

A laser flash photolysis study of magnetic field effects in photoinduced electron transfer between $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{N,N}'$ -dimethylviologen in micellar solutions

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The kinetics of electron transfer between photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{N,N}'$ -dimethylviologen (MV^{2+}) have been studied by means of laser flash photolysis in sodium dodecyl sulfate (SDS) and sodium laurate (SL) micelles. The decay of photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ follows first-order kinetics with $k_{\text{obs}} \approx 10^6$ – 10^7 s^{-1} , and dependences of k_{obs} versus surfactant and quencher concentrations were obtained. Analysis of the data showed that the quenching is mainly intramolecular. Although SDS solutions show no escape of the radicals MV^+ and $\text{Ru}(\text{bpy})_3^{3+}$ from the micelles, for solutions of SL micelles an escape value $\Phi_{\text{es}} \approx 0.08$ was determined. The dependences of Φ_{es} on the concentration of SL and SDS show a drop in the vicinity of the cmc. Radical MV^+ is not incorporated into the SL micelles. An increase of Φ_{es} in the SL micelles up to 20–25% was observed under application of an external magnetic field ($B=0.2$ – 0.47 T) during steady-state irradiation and laser flash photolysis studies. The magnetic field effect is mainly described according to a hyperfine coupling mechanism. Geminate recombination kinetics of the pair $^3[\text{MV}^+, \text{Ru}(\text{bpy})_3^{3+}]$ was observed in both SDS and SL micelles. Pertinent kinetic analyses were made and the requirements for geminate recombination kinetics observations were discussed.

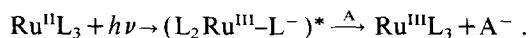
1. Introduction

The kinetics of photoinduced electron transfer (ET) reactions in microheterogeneous environments such as micelles and polyelectrolytes are active areas of investigation [1–12]. The main goal of this research is the possible control of the ET rate and product yield by the choice of reaction medium and by physical methods.

This paper is devoted to photoelectron transfer in the well-known system of tris(2,2'-bipyridyl)ruthenium (II) [$\text{Ru}(\text{bpy})_3^{2+}$] and $\text{N,N}'$ -dimethylviologen (MV^{2+}) in micellar microenvironments [7–25]. The kinetics of the photochemical reactions of these complexes should also give valuable information on the dynamic behavior of photoexcited probes in microenvironments.

The photochemistry of ruthenium (polypyridine)

complexes has been a topic of intense interest during the past twenty years, see for a review refs. [2,17]. These complexes possess a MLCT excited state, which results from an electron transfer excitation from metal to ligand (L) under excitation [17]. The redox properties of photoexcited RuL_3 differ markedly from those of ground-state RuL_3 ; in particular, the MLCT excited state becomes a more powerful reductant than the ground state, capable of reducing many acceptors, and in particular MV^{2+} [17,18]. Thus the photoreduction of an acceptor A by a RuL_3 complex may be represented by



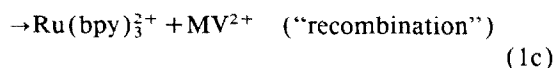
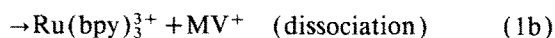
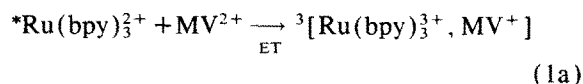
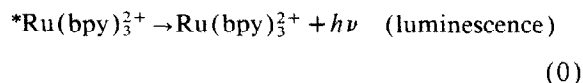
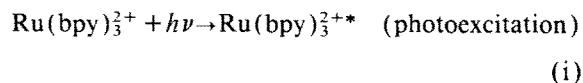
Solar energy can possibly be captured by such ruthenium complexes, stored, and released under controlled conditions.

The photochemical system $\text{Ru}(\text{bpy})_3^{2+}$ – MV^{2+} has been studied in detail in water, and the laser flash photolysis technique has been shown to be very use-

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ful for its study [17–25]. The following processes occur in the system when Ru(bpy)₃²⁺ is irradiated with visible light in the presence of MV²⁺:



Square brackets denote the solvent cage or the existence of radicals in the form of a radical pair (RP). The radicals that leave the cage recombine (or participate in back electron transfer, BET) in water in random pairs. Much effort was given to prevent BET and to store solar energy in such a way as to prevent it [2,11–13,17,25–27]. Certain progress was achieved with the use of micellar solutions and amphiphilic derivatives of MV²⁺ [13], with such derivatives of Ru(bpy)₃²⁺ [11,12], and sacrificial donors oxidized by Ru(bpy)₃³⁺ [25]. The geminate recombination kinetics of the compartmentalized radicals has been reported [10].

The effect of a permanent external magnetic field on the rate of reaction (1) was studied. A small negative magnetic field effect (MFE) on radicals escaping from the solvent cage in homogeneous solution was observed [20,21]. Observation of the kinetics of geminate reactions in micelles and the search for physical methods affecting charge separation in this reaction are of obvious importance. The present research is concerned with the kinetics of direct and geminate BET in SDS and SL micelles and to the MFE in Ru(bpy)₃²⁺ photoreduction by MV²⁺ in micelles.

2. Experimental

2.1. Devices and procedures

Nanosecond laser flash photolysis installation described elsewhere [28] was used. Solutions were

photoexcited with the third harmonic of a YAG laser ($\lambda_{\text{ex}} = 354.5 \text{ nm}$), laser energy 10–12 mJ. Quartz cells (1 × 1 cm section) were used. Kinetic measurements were performed in the time interval 0.05–20 μs after the flash. Kinetic traces were approximated to a single exponential; correlation coefficients of such approximations were not less than 0.98. Five–ten kinetic runs were recorded (each run having five laser shots), and the average rate constant values (k in s^{-1}) were computed. The usual time duration of kinetics observation was two–three half-lives. Typical experimental error limits of the estimation of the rate constants are 10–15%. When necessary the absorption spectra of transients were obtained for their identification using spectrophotometric registration. The radical escape values, Φ_{es} (see below), were determined from kinetic traces with smaller error limits, typically 5–10%. In the case of the MFE study on fast kinetics the reaction cell was positioned between the poles of a permanent magnet ($B = 0.34 \text{ T}$); about ten experiments were run (five in the presence and five in the absence of a permanent magnet).

The MFE experiments were also conducted in a flow system, very similar to that described in ref. [20]. Flowing deoxygenated solutions were irradiated with the full light of a mercury lamp or by filtered ($\lambda > 400 \text{ nm}$) light. The influence of a MF ($B = 0.005\text{--}0.47 \text{ T}$) on the optical density of the photolyzed solution due to a methylviologen radical-cation (MV⁺) at its absorption maxima at $\lambda = 395 \text{ nm}$ ($\epsilon = 4.21 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ [22,23]), and $\lambda = 600 \text{ nm}$ ($\epsilon = 1.13 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ [22,23]) was measured.

2.2. Kinetic analysis and cage escape values

The absorption spectra of the starting (Ru(bpy)₃²⁺, MV²⁺) and transient (Ru(bpy)₃³⁺, MV⁺) compounds are well known (cf. refs. [17–20,22–24]), and the loci of the transient absorption maxima and pertinent extinction coefficients of the transients presented by various researchers are in rather good agreement. Reaction kinetics have been monitored at characteristic wavelengths $\lambda = 313, 360, 395, 452, 600$ and 610 nm , see below. The absorption maximum of Ru(bpy)₃²⁺ in the visible region lies at $\lambda = 452 \text{ nm}$, $\epsilon = 1.47 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ [17,18,22,23]. Excitation of Ru(bpy)₃²⁺ leads to the formation of ^{*}Ru(bpy)₃²⁺ with absorption maxima at $\lambda = 360$ and

313 nm; $\epsilon = 2.6 \times 10^4$ and 2.8×10^4 M⁻¹ cm⁻¹, respectively [17,18,22,23]. Kinetic traces of *Ru(bpy)₃²⁺ decay in water and sodium laurate (SL) micelles show plateaus resulting from the absorption of the product of reactions (1a) and (1b), i.e. Ru(bpy)₃³⁺ and MV⁺ [17,18,20]. Their recombination in solvent bulk in a second-order reaction occurs at much longer times.

We shall define the rate constant of *Ru(bpy)₃²⁺ decay in reactions (0) and (1a) as k_{obs} . Strictly speaking, it can be obtained only from the luminescence decay traces ($\lambda_{\text{max}} \approx 610$ nm [17,18]), because at $\lambda = 313$ and 360 nm, the decay of *Ru(bpy)₃²⁺ is accompanied by a recovery of the ground-state absorption and the appearance of Ru(bpy)₃³⁺ and MV⁺ absorption. However, assuming that any new absorption appears by first-order law kinetics with the same rate constant, the k_{obs} value may be calculated from a kinetic trace, using the absorption at the plateau as the base line [29]. In the present work we used a luminescence decay and *Ru(bpy)₃²⁺ absorption decay measured at $\lambda = 360$ and 313 nm, respectively, for the calculation of k_{obs} , and the rate constants obtained coincided within the experimental error (about 10% of the values).

It is known that MV²⁺ quenches an excited *Ru(bpy)₃²⁺ only via electron transfer (1a), so the radicals' cage escape value, Φ_{es} , may be obtained by using the following equation [17,18]:

$$\Phi_{\text{es}} = \frac{[\text{Ru(bpy)}_3^{3+}]k_{\text{obs}}}{(k_{\text{obs}} - k_0)[*\text{Ru(bpy)}_3^{2+}]_0}, \quad (2)$$

where $[\text{Ru(bpy)}_3^{3+}]$ is the concentration of Ru(III) which leaves the cage (it manifests absorption at the plateau region of a kinetic trace and has an optical density denoted OD_{∞}), and $[\text{*Ru(bpy)}_3^{2+}]_0$ is the initial concentration of photoexcited Ru(II), which has an optical density of OD_0 . The measurement of Φ_{es} from the single kinetic trace is rather precise, and we found it convenient to measure Φ_{es} at $\lambda = 313$ and 452 nm. In order to obtain concentrations for eq. (2) from kinetic traces, it is necessary to take into account absorptions of Ru(bpy)₃³⁺, *Ru(bpy)₃²⁺ and Ru(bpy)₃²⁺, some of which contribute simultaneously to the absorption at these wavelengths. The following extinction coefficients ($\epsilon \times 10^{-4}$ M⁻¹ cm⁻¹) were used: $\epsilon_{452}[\text{Ru(bpy)}_3^{3+}] = 0.15$; $\epsilon_{313}[\text{Ru(bpy)}_3^{3+}] = 4.3$; $\epsilon_{452}[*\text{Ru(bpy)}_3^{2+}] = 0.45$; $\epsilon_{313}[\text{Ru(bpy)}_3^{2+}] = 1.2$ [17,18]. Thus, eq. (2) can be re-

written as

$$\Phi_{\text{es}} = \frac{F \text{OD}_{\infty} k_{\text{obs}}}{(k_{\text{obs}} - k_0) \text{OD}_0}, \quad (3)$$

where F is the coefficient depending on the extinction coefficients of stable and labile compounds, which absorb light at the given wavelength [17,18,22,23]. Using the ϵ -values presented above, we obtain $F_{452} = 0.76$ and $F_{313} = 0.52$; these F values were used for Φ_{es} -values evaluation. Rate constants k_0 and k_{obs} (eq. (2)) were determined by experiments in the same solution in the absence and in the presence of MV²⁺, respectively. Cage escape values measured at different wavelengths and in the presence of varying MV²⁺ concentrations matched within the experimental error. Fast BET (eq. (1c)), i.e. geminate recombination kinetics, was monitored as the MV⁺ decay at its absorption maxima at $\lambda = 395$ and 600 nm.

2.3. Reagents and solutions

Tris(2,2'-bipyridyl)ruthenium (II) chloride hexahydrate $[\text{Ru(bpy)}_3^{2+}]$ and N,N-dimethylviologen dichloride trihydrate (MV²⁺) (Aldrich Chemical Company) were used as received; sodium laurate (SL) (Sigma) and sodium dodecylsulfate (SDS) (Bio-Rad Laboratories) were used in the following way: SL and SDS were purified by recrystallization from a water-ethanol solution.

The reagents Ru(bpy)₃²⁺ and MV²⁺ were dissolved in micellar solutions; typical concentrations were $\approx 10^{-5}$ and 10^{-3} – 10^{-2} M, respectively. Micellar solutions were ultrasonicated before photolysis.

Deionized water was used. Organic solvents and inorganic salts were of reagent grade. Buffer solutions of pH 7.0 and 10.0 (both 0.05 M) were purchased from Fisher.

The micelle concentration was calculated according to the known equation: $[M] = \{[S] - \text{cmc}\}/N$, where $[S]$ is the concentration of the dissolved surfactant and N is the aggregation number. The following values were borrowed from the literature [30,31]: for SDS $\text{cmc} \approx 8.2 \times 10^{-3}$ M, $N = 64$; for SDS in the presence of 0.1 M NaCl $\text{cmc} = 1.5 \times 10^{-3}$ M, $N = 88$; the same cmc and N were used for SDS in the presence of 0.08 M LiCl; for SL $\text{cmc} = 0.024$ M, $N = 56$. Ru(bpy)₃²⁺ was dissolved in micellar solutions in

such concentrations that $[\text{Ru}(\text{bpy})_3^{2+}]/[\text{M}]$ was less than 0.1.

All solutions were deoxygenated by prolonged argon or nitrogen bubbling. All experiments were performed at room temperature.

3. Results

3.1. Kinetics of reaction (1a) and cage escape values in aqueous and micellar solutions

The decay kinetics of $^*\text{Ru}(\text{bpy})_3^{2+}$ in all solutions under investigation obeyed first-order kinetics. Published data for reaction (1a) [17–20,22–24] is reproduced; these data are in reasonable agreement with each other. The k_{obs} - and Φ_{es} -values for several aqueous solutions of $\text{Ru}(\text{bpy})_3^{2+}$ and MV^{2+} are presented in table 1. Rate constants of reaction (1a) as well as cage escape values (table 1) are affected by ionic strength (strong inorganic electrolytes) presence in accordance with previous observations [22–24]. Kinetics and Φ_{es} -values in aqueous solutions

Table 1

Rate constants k_{obs} of $^*\text{Ru}(\text{bpy})_3^{2+}$ decay in different microenvironments and aqueous solution in the presence of MV^{2+} (5×10^{-3} M) and cage escape values Φ_{es}

Environment	$k_{\text{obs}}^{\text{a)}$ (10^{-6} s^{-1})	$\Phi_{\text{es}}^{\text{b)}$
water	3.6	0.26
water, pH 7.0	5.6	0.23
water, NaCl (0.1 M)	5.0	0.18
water, pH 7.0, LiCl (0.08 M)	4.7	0.20
water, pH 7.0, NaCl (0.4 M)	10.0	0.40
SDS (0.1 M)	3.6	~0
SDS (0.1 M), NaCl (0.1 M)	4.5	~0
SDS (0.1 M), LiCl (0.08 M)	4.5	~0
SDS (0.015 M) ^{c)}	9.3	~0
SL (0.1 M)	2.6	0.08
SL (0.1 M), NaCl (0.1 M)	5.2	0.06
SL (0.026 M), pH 7.0, glycerol 2% v/v ^{d)}	7.0	0.09
SL (0.03 M) ^{e)}	13	0.08

^{a)} Determination error about 10%.

^{b)} Determination error about 5%.

^{c)} Here $[\text{MV}^{2+}] = 1 \times 10^{-3}$ M.

^{d)} Here $[\text{MV}^{2+}] = 2.5 \times 10^{-3}$ M.

^{e)} Here $[\text{MV}^{2+}] = 2.0 \times 10^{-3}$ M.

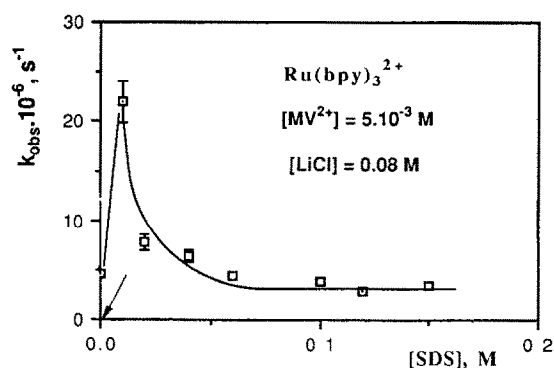


Fig. 1. The dependence of k_{obs} on SDS concentration. Obtained by laser flash photolysis of $\text{Ru}(\text{bpy})_3^{2+}$ in the presence of MV^{2+} (5×10^{-3} M) and LiCl (0.08 M). Arrow indicates the literature cmc value, see section 2.

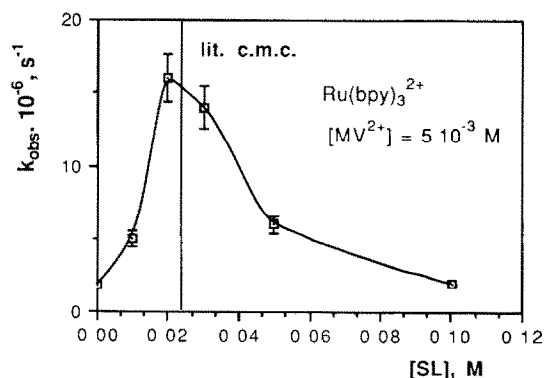


Fig. 2. The dependence of k_{obs} on SL concentration. Obtained by laser flash photolysis of $\text{Ru}(\text{bpy})_3^{2+}$ in the presence of MV^{2+} (5×10^{-3} M). Vertical line represents the literature cmc value, see section 2.

were the references for comparison with those in micellar solutions. The data in table 1 are presented mainly for one concentration of MV^{2+} (5×10^{-3} M), which is usually sufficient for the reduction of the $^*\text{Ru}(\text{bpy})_3^{2+}$ lifetime two to four times. Figs. 1 and 2 present the dependence of k_{obs} on a surfactant concentration with fixed $[\text{MV}^{2+}]$, and figs. 3 and 4 show the dependence of k_{obs} on $[\text{MV}^{2+}]$ with a fixed surfactant concentration.

The dependence of k_{obs} on [SDS] (fig. 1) was re-plotted also as k_{obs} versus $\langle r \rangle = [\text{MV}^{2+}]/[\text{M}]$, the occupancy number or Poisson statistics, i.e. average number of quencher molecules per micelle [10], cf. fig. 5. The micelle concentration [M] was calculated

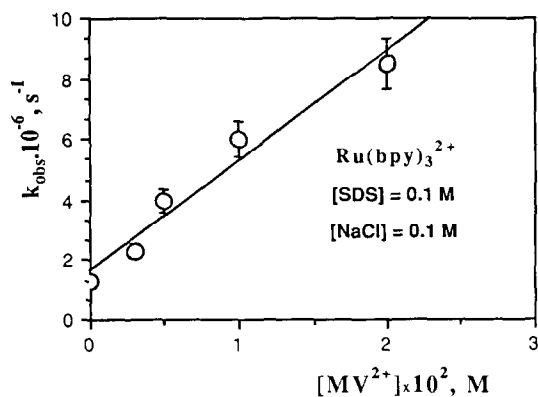


Fig. 3. The dependence of k_{obs} on MV^{2+} concentration. Obtained by laser flash photolysis of $\text{Ru}(\text{bpy})_3^{2+}$ in the presence of MV^{2+} and NaCl (0.1 M) in SDS (0.1 M) micelles.

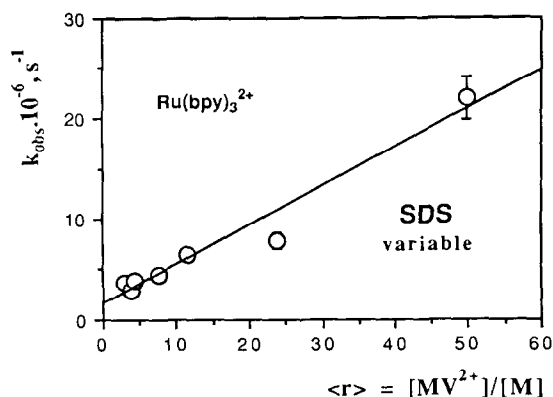


Fig. 5. The dependence of k_{obs} on SDS micelles occupancy number of MV^{2+} . These are the experimental data of fig. 1, cf. the caption of fig. 1.

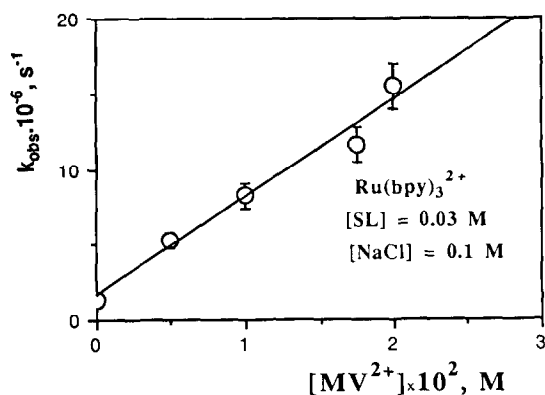


Fig. 4. The dependence of k_{obs} on MV^{2+} concentration. Obtained by laser flash photolysis of $\text{Ru}(\text{bpy})_3^{2+}$ in the presence of MV^{2+} and NaCl (0.1 M) in SL (0.03 M) micelles.

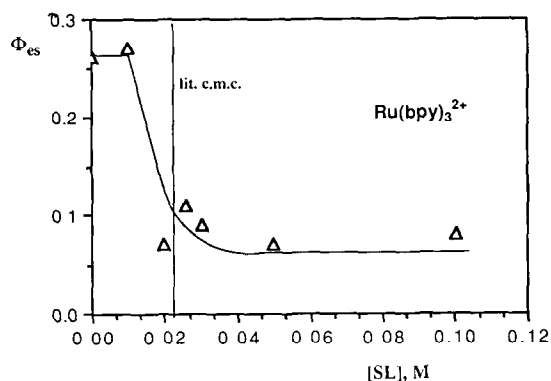


Fig. 6. The dependence of micelle escape value Φ_{es} on SL concentration. Obtained by laser flash photolysis of $\text{Ru}(\text{bpy})_3^{2+}$ in the presence of MV^{2+} ($5 \times 10^{-3} \text{ M}$).

as explained above in section 2.

Cage escape values Φ_{es} strongly depend on surfactant concentrations, cf. table 1 and fig. 6.

3.2. Geminate recombination kinetics

In the case of a relatively fast reaction (1a), which occurs under high $\langle r \rangle$ for $[\text{MV}^{2+}]$ and/or in the presence of an inorganic salt (salt effect), it is possible to observe geminate recombination kinetically. Figs. 7 and 8 present kinetic traces due to a geminate recombination in SDS and SL micelles, respectively.

The descending part of the traces were approximated by exponents, and pertinent geminate kinetics constants $k_{\text{bc}} (\text{s}^{-1})$ were obtained (table 2). In the case of SL, where the escape from micelles occurs, the observed plateau was taken as a baseline for the calculation of k_{bc} (fig. 8) [32]; furthermore, $k_{\text{bc}} = k_{1\text{b}} + k_{1\text{c}}$, cf. eq. (1). The use of a measured value for k_{bc} and Φ_{es} (table 2) for SL micelles and eq. (4) enables one to obtain $k_{1\text{b}}$ and $k_{1\text{c}}$ values [32], see table 2. In the case of SDS $k_{1\text{b}} \ll k_{1\text{c}}$

$$\Phi_{\text{es}} = \frac{k_{1\text{b}}}{k_{1\text{b}} + k_{1\text{c}}} \quad (4)$$

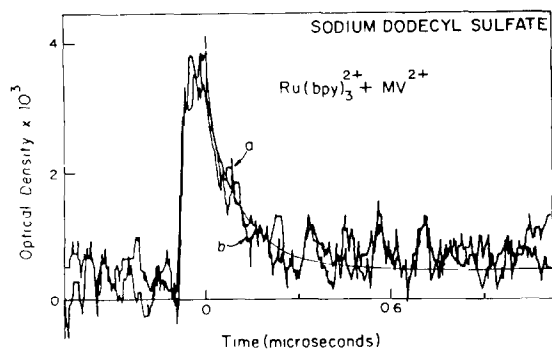


Fig. 7. Kinetic trace at $\lambda=395$ nm showing geminate recombination kinetics of RP $[\text{MV}^{\bullet+}, \text{Ru}(\text{bpy})_3^{\bullet+}]$ in SDS (0.015 M) micelles. Obtained by laser flash photolysis of $\text{Ru}(\text{bpy})_3^{2+}$ in the presence of MV^{2+} (1×10^{-3} M); trace (a) is in the presence of an external magnetic field $B=0.34$ T, trace (b) is in the Earth's field

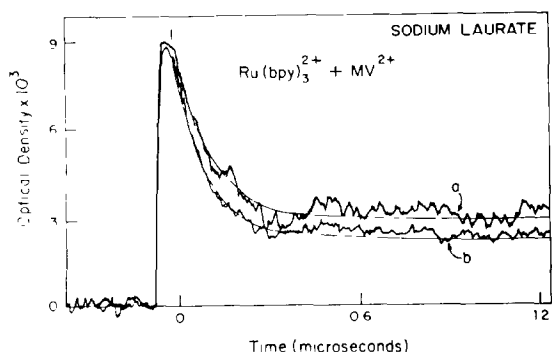


Fig. 8. Kinetic traces at $\lambda=395$ nm showing geminate recombination kinetics of the RP $[\text{MV}^{\bullet+}, \text{Ru}(\text{bpy})_3^{\bullet+}]$ in SL (0.03 M) micelles. Obtained by laser flash photolysis of $\text{Ru}(\text{bpy})_3^{2+}$ in the presence of MV^{2+} (2×10^{-3} M); trace (a) is in the presence of an external magnetic field $B=0.34$ T, trace (b) is in the Earth's field.

3.3. Magnetic field effect

A positive magnetic field effect (MFE), i.e. an increase in Φ_{es} , was observed in SL micelles (fig. 8). The MFE in SL was studied in more detail with a flow system, the precision of which is higher than that of laser flash photolysis experiments. In the basic media the MV^+ radical-cation is rather stable [25,27], so that the experiments were performed at pH 10.0 in SL (0.026 M) solutions, containing $\text{Ru}(\text{bpy})_3^{2+}$ (1.0×10^{-5} M) and MV^{2+} (1×10^{-3} M). The MFE Φ_B is defined as the relative change in the concentra-

Table 2

Rate constants k_{bc} of radical pairs decay in SL and SDS micelles

Micelles	$[\text{MV}^{2+}]$ (M)	k_{bc} ^{a)} (10^{-6} s^{-1})
SL (0.026 M), pH 7.0, glycerol 2% v/v	2.5×10^{-3}	5.0
SL (0.03 M) ^{b)}	2.0×10^{-3}	6.5 (= 5.9 + 0.6) ^{c)}
SL (0.03 M)	2.0×10^{-3}	7.6 (= 7.0 + 0.6) ^{c)}
SL (0.026 M), pH 7.0	0.02	5.5
SDS (0.015 M)	1.0×10^{-3}	6.8
SDS (0.01 M), LiCl (0.08 M)	5.0×10^{-3}	5.8
SDS (0.08 M) ^{d)}	0.015	5.66

^{a)} Determination error is 15–20%.

^{b)} In the presence of an external magnetic field $B=0.34$ T.

^{c)} Here $k_{\text{bc}} = k_{1c} + k_{1b}$.

^{d)} Data of ref. [10].

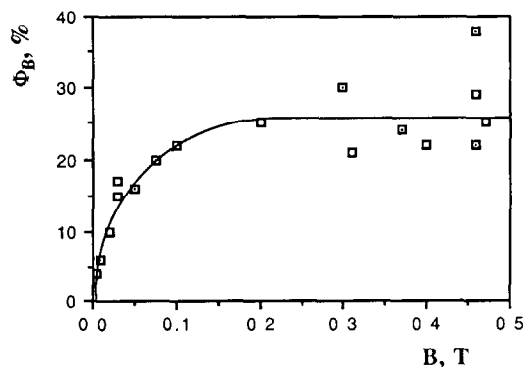


Fig. 9. The dependence of MFE Φ_B on field flux. Obtained during steady-state photolysis of $\text{Ru}(\text{bpy})_3^{2+}$ (1×10^{-5} M) and MV^{2+} (2.5×10^{-3} M) in SL (0.03 M) micellar solution of pH 10.0.

tion, C , (or absorption) of MV^+ in the presence of MF.

$$\Phi_B = \frac{C_B - C_0}{C_0} \quad (5)$$

A significant MFE was observed; fig. 9 shows the field dependence of Φ_B .

In time-resolved experiments (fig. 8), $C_B(C_0)$ was measured at the plateau region of a kinetic trace at $t \geq 0.5 \mu\text{s}$. Laser flash photolysis experiments in various SL solutions also show a significant MFE ($\Phi_B \approx 20\%$). (The compositions of these SL solutions can be found in tables 1 and 2.) Irreversible reactions leading to an accumulation of MV^+ were observed in SL micelles. No MFE within the experimental error

limits was observed in SDS micellar solutions, cf. fig. 7.

4. Analysis and discussion

4.1. Quenching of $^*\text{Ru}(\text{bpy})_3^{2+}$ in aqueous and micellar solutions

In all aqueous and micellar solutions under investigation the decay of $^*\text{Ru}(\text{bpy})_3^{2+}$ was fairly well approximated by first-order kinetics, see section 2. Table 1 lists the derived first-order rate constants obtained for $^*\text{Ru}(\text{bpy})_3^{2+}$ decay. Further mechanistic insight was obtained from measurement of the dependences of k_{obs} on surfactant (S) and MV^{2+} concentrations (figs. 1–5). The dependences of k_{obs} on [S] show the anticipated behavior, namely acceleration of the reaction under an increase in [S] up to concentrations close to the cmc and deceleration of the reaction rate under a further increase in [S] (figs. 1, 2) ^{#1}.

The main expected effect of micellar formation is the increase in the local reagents' concentration and thus a potential increase in the reaction rate [8,10]. At the same time at least two other circumstances appear, namely a change of reaction thermodynamics due to a solvent change (it can become more or less exergonic) and the change of the mutual diffusion coefficient D . According to the literature [7–9,14] the probe and the quencher are located in the Stern layer in a negatively charged ionic atmosphere in SDS and probably other anionic micelles, and their diffusion occurs over the surface of the micelle. Such diffusion leads to the formation of an encounter complex, and ET occurs with a certain probability p . The numerical values of D are not known ^{#2}. As a result of the influence of all these circumstances, the pseudo-first-order reaction can accelerate at $[\text{S}] \approx \text{cmc}$ in comparison with an aqueous solution under the same

concentration of quencher, and this was observed (figs. 1 and 2).

Further increase of [S] ($[\text{S}] > \text{cmc}$) under constant quencher concentration leads to a reasonable result, namely deceleration of the reaction (figs. 1 and 2) due to a dilution of the micelles of MV^{2+} . So, the intramicellar quenching process is considered to be the most important. It is also quite reasonable that, under constant surfactant concentration, k_{obs} linearly increases with $[\text{MV}^{2+}]$, cf. figs. 3, 4.

For intramicellar quenching the following equation may be proposed, being based upon the treatment in ref. [10]:

$$k_{\text{obs}} = k_0 + k_r [\text{MV}^{2+}] / [\text{M}], \quad (6)$$

where [M] is the micellar concentration (see section 2). The value of $[\text{MV}^{2+}] / [\text{M}] = \langle r \rangle$ (see section 3), all MV^{2+} is believed to be incorporated into the micelles. The k_r value has the sense of a first-order rate constant of the reaction between fluorophore and quencher within the micelle. Certainly, eq. (6) ought to be valid in a limited range of $[\text{MV}^{2+}]$ due to the limited facility of the micelles to incorporate a quencher, and deviations from linearity between k_{obs} and the calculated $\langle r \rangle$ were observed [10]. Probably, such deviations may be used for the evaluation of the capacity of the micelles.

The general scheme of fluorescence quenching in the micelles is presented in refs. [6–9] under a number of assumptions leading to eq. (6). These assumptions are known [7–9] and they can be summarized when the fast intramicellar quenching between reagents strongly bound to a micelle is considered. Then the excited state decay kinetics should be of first order, and k_{obs} is expressed by eq. (6).

The elementary rate constant k_r obtained in a different way (figs. 1 and 3) is approximately the same, $k_r \approx 4.0 \times 10^5 \text{ s}^{-1}$. This fact confirms the validity of our present description.

The use of the data in fig. 2, eq. (6) and the k_0 value for SL micelles enables us to make three rough statements about k_r ; (1) the order of magnitude is beyond doubt; (2) the average value of $k_r = (3.5 \pm 1.0) \times 10^5 \text{ s}^{-1}$; and (3) the satisfactory description of the observed kinetics with a single exponent also supports the correctness of eq. (6).

The rate constant, k_r , can be evaluated by using Tachia's [33,34] model of diffusion-controlled bi-

^{#1} A relatively high rate of reaction (1a) in the presence of SDS under $[\text{SDS}] < \text{cmc}$ due to submicellar aggregate formation was found in ref. [10].

^{#2} The D values may be obtained in the course of study of a Heisenberg spin exchange between paramagnetic particles attached to the surface of a micelle. It is difficult to compare numerical values of these two-dimensional diffusion coefficients on a sphere with the "usual" three-dimensional diffusion coefficients.

molecular reactions on a micellar surface, provided that the reaction probability at contact $p = 1$, the value of the mutual diffusion coefficient D , and the micelle's and reagents' radii are known [6,9]. However, in the present case the D value is not known; in aqueous solutions $p < 1$ (see above), and it is not obvious that $p = 1$ for the same system in micelles. The use of Tachia's model is therefore not appropriate in the present situation.

The data on $\text{Ru}(\text{bpy})_3^{2+}$ luminescence quenching by MV^{2+} in SDS micelles is in reasonable agreement with that previously published [7,8,10–12]. For example, in agreement are k_{bc} values for SDS micelles obtained in the present work and in ref. [10], see table 2.

Acceleration of reaction (1c) due to a kinetic salt effect is observed not only in water but also in micelles. Under the same concentration of MV^{2+} the k_{obs} values are higher in the presence of 0.1 M NaCl or 0.08 M LiCl, which most probably is due to a salt effect (cf. the data in table 1 for SDS and SL). However, it should be noted that the properties of the micelles in the presence of a salt are changed [30,31], and that such a change may influence the kinetics.

Contrary to the case for SDS micelles, radicals exit from SL micelles at a measurable rate (table 1). Fig. 6 presents a dependence of Φ_{es} on [SL]. The curve has quite a reasonable shape with a drop in the vicinity of the cmc. Such experiments can manifest themselves as a convenient way of determining the cmc in similar experiments. The variation of surfactant concentration allows one to change the radicals' escape into the solvent bulk, other conditions being equal. Φ_{es} values determined for SL micelles do not depend on $[\text{MV}^{2+}]$ within the range of concentrations used ($[\text{MV}^{2+}] \leq 0.02 \text{ M}$); this fact confirms once more the validity of the simple (pseudo)-first-order kinetic treatment of photoelectron transfer. A similar dependence of Φ_{es} on [S] was obtained for SDS micelles. $\Phi_{es} \approx 0$ under $[\text{SDS}] \geq 0.01 \text{ M}$.

Thus SL and SDS micelles manifest different behavior, the latter micelles keeping MV^{2+} (most probably also in the Stern layer, see above), whereas SL micelles allow the escape of MV^{2+} . The question arises: does all the MV^{2+} escape or does a measurable fraction of it remain in the micelles? Kinetics curves, which measure the total absorption of MV^{2+} , do not allow us to distinguish between these two situations.

ESR spectra of MV^{+} produced by the chemical reduction of MV^{2+} in micellar solutions provide an answer to this question [35]. ESR spectra of MV^{+} in the presence of SL micelles show no difference compared to water. So, there is no reason to state that any measurable amount of MV^{+} is incorporated into SL micelles. At the same time similar measurements with SDS micelles show broadened ESR spectra of MV^{+} , which is definitely located in the micellar phase [35].

Two main factors are known to influence the thermodynamics of charged compounds binding to micelles, namely hydrophobicity and Coulomb interaction [1]. In the case of SDS and SL, which are both C12 micelles, the hydrophobic interaction may be considered approximately the same. These two sorts of micelles give an instructive example of the effect of a terminal group. Sodium laurate, the salt of a weak acid and a strong base, hydrolyzes effectively in water and shows a pH of 9–11 (depending on the concentration of SL). Thus, a significant fraction of carboxylate groups may be protonated and may result in the weakened binding of MV^{+} to laurate micelles. The essential difference between the sodium ion binding to SL and SDS micelles is revealed in ^{23}Na NMR experiments [36]. These data demonstrate a partial penetration of sodium ions among the surfactant polar group in the case of SL micelles [36]. This phenomenon should result in expelling MV^{+} radicals from the SL micelle, and probably only thrice-charged $\text{Ru}(\text{bpy})_3^{3+}$ remains in the micelles. Therefore, reaction (1) in SL micelles leads to a charge separation in contrast to a run of reactions in an aqueous solution of SDS micelles (table 1).

4.2. Geminate recombination

Not only reaction (1a), but also reactions (1b) and (1c) may be observed in the present system after a laser pulse. In order to observe the kinetics of geminate (or cage) recombination and dissociation it is necessary to produce a pair of reactive reagents in sufficient concentration. This task is simpler for photodissociation reactions. For bimolecular reactions such as (1) it is necessary to make the electron transfer reaction (1a) as fast as possible [32]; this can be realized using solutions with as parameter $\langle r \rangle$ (see above) as high as possible. Reaction (1a) is of pseudo-first-order, cf. previous section. The theory

predicts that a geminate recombination in micelles is also a first-order process except at very short times (due to "transient effects") [33,34]. So, the overall process may be represented as two consecutive first-order reactions; the description of such a process is rather simple, see e.g. ref. [37]. It is important that the concentration of the intermediate product (radical pair (RP) in our case) reaches its maximum, the descending part of the curve perhaps approximated by an exponential law $[RP] \approx \exp(-k_{bc}t)$. The higher the k_{obs}/k_{bc} value and the further from the maximum the approximation begins, the more precise is the approximation [37].

Figs. 7 and 8 show the kinetic runs of geminate recombination in SDS and SL micelles. The descending part of the curve was approximated by an exponential decay, and the k_{bc} values were obtained (table 2). The k_{obs} values, i.e. the rate constants of RP formation for the same solutions, can be found in table 1.

Kinetic analysis of the system enables one to suggest equations for the time (t_{max}) of reaching the maximum concentration of RP (or MV⁺). The following equation must hold for SDS micelles, where no escape is observed [37]:

$$t_{max} = \frac{\ln(k_{obs}/k_{bc})}{k_{obs} - k_{bc}}. \quad (7)$$

The following equation was obtained for the maximum concentration of MV⁺ in SL micelles, where escape was observed:

$$t_{max} = \frac{\ln[(k_{obs} - k_{lb})/(k_{bc} - k_{lb})]}{k_{obs} - k_{bc}}. \quad (8)$$

The maximum in [MV⁺] can be observed under the condition of $k_{obs} > k_{lb}$; this was the case in the present study (cf. tables 1 and 2). Eqs. (7) and (8) can be used to check the validity of the kinetic measurements and analysis. The substitution of the pertinent rate constants (tables 1 and 2) into eqs. (7) and (8) leads to $t_{max} = 125$ ns (SDS) and $t_{max} = 100$ ns (SL). The corresponding experimental t_{max} are 75–100 ns for SDS solutions (cf. fig. 7) and about 50 ns for SL solutions (cf. fig. 8) are in reasonable agreement with the calculated ones. The important peculiarity, i.e. the appearance of MV⁺ at maximum absorption with a delay is clearly seen in figs. 7 and 8.

It was mentioned above that the reaction between Ru(bpy)₃³⁺ and MV⁺ in water is diffusion-controlled, which means that the reagents are extremely reactive towards each other. The obvious questions arise: why don't they react immediately as a contact pair? Why is it that in water $\Phi_{es} > 0$? Why does reaction (1c) last as long as about 10⁻⁷ s in micelles?

The following explanations are plausible:

(i) The reagents are characterized by reaction anisotropy and are initially generated in an unfavorable atmosphere for reaction at the mutual orientation, see for details refs. [24,32].

(ii) The reagents are not generated in the contact. This is possible, because, in very viscous media, long-distance electron transfer occurs in this system [38]. However the BET may also be a noncontact reaction, and this reason probably is not essential.

(iii) Spin prohibition of the reaction, i.e. formation of the triplet pair which should interconvert into a singlet state before reaction, seems to be the most probable reason for the relative ineffectiveness of BET. Moreover, the experimental observation of MFE testifies to this interpretation (see next section). Even if generated as a contact pair, the reagents react with a probability less than unity. Despite previous attempts [9], this fact, i.e., moderate reactivity of reagents, prevents the use of Tachia's [33,34] model for analysis of the data. (The model [33,34] considers a reaction to occur with unit probability at the contact and obviously predicts an infinite reaction rate for reagents generated in contact.)

With regard to an aqueous solution it is necessary to mention that the very short lifetime of the cage $\tau \approx 10^{-10}$ – 10^{-11} s does not allow observation of the geminate recombination, whereas in micelles due to a rather long lifetime of the pair, this observation is possible. Not all of the triplet RPs formed in water dissociate ($\Phi_{es} < 1$, see table 1 and refs. [17–24]); the most probable reason for this observation is the spin-orbit coupling (SOC) induced recombination of contact RPs [19].

4.3. Magnetic field effect

Reaction (1) was shown to be magnetosensitive in water and in a water/ethylene glycol binary mixture (viscosity $\eta \lesssim 2.5$ cP) [20]. *Ru(bpy)₃²⁺ reacts in a triplet state, and the radical pair (RP), the primary

product of ET, is also in a triplet (or nominal triplet) state [20], eq. (1). A small *negative* MFE on Φ_{es} has been reported [20,21]. Steiner et al. [20] unequivocally demonstrated that this MFE is due to an increase of the BET rate in the RP and the sign of the MFE is consistent with that according to a triplet or Δg mechanism. The radical-cation MV^+ manifests hyperfine coupling (HFC) [39]; $\text{Ru}(\text{bpy})_3^{3+}$ does not [43]. The *positive* MFE on Φ_{es} according to a HFC mechanism can be expected for reaction (1) proceeding via triplet RPs formation, and that was found to be the case (figs. 8 and 9, table 2). Similar behavior of triplet RPs has been found earlier: the reactions which show a negative MFE due to a triplet mechanism, being run in micelles, show no MFE at all or show a positive MFE due to a HFC mechanism, which dominates over the triplet mechanism [40]. The theoretical $B_{1/2}$ value, i.e. magnetic field strength corresponding to Φ_B equal to half of its maximum value, should be calculated according to the following equation [41]:

$$B_{1/2} = 2 \left[\sum_n A_n^2 I_n (I_n + 1) \right]^{1/2} \approx 0.003 \text{ T}, \quad (9)$$

where A_n is the HFC constant of the n th atom of MV^+ with a magnetic nucleus with spin I_n . (The numerical values of isotropic HFC constants of MV^+ were taken from ref. [39].) The characteristic triplet (T)–singlet (S) evolution time for an RP with such a HFC constant is about 10^{-8} s [41], and the increase in lifetime of the RP under its inclusion into the micelle allows the realization of a positive MFE according to the HFC mechanism.

The experimental $B_{1/2}$ value is about 0.027 T (fig. 9), i.e. approximately nine times larger. Such a discrepancy, i.e. the significant excess of experimental over calculated $B_{1/2}$ values has been found many times, see e.g. refs. [32,42]. One of possible reasons leading to an increase in experimental $B_{1/2}$ is the action of a relaxation mechanism, i.e. retardation of the relaxation, caused by HFC anisotropy, with a field flux increase [32,42].

The present system is rather complicated, and it is a challenge to the theory of magnetokinetic phenomena. It has the following peculiarities: a very strong anisotropy of the g -factor of the $\text{Ru}(\text{bpy})_3^{3+}$ radical ($g_{\parallel} = \pm 1.14$, $g_{\perp} = 2.64$ [20,43]); a strong spin-orbit

coupling (SOC) due to the heavy atom Ru (SOC constant of Ru $\xi = 1100 \text{ cm}^{-1}$ [19]), which, apart from g -factor anisotropy, must lead to T–S-transitions in contact RPs; and indefinite singlet and triplet states of RPs [20]. The large difference between the g -tensor components of $\text{Ru}(\text{bpy})_3^{3+}$ and the g -factor of MV^+ may result in the contribution of another negative MFE, namely the Δg -mechanism [41].

The most serious obstacle to observation of a MFE is the strong anisotropy of the g -factor, which should result in a fast paramagnetic relaxation of RPs which can diminish or completely destroy the MFE [44]. We present below some semiquantitative estimations of relaxation rates. The overall rate of relaxation is given by the sum of the field independent spin-rotation relaxation (SR) and relaxation due to the g -factor anisotropy:

$$k_{\text{rel}} = (T_1^{\text{SR}})^{-1} + (T_1^g)^{-1} \text{ s}^{-1}. \quad (10)$$

For $(T_1^{\text{SR}})^{-1}$ the following holds [44,45]:

$$(T_1^{\text{SR}})^{-1} \approx \delta g^2 / 9 \tau_c, \quad (11)$$

where $\delta g^2 = 2(g_s - g_{\perp})^2 + (g_s - g_{\parallel})^2$, g_s is the isotropic g -factor of $\text{Ru}(\text{bpy})_3^{3+}$, and τ_c is the rotational correlation time. Using the g_{\perp} and g_{\parallel} values presented above we estimate $\delta g^2 \approx 1$, and re-write eq. (11) as:

$$(T_1^{\text{SR}})^{-1} \approx 0.1 / \tau_c. \quad (12)$$

The following expression should be used for $(T_1^g)^{-1}$ [42,45]:

$$(T_1^g)^{-1} = \omega_0^2 \tau_c \delta g^2 / [5g_s^2(1 + \omega_0^2 \tau_c^2)], \quad (13)$$

where ω_0 is the Larmor frequency. For the field flux region $B > 0.05 \text{ T}$, where significant MFE was observed (fig. 9), the value of $\omega_0 > 10^{10} \text{ s}^{-1}$. According to ref. [46] for nitroxyl free radicals (TEMPO and its simple derivatives) in SDS micelles $\tau_c \approx 10^{-10} \text{ s}$, and we shall use this estimation for a beginning as τ_c of $\text{Ru}(\text{bpy})_3^{3+}$. So, under conditions of $B > 0.05 \text{ T}$ and $\tau_c \approx 10^{-10} \text{ s}$, formula (13) can be simplified:

$$(T_1^g)^{-1} \approx 0.1 / \tau_c. \quad (14)$$

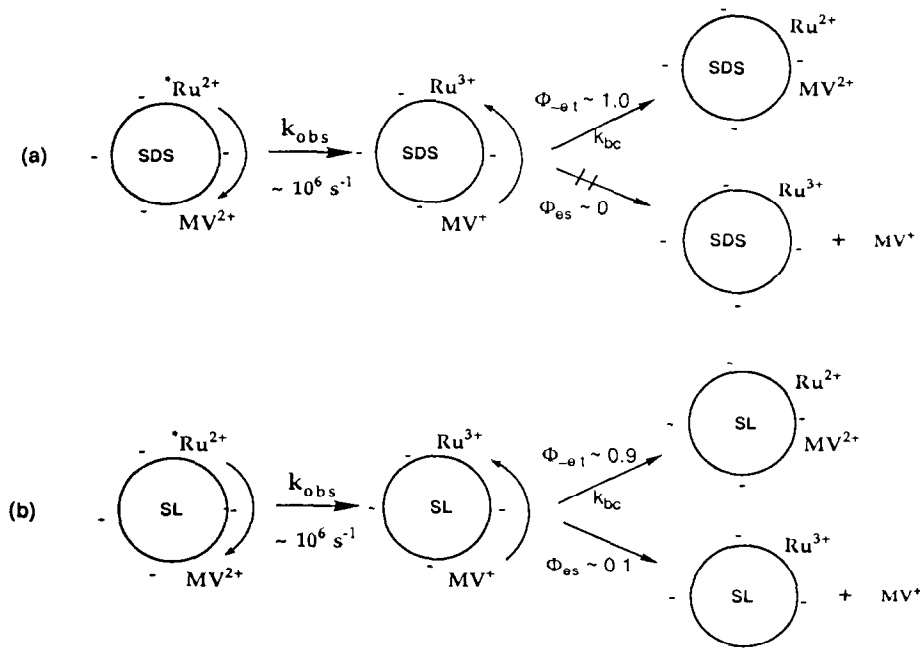
It is obvious that the τ_c value is crucial for a k_{rel} estimation according to eqs. (12) and (14) under the present conditions ($\delta g^2 \approx 1$ and $B = 0.1\text{--}0.5 \text{ T}$). The k_{rel} should not be much higher than the rate of geminate recombination ($k_{\text{bc}} \approx 10^6\text{--}10^7 \text{ s}^{-1}$, table 2) for

the existence of MFE. This demand can be fulfilled only under a very large τ_c value. In fact, it seems obvious that $\text{Ru}(\text{bpy})_3^{3+}$ has a larger rotational correlation time due to its larger radius than that for TEMPO and its simple derivatives. According to the Stokes–Einstein–Debye formula, τ_c is proportional to the radius of the molecule in the third power. $\text{Ru}(\text{bpy})_3^{3+}$ is more than two times larger than TEMPO; this fact alone should give a one order of magnitude increase in τ_c compared to TEMPO. Recent estimations of τ_c for TEMPO attached by a flexible $(\text{CH}_2)_4$ chain to $\text{Ru}(\text{bpy})_3^{2+}$ in SDS micelles show that this value is about 10^{-9} s [35]; so that it is highly probable that $\text{Ru}(\text{bpy})_3^{3+}$ itself has essentially a larger τ_c than this tethered TEMPO.

The second important factor is the charge of $\text{Ru}(\text{bpy})_3^{3+}$, which is located in a negatively charged Stern layer of micelles (see above), and this non-uniformly charged particle rotates in a strong Coulomb field. It was shown that τ_c values for nitroxyls which have a single positive charge are, on average, one order of magnitude larger than for neutral radicals of similar structure [46]. As a result, one can finally suggest that τ_c of $\text{Ru}(\text{bpy})_3^{3+}$ is not less than 10^{-8} s, leading to the estimate of $k_{\text{rel}} \lesssim 10^7 \text{ s}^{-1}$, which validates the existence of MFE.

5. Conclusions

In the present work the kinetics of a photoelectron transfer reaction between $^*\text{Ru}(\text{bpy})_3^{2+}$ and MV^{2+} were studied in SDS and in SL, cf. scheme 1. The quenching of a photoexcited probe in water by MV^{2+} is accelerated in the presence of these surfactants. The k_{obs} versus surfactant concentration dependences show a maximum in the vicinity of cmc. The transfer of the bimolecular reaction from the solvent bulk to the reaction on a micelle surface leads to its acceleration under the same initial concentrations of reagents. The descending part of the curve reflects a dilution of micellar solution with quenchers. Dependences of quenching rate constants on the surfactant concentration (at constant quencher concentration) as well as on quencher concentration (at constant surfactant concentration) have been obtained for SDS and SL solutions. Elementary intramicellar quenching rate constants $k_r \approx 10^5 \text{ s}^{-1}$ were obtained with the use of such plots and eq. (6). Eq. (6) can be obtained from a more general treatment of luminescence quenching in micellar solutions under several assumptions, such as: (1) quenchers are strongly associated with micelles; (2) the quencher-exchange process is negligible for this submicrose-



Scheme 1.

cond microreactor; and (3) quenching is monitored at time less than about one microsecond.

The obtained data (figs. 1–5) enable us to draw a general conclusion on the influence of a micellar microenvironment on photoinduced electron transfer rates. In order to increase the rate under the same concentration of reagents, it is necessary to have a rather high concentration of quencher per micelle $\langle r \rangle$. For SDS micelles the rate constant of quenching was shown to be linearly dependent on $\langle r \rangle$ within a rather wide range, namely up to $\langle r \rangle \sim 10$.

The quenching reaction is accelerated in the presence of inorganic salts in micellar solutions probably due to a kinetic salt effect on the reaction between the two twice positively charged reagents.

Radicals do not exit from SDS micelles, the cage escape value $\Phi_{\text{es}} \approx 0$. On the contrary, $\Phi_{\text{es}} > 0$ ($\Phi_{\text{es}} \approx 0.08$) for SL micelles. The difference in the properties of SDS and SL (both are C12) may be ascribed to the difference in the chemical properties of their terminal groups. The dependence of Φ_{es} on [SL] has a sharp drop in the vicinity of cmc. Such dependences may be used for the determination of the cmc of micelles in kinetic laser flash photolysis experiments.

The kinetics of geminate recombination of a triplet RP [$\text{Ru}(\text{bpy})_3^{3+}$, MV^+] was observed in SL and SDS micelles. The pertinent kinetic analysis was presented, and conditions for the observation of geminate recombination were discussed. The kinetics of geminate recombination is well described by a first-order law. Rate constants k_{bc} (s^{-1}) do not depend on the concentration of the quencher and may be used as representative dynamic characteristics of micelles.

A significant positive magnetic field effect $\Phi_B \approx 20$ –25% was observed during the steady-state or laser flash photolysis of $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$ in SL micelles. The field dependence of Φ_B reached a plateau at $B \gtrsim 0.1$ T. The origin of the positive field effect is the action of a HFC mechanism of triplet–singlet evolution. This observation seems to be important demonstrating that MFE exists in reactions with radicals centered on the heavy (Ru) atom despite the action of spin–orbit coupling in the RP. The strong anisotropy of the g -factor of the Ru-centered radical does not lead to an effective paramagnetic relaxation probably due to its hindered rotation in a micelle.

Irreversible reactions, leading to the appearance of

a blue MV^+ radical-cation have been observed in SL micelles. There is an essential interest in charge separation in the present system, in preventing BET and in creating in such a way a photo-“diode” [11–13, 17, 25–27, 47]. One of the possible realizations of such an idea is the use of a solution of SL micelles, which keeps $\text{Ru}(\text{bpy})_3^{3+}$ and serves as sacrificial donor. The application of an external magnetic field decelerates intramicellar recombination, increases MV^+ yield into solvent bulk, and makes charge separation more efficient.

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