rhodamine B for 500-600 nm and with methylene blue for 550-700 nm range.¹³ The calibration data in overlapping region (550-600 nm) matched well for both dyes. Life-time measurements were made by using a time-correlated single photon counting system with ps-laser pulse excitation. Absorption spectra were taken with a Beckman DU-8B spectrophotometer.

Determination of Rate Constants for Quenching Reactions. The bimolecular quenching rate constants k_q were calculated from Stern-Volmer equation,¹⁴

$$I_0/I = 1 + k_q \tau_0 [Q] \quad (1)$$

where I_0 and I are the emission intensities in the absence and presence of quencher Q , respectively; τ_0 is the excited life-time of the luminesphore in the absence of Q .

Binding of O_2 and Nitrobenzene with SDS Micelle. Solubilities of nitrobenzene were determined at various SDS concentrations by absorbance measurement of the aqueous phase after shaking nitrobenzene with appropriate SDS solu-

tion. Molar absorptivity of nitrobenzene in SDS solution was determined from standard solution and found to be $5,700 \text{ M}^{-1}\text{cm}^{-1}$ at 257 nm. Solubility data of O_2 in SDS micelle were taken from literature.¹⁵ The binding constants of the quenchers with SDS micelle were calculated from the solubility data (For details, see results section).

Results

Spectral Behaviors and Quenching by O_2 . Tris(α , α' -diimine)ruthenium(II) complexes show a very similar metal-to-ligand charge transfer (MLCT) absorption band near 450 nm and an emission band near 600 nm. Upon addition of SDS, the absorption band is little affected. However, the emission band shifts to longer wavelength with concomitant increase in emission intensity as the concentration of SDS is increased.¹⁶ The luminescence titration of Ru(II) complexes with SDS in 0.1 M NaCl showed that the spectral changes level off when the concentration of SDS exceeds 2 mM. Deoxygenation of the solutions of Ru(II) complexes enhances the emission intensity without noticeable change in spectral shape.

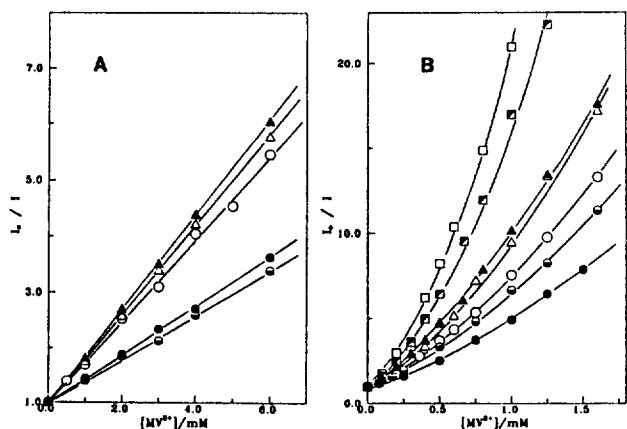
The life-times of photo-excited RuL_3^{2+} in air-saturated solutions (τ_{air}) in the absence and presence of 10 mM SDS were determined. The life-times in deaerated solutions ($\tau_{\text{de aer}}$) were calculated from the life-time data obtained in air-saturated solutions and emission intensity data by using the relationship of $\tau_{\text{de aer}} = (I_{\text{de aer}}/I_{\text{air}}) \cdot \tau_{\text{air}}$. The results are listed in Table 1. The life-times of Ru(II) complexes in deoxygenated solutions calculated from this method agree well with the values reported from luminescence decay curves of the corresponding complexes from deoxygenated solutions (see, Table 1). Also the ratio of life-times of each Ru(II) complex in SDS-free solution relative to that in SDS solution accords well with the ratio of emission intensities at emission maxima of corrected luminescence spectra of the corresponding solutions.

Enhancement of emission intensity and thus longer life-time of RuL_3^{2+} upon deaeration of the solution reflects quenching reaction between the photoexcited RuL_3^{2+} and molecular oxygen (O_2) in air-saturated solutions. The concentration of O_2 in air-saturated 0.1 M NaCl solution is $2.48 \times 10^{-4} \text{ M}$.¹⁸ Matheson and King^{15a} demonstrated experimentally that the concentration of SDS micellized oxygen $[\text{O}_2]_{\text{mic}}$ is given by

Table 2. Apparent Bimolecular Quenching Rate Constants ($k_q \times 10^{-9}/\text{M}^{-1}\text{s}^{-1}$) of RuL_3^{2+} by O_2 , Dimethylviologen (MV^{2+}), Cu^{2+} , and Nitrobenzene (NB)^a

<i>L</i>	<i>Q</i>	<i>E</i> ^{ob}	[SDS]=0 mM				[SDS]=10 mM			
			O_2	MV^{2+}	Cu^{2+}	NB	O_2	MV^{2+}	Cu^{2+}	NB
bpy		-0.84	3.7	0.98	0.09	4.0	2.9	13	0.86	2.2
Me_2bpy		-0.94	3.9	1.6	0.15	4.6	2.6	15	0.84	4.3
phen		-0.87	4.1	1.5	0.12	4.6	3.1	8.4	0.34	3.2
Mephen		-0.90	4.5	1.6	0.12	5.2	3.1	11	0.39	3.3
Me_2phen		-0.93	5.0	1.5	0.13	5.7	3.2	9.5	0.44	4.6
ph_2bpy		-0.85	(4.7) ^c	—	—	—	2.6	29	0.96	0.23
ph_2phen		-0.90	(4.5) ^c	—	—	—	3.0	19	0.30	0.34

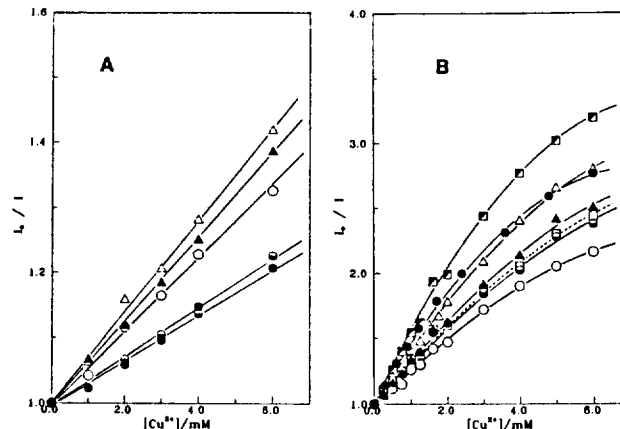
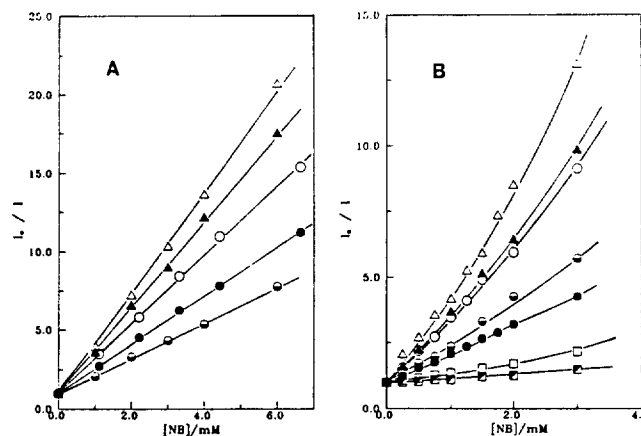
^aReduction potentials of quenchers are -0.33 V for O_2 , -0.45 V for MV^{2+} , 0.152 V for Cu^{2+} and -0.56 V for nitrobenzene (see, text). ^bV vs. NHE and taken from ref. 5. ^cCalculated from life-time data.

**Figure 2.** Stern-Volmer plots for quenching of the luminescence of RuL_3^{2+} by methyl viologen in homogeneous (A) and 10 mM SDS micellar (B) solutions. *L* are bpy (●), phen (○), Me_2bpy (◐), Mephen (△), Me_2phen (▲), ph_2bpy (◼), and ph_2phen (□).

$$[\text{O}_2]_{\text{mic}} = a([\text{SDS}] - \text{cmc})P_{\text{O}_2} \quad (2)$$

where a is $1.04 \times 10^{-3} \text{ atm}^{-1}$. Taking cmc of SDS in 0.1 M NaCl solution as $1.5 \times 10^{-3} \text{ M}$ ²⁰ and P_{O_2} as 0.21 atm of air. $[\text{O}_2]_{\text{mic}}$ of air-saturated 10 mM SDS solution becomes $1.9 \times 10^{-6} \text{ M}$. Thus the total concentration of O_2 in 10 mM SDS is $2.50 \times 10^{-4} \text{ M}$. The apparent bimolecular quenching rate constants k_q for the quenching reactions with O_2 were calculated by substituting life-time and emission intensity data (Table 1) into the Stern-Volmer equation (Eq. 1). For $\text{Ru}(\text{ph}_2\text{bpy})_3^{2+}$ and $\text{Ru}(\text{ph}_2\text{phen})_3^{2+}$, of which emission intensity could not be measured with reasonable accuracy in the absence of SDS due to adsorption of the complexes, we used $\tau_{\text{deact}}/\tau_{\text{air}}$ values instead of I_0/I in Eq. (1). The k_q values are summarized in Table 2.

Quenching by Dimethylviologen (MV^{2+}), Cu^{2+} , and Nitrobenzene. Figures 2-4 show Stern-Volmer plots (Eq. 1) of emission quenching data of RuL_3^{2+} by MV^{2+} , Cu^{2+} , and nitrobenzene, respectively. In the absence of SDS, the plots gave good linearity. By dividing the slope of each Stern-Volmer plot by life-time of the corresponding $\text{Ru}(\text{II})$ complex, k_q values of the quenching reactions were calculated. The results are given in Table 2. The k_q values decrease in order of $\text{NB} > \text{O}_2 > \text{MV}^{2+} > \text{Cu}^{2+}$.

**Figure 3.** Stern-Volmer plots for quenching of the luminescence of RuL_3^{2+} by Cu^{2+} in homogeneous (A) and 10 mM SDS micellar (B) solutions. *L* are bpy (●), phen (○), Me_2bpy (◐), Mephen (△), Me_2phen (▲), ph_2bpy (◼), and ph_2phen (□).**Figure 4.** Stern-Volmer plots for quenching of the luminescence of RuL_3^{2+} by nitrobenzene (NB) in homogeneous (A) and 10 mM SDS micellar (B) solutions. *L* are bpy (●), phen (○), Me_2bpy (◐), Mephen (△), Me_2phen (▲), ph_2bpy (◼), and ph_2phen (□).

The Stern-Volmer plots for the emission quenching in SDS solutions showed deviation from linearity. However, the pattern of deviation differs depending on quenchers: the plots show positive deviation for MV^{2+} (Figure 2B), whereas the

plots for Cu^{2+} show negative deviation from linearity (Figure 3B). The Stern-Volmer plots for quenching by NB in SDS solutions (Figure 4B) also showed positive deviation, but extent of deviation was much less than that observed with MV^{2+} . The apparent K_{SV} , which is $k_q \cdot \tau_0$ in Eq. 1, were estimated at 1.0 mM for MV^{2+} and at 2.0 mM for Cu^{2+} and NB. The k_q values were calculated from the K_{SV} values and life-times in SDS solutions (Table 1) and included in Table 2. In SDS solutions, k_q decreases in order of $\text{MV}^{2+} > \text{NB} > \text{O}_2 > \text{Cu}^{2+}$.

Binding Constants of Quenchers to SDS Micelle.

By assuming multi-step equilibrium for binding of quenchers with micelles and Poisson distribution of quencher molecules among micelles, the total concentration of quencher $[Q]_T$ is given by¹⁹

$$[Q]_T = [Q] + K[Q][M] \quad (3)$$

where $[Q]$ is the concentration of quencher in aqueous phase, $[M]$ is the concentration of micelle. $[M]$ is calculated from the relationship $[M] = ([\text{surf}] - \text{cmc})/n$ by using $\text{cmc} = 1.5 \times 10^{-3}$ M and aggregation number of the micelle (n) = 91 for SDS in 0.1 M NaCl.²⁰ The binding constant of O_2 to SDS micelle was calculated from Eq. (4) using aforementioned solubility data of O_2 to be 84 M^{-1} .

The solubility of nitrobenzene at 25°C varied linearly with the concentration of SDS and the following relationship was obtained.

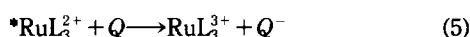
$$[\text{NB}]_T = 0.0184 + 0.76[\text{SDS}] - \text{cmc} \quad (4)$$

By correlating this relationship with Eq. (3), the binding constant of NB on SDS was calculated to be 4000 M^{-1} .

Discussion

All the Ru(II) complexes studied in this investigation are completely micellized when the concentration of SDS exceeds 2.0 mM. The emission band of Ru(II) complexes bound to SDS micelle appears at longer wavelength than that in aqueous phase. This was ascribed to the energy stabilization of thermally equilibrated emitting metal-to-ligand charge transfer (MLCT) state, relative to the initially formed excited state.²¹ Upon binding of Ru(II) complexes to SDS micelle, the excited life-times of the complexes become longer. This may be due to diminution of non-radiative decay of the Ru(II) complexes bound to SDS micelle by solvent molecules. A solvent exposure study by Hauenstein *et al.*⁷ indicated that only 10-30% of the surface of RuL_3^{2+} is exposed to water. Thus, it is expected that RuL_3^{2+} bound to micelle is shielded fairly well against quenching from species in bulk medium.

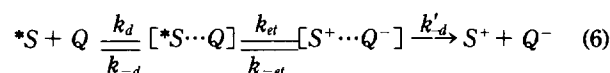
The redox potentials of $\text{RuL}_3^{3+}/\text{RuL}_3^{2+}$ couples are in range of 0.84-0.94 V vs. NHE (Table 1), whereas the redox potentials of O_2/O_2^- , $\text{MV}^{2+}/\text{MV}^+$, $\text{Cu}^{2+}/\text{Cu}^+$, and $\text{C}_6\text{H}_5\text{NO}_2/\text{C}_6\text{H}_5\text{NO}_2^-$ couples are -0.33 V ,²² -0.45 V ,^{23,24} 0.152 V ,²⁵ and -0.56 V ,²⁶ respectively. Thus, electron-transfer quenching by the quencher (Eq. 5) is energetically allowed for RuL_3^{2+} .



The excitation energy of ground-state triplet oxygen to singlet oxygen is 0.98 eV (1260 nm).²⁷ Experimental results indicated that the quenching of Ru(II) complexes by oxygen

is dominated by energy-transfer, rather than electron-transfer mechanism.^{5,28} On the other hand, the absorption maxima of both MV^{2+} and nitrobenzene are located near 257 nm and the energy-transfer quenching pathway is excluded for the quenchers. The electron-transfer reaction between RuL_3^{2+} and MV^{2+} is basis for solar-energy conversion^{2,3} and photoinduced reduction of organic substrates using viologens as an electron mediator.²⁹ The electron-transfer quenching mechanism for aromatic nitro compounds including nitrobenzene is supported by the sensitivity of the quenching rate constant on the reduction potential of the quenchers.³⁰

The overall reaction scheme for the quenching reactions between RuL_3^{2+} (denoted by $*S$) and a quencher Q can be described as following:^{29d,32}



This scheme is written for electron-transfer quenching neglecting backreaction after separation of the reaction products.³¹ A similar scheme can be given for energy-transfer reaction by substituting the second step as energy-transfer step and $*Q$ for Q^- . By applying steady-state approximation, the overall bimolecular quenching rate constant k_q is given by Eq. (7).³¹

$$k_q = k_d \left[1 + \frac{k_{-d}}{k_{et}} \left(1 + \frac{k_{-et}}{k'_{-d}} \right) \right]^{-1} \quad (7)$$

When the quenching reaction is sufficiently exothermic, the rate of back-electron transfer in the initial charge-separated product (k_{-et}) is much smaller than the rate of diffusion apart of the products (k'_{-d}). For all reactions examined in this study, the difference between redox potentials of RuL_3^{2+} and quencher is greater than 0.29 V enabling the assumption operative.^{28d} In this case, Eq. (7) reduces to

$$k_q = k_d / \left(1 + \frac{k_{-d}}{k_{et}} \right) \quad (8)$$

The k_d is the bimolecular rate constant for diffusion-controlled reaction and expressed by Eq. (9) by Smoluchowski.³²

$$k_d = \frac{10^6 \cdot 2RT(r_s + r_q)^2}{3000\eta \cdot r_s r_q} \quad (9)$$

η being the bulk viscosity in SI unit. If ions are involved in the reaction, Eq. (9) should be modified to include the contribution of electrostatic interaction.³² Rough values of k_d are calculated for reactions with O_2 and nitrobenzene in homogeneous aqueous media ($\eta = 0.9 \times 10^{-3} \text{ N} \cdot \text{s} \cdot \text{m}^{-2}$ at 25°C) from Eq. (9) by assuming $r_s = 0.5$ - 0.6 nm and $r_q = 0.1$ - 0.2 nm . The estimated k_d values are in range of 0.9 - $1.5 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$. For the calculation of k_d using Eq. (9), we assumed the reaction radius as contact distance. In fact, many reactions which are energetically favored proceed at transfer distances larger than the contact distance of the reacting pair. In this sense, the above estimated k_d value is lower limit for rate constant of the diffusion-controlled reaction: Timpson *et al.*^{28d} evaluated k_d for the reaction between RuL_3^{2+} and O_2 to be $3.9 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ in acetone ($\eta = 1.316 \text{ cp}$ at 25°C), which allows us to estimate k_d in water to be $5.8 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ after correcting viscosity effect on the diffusion coefficient of oxygen molecule.³³ If charges of S and Q are completely shielded

at high ionic strength, the k_d for reactions with MV^{2+} and Cu^{2+} should be in the same range. The experimental k_q values (Table 1) are smaller than the diffusion limit. This indicates that only small fraction of encounter pair formed by diffusion-controlled reactions undergoes energy or electron-transfer reaction.

Table 1 shows that k_q for reaction with Cu^{2+} in homogeneous aqueous media is higher as the reducing power of $*RuL_3^{2+}$ is greater, i.e. as the reduction potential of $RuL_3^{3+}/*RuL_3^{2+}$ couple is more negative. It indicates that the variation of k_q with the ligand for the reaction with Cu^{2+} mainly arises from difference in k_d .

The correlation between k_q and redox potential of $*RuL_3^{2+}$ is less obvious for reactions with other quenchers. However a clear trend that k_q for O_2 and nitrobenzene is higher as the ligand is more hydrophobic is seen. This can be attributed to the interaction with RuL_3^{2+} by van der Waals and/or hydrophobic force. As a ligand is more hydrophobic, the interaction should be greater and result in greater stability of the encounter pair and thus smaller k_d value. This effect seems to outweigh the effect of reduction potential in variation of k_q with the ligand for the quenchers. MV^{2+} is less easily reduced than Cu^{2+} . Despite of this, the k_q value for MV^{2+} is about one order of magnitude greater than that for Cu^{2+} . This suggests that the RuL_3^{2+}/MV^{2+} encounter pair is also stabilized by the hydrophobic force. This conclusion accords with our previous one from a study on the emission quenching of $Ru(bpy)_3^{2+}$ by viologens of different alkyl chain.³⁴ Gains estimated that the ground association constant of $Ru(bpy)_3^{2+}$ with MV^{2+} is about 30 M^{-1} .³⁵

In the presence of SDS and at low concentration of quenchers, the Stern-Volmer plots for quenching reactions deviate from linearity. The upward curve in Stern-Volmer plot as observed for MV^{2+} and nitrobenzene is fairly common feature for quenching reactions in micellar media. Atik and Singer³⁶ have derived an equation (Eq. 10) which predict upward curve in Stern-Volmer plot of steady-state luminescence quenching data, under assumptions of multi-step equilibrium for binding of a quencher with micelles and intramolecular quenching. They also assumed Poisson distribution of quenchers among micelles.

$$I_0/I = (1 + \beta k_q K \tau [Q]_T) / (1 + \alpha \beta k_q K \tau [Q]_T) \quad (10)$$

where $\beta = (1 + K[M])^{-1}$ and α is the fraction of luminescence-occupied micelles that do not contain quencher.

The assumptions employed in the derivation of Eq. (10) may be approximately valid for nitrobenzene at low concentration. However, the assumptions do not hold for the binding of MV^{2+} and Cu^{2+} with SDS micelle, as electrostatic interaction is involved in the binding. It is well expected that the binding affinity of the cations is weaker as the coverage of the anionic micelle by the quenchers is higher. This explains the downward Stern-Volmer plot observed in the quenching by Cu^{2+} .

Several studies have shown that both MV^{2+} and Cu^{2+} have high binding constants to SDS micelle.³⁷⁻⁴¹ The binding constant of Cu^{2+} was reported to be 1.4×10^3 ,³⁷ $(0.88-1.1) \times 10^4$,³⁸ 2.0×10^4 ,³⁹ and $(6-9) \times 10^4\text{ M}^{-1}$,⁴⁰ the binding constant for MV^{2+} was reported to be 9×10^2 ,⁴¹ and $7 \times 10^4\text{ M}^{-1}$.³⁹ These widely varying values of binding constants are partly attrib-

utable to the use of different experimental methods and different kinetic model for data analysis. Thus it is inappropriate to compare the binding constants of MV^{2+} and Cu^{2+} obtained from different methods. Fortunately, Atherton *et al.* determined binding constants of MV^{2+} and Cu^{2+} by the same methods and showed that K of MV^{2+} ($7 \times 10^4\text{ M}^{-1}$) is 2.5 times greater than that of Cu^{2+} .³⁹ This is quite contrast to our expectation from charge density of the cations and suggest strongly that the binding mechanism of MV^{2+} to SDS micelle is quite different from that occurring with Cu^{2+} . A reasonable explanation for this is that the binding of Cu^{2+} is mainly electrostatic association, while that of MV^{2+} involves hydrophobic interaction as well as electrostatic interaction. Such an explanation is in accord with the conclusion from extramolecular probe luminescence study for binding of the cations to SDS micelle.⁴² Also a similar explanation was given to the binding of the cations to a amphiphilic polyelectrolytes, poly(styrenesulfonate) and poly(methacrylic acid).¹²

Contrast to the case of Cu^{2+} , the Stern-Volmer plots for quenching by MV^{2+} in SDS solutions show positive deviation from linearity at low quencher concentration region. Two possible explanations can be given for this. One is the difference in binding regions as expected from the large difference in binding constants of the cations. The binding region of Cu^{2+} on the SDS micelle is expected to be Stern layer, whereas MV^{2+} penetrates into micelles to hydrocarbon-water interfaces due to hydrophobic interaction.⁴² Since the surface charge of SDS micelle is neutralized and structure of the micelle is perturbed upon binding of RuL_3^{2+} , the sites remote from RuL_3^{2+} are the preferred binding sites for MV^{2+} . Obviously the binding to remote sites results in less efficient quenching than the binding to the adjacent sites. Heterogeneity in binding sites would be less pronounced for Cu^{2+} as the cations are condensed in the potential field of the anionic micelle. The other explanation can be given in terms of the difference in the binding affinity. As binding affinity of MV^{2+} to SDS micelle is high, most of MV^{2+} added to a SDS solution are bound to the micelle and they are statistically distributed among micelles. Thus, the dependence of K on the concentration of quencher is less important in affecting the shape of I/I_0 vs. $[Q]$ plot and the Stern-Volmer plot would show upward curvature as Eq. (10) predicts.

The enhancement of the apparent quenching rate constants by SDS is dependent on the ligands and is generally less as the ligand is more hydrophobic. This also seems to reflect a difference in the binding site of the quenchers and RuL_3^{2+} in a micelle. Table 2 shows that the enhancement of k_q with MV^{2+} and Cu^{2+} by SDS is greatest for $Ru(bpy)_3^{2+}$. A clear trend is also seen from Table 2 that the micellar enhancement of quenching rates with MV^{2+} and Cu^{2+} is less as the ligand is more hydrophobic. This trend is more pronounced for quenching by Cu^{2+} . This can be clearly attributed to a deeper embedment of a $Ru(II)$ complex of greater hydrophobic nature into micelle by hydrophobic interaction with hydrocarbon core of the micelle.

The luminescence quenching of RuL_3^{2+} by O_2 and nitrobenzene is attenuated by the presence of SDS, despite of substantial binding of the quenchers on micelle. The diffusion coefficient of a substrate bound on a micelle is much smaller than that in homogeneous medium due to high microviscosity of micellar surface and hydrocarbon core.¹¹ This

results in smaller intramolecular quenching rate constant, compared to that in homogeneous solutions. Unless the concentrating effect of a micelle on the rate of a reaction is large enough to compensate the viscosity effect, the reaction is retarded by the presence of a micelle. The quenching reactions of RuL_3^{2+} with O_2 and nitrobenzene appear to be this case.

Acknowledgements. This work was supported by the Basic Research Institute Program of the Ministry of Education of the Republic of Korea, 1990. We thank M. Kim and S. Koh for preparation of the Ru(II) complexes. The authors acknowledge Drs. D. Kim and M. Lee of the Korea Standard Research Institute for life-time measurements.

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