

YIELD OF IONS PRODUCED IN THE LUMINESCENCE QUENCHING OF TRIS (2,2'-BIPYRIDINE)RUTHENIUM(II) BY DICHLOROPHENOLATE IONS

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The electron-transfer quenching of $\text{Ru}(\text{bpy})_3^{2+}$ (tris(2,2'-bipyridine)ruthenium(II)) excited state by 2,4-dichlorophenol (2,4-DCP), 2,5-dichlorophenol (2,5-DCP) and 2,6-dichlorophenol (2,6-DCP), in their anionic forms, was studied in de-aerated solutions of neat methanol and 25, 50 and 75% v/v aqueous methanol at 30 °C. The quenching rate constants (k_q) were determined and their values range from 1×10^9 to $8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. In all the mixtures methanol: water the k_q values for 2,5-DCP were lower than for 2,4-DCP and 2,6-DCP. This result was discussed in terms of the effect of chloro atom on the quencher oxidation reaction. The photoredox product $\text{Ru}(\text{bpy})_3^+$ was observed by laser flash photolysis and its quantum yield ($\Phi_{\text{Ru}(\text{bpy})_3^+}$) calculated by using a comparative method with the formation of zinctetraphenylporphyrin triplet state. The yields of cage escape (Y_{ce}) for the different methanol/water mixtures were calculated from the obtained values of $\Phi_{\text{Ru}(\text{bpy})_3^+}$. Y_{ce} increases from 0.1-0.2 in 25% v/v aqueous methanol to 0.5-0.6 in neat methanol. This change of Y_{ce} with the solvent composition was discussed in terms of combined effects of viscosity and solvent cage on the rate constant of cage escape (k_{-d}) and the rate constant for back electron-transfer to the ground state from geminate pair (k_{bc}), respectively. The constants k_{-d} were calculated with the Eigen equation. The constants k_{bc} were estimated from Y_{ce} and k_{-d} by applying a simplified reaction scheme. The k_{bc} values range from 3.2×10^9 to $1.3 \times 10^{10} \text{ s}^{-1}$.

INTRODUCTION

Considerable progress has been made in the photochemistry of transition metal complexes during the last years as a result of many works published in this area.¹ Ru(II) complexes have been extensively used for experiments in photochemical energy storage because their lowest energy excited state is long-lived and able of a rapid electron-transfer reaction.²⁻⁵

Phenolate ions are typical electron donors. Reduction of the lowest excited state of tris(2,2'-bipyridine)ruthenium(II) [$(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$] can take place in the presence of phenolate ion. Strong support in favor of a reductive process was given by the formation of $\text{Ru}(\text{bpy})_3^+$ detected in the study of the luminescence quenching of $\text{Ru}(\text{bpy})_3^{2+}$ by phenol and substituted phenols.^{6,7} The quenching rate constant k_q increases on changing the solvent from water to methanol⁷ and also when the pH of the solution increases. The results of

the pH effect on k_q showed that the ionized form of phenolic derivative has a higher quenching efficiency than the neutral one and controls the apparent quenching rate constant at high pH values.⁸ The above-described reduction processes has been proposed as an initial step in the mechanism for the photodechlorination of polychlorophenolate ions sensitized by $\text{Ru}(\text{bpy})_3^{2+}$ studied from continuous and flash photolysis experiments.⁷ The values of yield of electron-transfer products and quantum yield of loss of polychlorophenol were lower for 2,6-dichlorophenol than for 2,4-dichlorophenol and 2,4,6-trichlorophenol.

The bimolecular electron-transfer reaction between a photoexcited compound and a quencher is followed by two reverse processes.⁹ One of them takes place within the solvent cage in the lifetime of the geminate ion pair. The other can be observed as a second order process with respect to the free radical ions in the bulk. Both processes dissipate the excitation energy as heat. Independent ions or electron-transfer products can be formed by a diffusional process from the geminate pair. A small yield of the electron-transfer products in the

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bulk is generally ascribed to a fast reverse electron-transfer in the geminate pair.¹⁰ Therefore, the study of the influence of different parameters on the rate of back electron-transfer to the ground state within the geminate pair is an interesting subject.¹¹

In the present paper we report results of emission quenching and quantum yield of formation of Ru(bpy)₃²⁺ obtained in de-aerated alkaline solutions of Ru(bpy)₃²⁺ and 2,4-dichlorophenol (2,4-DCP) 2,5-dichlorophenol (2,5-DCP) or 2,6-dichlorophenol (2,6-DCP) in neat methanol and 25, 50 and 75% v/v aqueous methanol. The cage escape yield or formation of electron-transfer products in the bulk and the rate constant for back electron-transfer to the ground state have been determined from the quantum yield of formation of Ru(bpy)₃²⁺ measured by microsecond-laser flash photolysis.

EXPERIMENTAL

Apparatus and materials

Luminescence spectra of Ru(bpy)₃²⁺ were obtained from an Aminco Bowman spectrofluorometer. The luminescence lifetime determinations in the quenching experiments were carried out as described previously.¹² The determinations of transient absorptions were made by the flash photolysis technique using a nitrogen laser as excitation source. The details of the laser and the monitoring apparatus have been described elsewhere.⁷ The incident light intensity on the samples was attenuated in a controlled way by inserting filters of transmittance 16, 21, 48, 51, 84 and 87% at 337 nm.

Tris(2,2'-bipyridine) ruthenium (II) dichloride from Baker was used as received. 2,4-dichlorophenol, 2,5-dichlorophenol and 2,6-dichlorophenol from Sigma Co. were purified by vacuum sublimation. Zinctetraphenylporphyrin (ZnTPP) from Aldrich was purified following the procedure developed by G. H. Barnett *et al.*¹³ Sodium hydroxide (Carlo Erba), benzene (Merck, HPLC grade) and methanol (Cicarelli, p.a.) were used without further purification. Triple-distilled water was employed.

Procedure

In the quenching experiments, the concentration of Ru(bpy)₃²⁺ was in the (1–2) × 10⁻⁵ M range, whereas the concentration of the phenolic compounds ranged from 1 × 10⁻⁴ to 6 × 10⁻³ M according to their efficiency as quenchers. In the flash-photolysis experiments, Ru(bpy)₃²⁺ was in the (1–2) × 10⁻⁴ M range and the phenolic compounds were 1 × 10⁻² M. The dichlorophenols were dissolved in their acid form in the solution of Ru(bpy)₃²⁺ and sodium hydroxide 1 × 10⁻² M. This NaOH concentration insured that the DCP was converted to its basic form. The pK_a values

for 2,4-DCP and 2,6-DCP in water are 7,7 and 6,8 respectively¹⁴ and a similar value should be expected for 2,5-DCP. Then, the hydrolysis of anion dichlorophenolate and thus the concentration of the quencher in its acid form in our experimental conditions may be considered negligible.

The quenching rate constants were determined from Stern–Volmer plots of emission intensity or lifetime data, as described previously.⁷

Ru(bpy)₃²⁺ was measured spectrophotometrically. Two procedures were used to determine the amount of Ru(bpy)₃²⁺ produced by the laser flash excitation. In the first the oscilloscope sweep rate was expanded to cover 20 μs of reaction after the laser pulse. On these expanded sweeps a linear extrapolation of the intensity–time data could be used to obtain the intensity and thus the absorbance at zero time. In the second procedure the intensity was measured to 2 μs after the laser pulse on the decay traces. This time corresponds to approximately five or more lifetimes of the (³CT)Ru(bpy)₃²⁺ precursor in the presence of the quencher. When using the first procedure to obtain the absorbance of ZnTPP triplet at zero time, the oscilloscope sweep rate was expanded to cover 5 μs of reaction after the laser pulse.

The quantum yield of formation of Ru(bpy)₃²⁺, Φ_{Ru(+)}, was calculated from the absorbance increase (ΔA) at 510 nm, corresponding to the maximum of its absorption by using a comparative method.¹⁵ The triplet quantum yield of ZnTPP in solution of benzene was used as a standard reference. At the laser wavelength, the absorbances of the two initial solutions were approximately the same.

The absorbance increase for the Ru(bpy)₃²⁺/DCP⁻ ion systems at 510 nm as a function of the laser dose was measured by adjusting the incident intensity by means of a set of filters, as described in the above section. For the reference system, the absorbance increase was also measured at the triplet–triplet absorption maximum at 470 nm as a function of the laser dose.

Both absorbance increase measurements were always carried out immediately after each other to minimize changes in laser output and/or beam alignment. All the experiments were carried out at 30 °C with solutions de-aerated by bubbling nitrogen through them. Typically, 16 laser shots were averaged in order to set a proper signal-noise ratio. The reagents depletion in the Ru(bpy)₃²⁺/DCP⁻ ion systems was lower than 5% when the laser light intensity was used with no attenuation. Therefore, corrections were not necessary.

RESULTS AND DISCUSSION

Quenching of the emission of (³CT)Ru(bpy)₃²⁺ was observed in the presence of 2,4-DCP, 2,5-DCP and 2,6-DCP in alkaline solutions of neat methanol and 25, 50

and 75% v/v aqueous methanol. For each quencher, the Stern–Volmer plots of luminescence intensity measurements were obtained and all were linear over the used concentration ranges in the different methanol/water mixtures. The same procedure was followed with the dynamic measurements and equivalent results were obtained. This fact allowed us to discard the association in the ground-state between $\text{Ru}(\text{bpy})_3^{2+}$ and the anionic DCP as quenching mechanism.

The linearity of Stern–Volmer plots indicates the absence of other two possible causes of deviations. One of them can be derived from the marked decrease of the quenching rate constant (k_q) with the lowering of the pH already observed in earlier studies.^{7,8} However, in $\text{NaOH } 1 \times 10^{-2} \text{ M}$ the acid–base equilibrium of DCPs is displaced toward the ionized or basic form. Therefore, the ionized form controls the k_q in our experimental conditions. The second one is the effect of ionic strength on the quenching kinetics between oppositely charged ions which produces a decrease of the rate constant as the ionic strength is increased. In this work, the ionic strength in the quenching experiments was approximately 0.01 M ($\text{NaOH } 0.01 \text{ M}$) in the absence of quencher and increased to 0.016 M for the highest quencher concentration used. The variation of k_q with the ionic strength and a behavior similar to that of *p*-methoxyphenolate as given in Ref. 6 were taken into account. The estimated difference between the k_q values for both ionic strengths was about 5% and therefore lies within experimental error. Therefore, a deviation of the linearity in the Stern–Volmer plots from the effect of ionic strength should not be observed. For instance, the plots for the studied DCPs in some methanol/water mixtures are shown in Figure 1. The quenching rate constants are collected in Table 1.

The observed decrease in the k_q values with the increase in the proportion of water in the methanol/water mixtures was also observed in a previous work.⁷ In all the mixtures the k_q values for 2,5-DCP were lower than those for 2,4-DCP and 2,6-DCP. A similar result was obtained in the study of luminescence quenching of tris(1,10-phenanthroline) chromium(III) by phenol derivatives.¹⁶

It is necessary to know the reduction potential of the quencher in order to explain the above results in terms of the Marcus–Hush theory. These potentials for dichlorophenols in methanol/water mixtures are not reported in the literature. However, it is known that the metachlorophenol is the most difficult compound to oxidize within the monochloro phenols.¹⁷ Therefore, by assuming that a similar effect is brought about by the substitution of hydrogen atom with a second chloro atom in position *meta* in the orthochlorophenols, we can explain the reduction in the k_q values obtained for 2,5-DCP with respect to the ones for 2,4- and 2,6-DCP.

The transient species observed by flash photolysis in solutions of $\text{Ru}(\text{bpy})_3^{2+}/\text{DCP}^-$ ions exhibits an absorption spectrum with a maximum at 510 nm which is similar to that of $\text{Ru}(\text{bpy})_3^+$ reported by other authors.^{6,18} This result provided clear evidence that net electron-transfer had occurred in the quenching process.

The contact ion pairs (CIP) and solvent-separated ion pairs (SSIP) have been proposed as intermediaries in the photo-induced bimolecular electron-transfer reactions. These are of particular significance in the study of the decay kinetics of the ion pairs (IP) in polar solvents.¹⁹ The specific rate constants are generally in the order of 1×10^9 to 10^{10} s^{-1} and then the IP lifetimes are in the range ns to ps.

In the resolution time of our laser flash photolysis

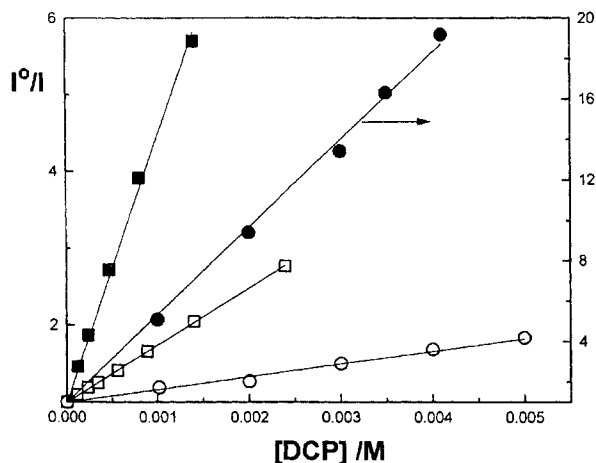


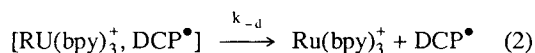
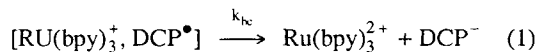
Figure 1. Stern–Volmer plots for the quenching of $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$ by DCP in methanol/water solutions ($\text{NaOH } 0.01 \text{ M}$). (O) 2,5-DCP, methanol 50% v/v; (□) 2,4-DCP, methanol 50% v/v; (●) 2,6-DCP, methanol 100% v/v; (■) 2,4-DCP, methanol 100% v/v.

Table 1. Quantum yield of formation of Ru(bpy)₃⁺, cage escape yield, rate constants of quenching and back electron-transfer in the quenching of (³CT)Ru(bpy)₃²⁺ by dichlorophenolate ions at 30 °C in methanol/water solutions (NaOH 0.01 M)

Phenolic compound	Methanol in water % (v/v)	$\phi_{\text{Ru}(+)}$ ^a	Y_{cc} ^b	$k_q^b \times 10^{-9}$ [M ⁻¹ s ⁻¹]	$k_{\text{bc}}^b \times 10^{-9}$ [s ⁻¹]
2,4-DCP	25	0.13	0.19	0.29	9.0
	50	0.23	0.25	1.2	5.6
	75	0.32	0.33	3.2	4.8
	100	0.51	0.52	8.4	4.8
2,5-DCP	25	—	—	0.01	—
	50	0.12	0.17	0.28	9.2
	75	0.28	0.34	0.52	4.6
	100	0.57	0.62	1.56	3.2
2,6-DCP	25	0.08	0.14	0.17	13
	50	0.23	0.26	0.98	5.5
	75	0.39	0.42	1.8	3.4
	100	0.50	0.51	7.2	5.0

Estimated variations based on three measurements are: ^a ±5%, ^b ±10%.

device ($\approx 1 \mu\text{s}$), the Ru(bpy)₃⁺ ions observed are those that escape to the cage recombination process. We propose the following simplified reaction scheme with two competing processes in order to explain our results of cage escape yield:



where [Ru(bpy)₃⁺, DCP[•]] is the geminate pair; DCP[•] and DCP⁻ are the ionized form and the radical derived from the phenolic quencher. k_{-d} and k_{bc} are the rate constants of cage escape and back electron-transfer to the ground state from the geminate pair, respectively.

The electron-transfer product Ru(bpy)₃⁺ could be formed in either of the two following ways. In the first, Ru(bpy)₃⁺ is formed from reductive quenching of the charge transfer excited state (³CT)Ru(bpy)₃²⁺. In the second way, Ru(bpy)₃⁺ is formed from triplet-triplet energy transfer between (³CT)Ru(bpy)₃²⁺ and DCP⁻ followed by an electron-transfer process between the triplet state of DCP⁻ and Ru(bpy)₃²⁺. The energy of the triplet state of the quenchers used in this work is not known. The available data for phenol is 81.7 Kcal mol⁻¹^{20a} and from the substitution on the ring, lower triplet state energies in the substituted phenols and their phenolate ions could be expected. Whichever is the case, the magnitude of the lowering of the triplet state energy is assumed to be less than 30 Kcal mol⁻¹.⁶ Therefore, the electronic energy transfer should be an energetically unfavorable process for all the systems examined because the energy of the excited state (³CT)Ru(bpy)₃²⁺ (49 Kcal mol⁻¹)^{20b} is lower than that for the substituted phenols. Therefore,

the role of this path in the quenching process may be considered negligible.

The transient Ru(bpy)₃⁺ undergoes decay in several hundred of microseconds under our experimental conditions as it can be seen in the corresponding trace (inset in Figure 2). Therefore, it is possible to measure its absorbance increase at 510 nm before significant decay takes place. However, it is necessary to take into account that the decay is a function of the initial concentration of Ru(bpy)₃⁺ and is thus dependent on the intensity of the laser pulse and the quenching efficiency. Therefore, the absorbance increase of Ru(bpy)₃⁺ or the ZnTPP triplet was measured from the two procedures described in the experimental section. In a number of test cases, we used both procedures and the obtained values of $\Phi_{\text{Ru}(+)}$ were consistent within experimental error.

The absorbance increase of Ru(bpy)₃⁺ as a function of the laser dose observed in the flash photolysis experiments for 2,6-DCP, in methanol/water 25, 50, 75 and 100% v/v, is shown in Figure 2. A linear plot was obtained as expected for the formation of products via a photochemical primary process. Similar results were obtained for 2,4-DCP and 2,5-DCP except for 2,5-DCP in methanol/water 25% v/v. In this case, the ΔA of Ru(bpy)₃⁺ measured with the laser intensity attenuated was within experimental error and therefore the $\Phi_{\text{Ru}(+)}$ could not be determined.

A linear dependence was also found for the formation of triplet state of ZnTPP which is showed join to its decay in Figure 3. These results correspond to the experiments for two solutions of ZnTPP in benzene with different absorbances (0.289 and 0.479) at the excitation laser wavelength. The ratio of the slopes derived from these plots is in good agreement with the

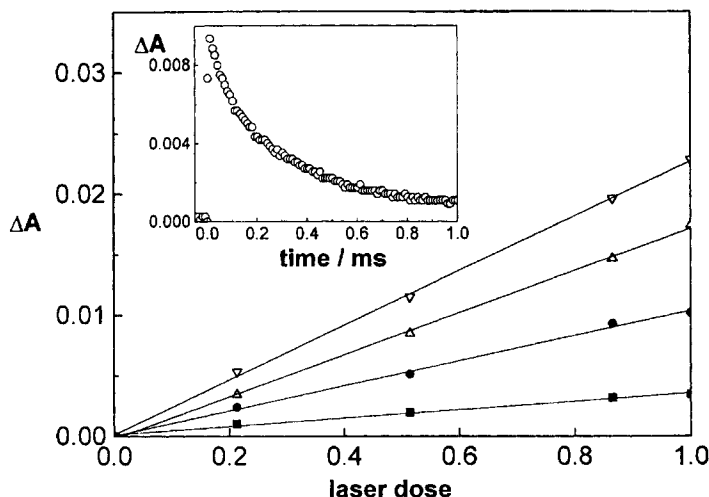


Figure 2. Absorbance changes monitored at 510 nm as a function of 337 nm laser dose for $\text{Ru}(\text{bpy})_3^+$ in methanol/water solutions (NaOH 0.01 M), 2,6-DCP, 10 mM. Methanol % v/v: (■) 25; (●) 50; (Δ) 75 and (▽) 100. Inset: a decay trace for $\text{Ru}(\text{bpy})_3^+$ monitored at 510 nm, 2,6-DCP concentration 10 mM in 75% v/v aqueous methanol, laser dose 0.48.

value for the ratio of the respective absorbances. The $\Phi_{\text{Ru}(+)}$ was then calculated from the ratio of slopes of the plots obtained for ZnTPP and the DCPs, similar to those shown in Figures 2 and 3, by using the method outlined in the paper by Hurley *et al.*¹⁵ The slopes were previously divided by the corresponding fractional absorption of the exciting light at 337 nm. It should be noted that the analysis yields the product of the transient extinction coefficient $\epsilon_{\text{Ru}(+)}$ multiplied by its quantum yield of formation $\Phi_{\text{Ru}(+)}$. This product can be

expressed:

$$\epsilon_{\text{Ru}(+)}\Phi_{\text{Ru}(+)} = (S_{\text{Ru}(+)}/S_r)\epsilon_r\Phi_r \quad (3)$$

where $S_{\text{Ru}(+)}$ and S_r are slopes for sample and reference, respectively. Φ_r is the quantum yield for the formation of ZnTPP triplet state, having a value of 0.83 according to Ref. 14 and ϵ_r is its extinction coefficient in benzene solution. It should be noted that $\epsilon_{\text{Ru}(+)}$ and ϵ_r are really the differences between the molar absorption coefficients on going from ground state $\text{Ru}(\text{bpy})_3^{2+}$ to

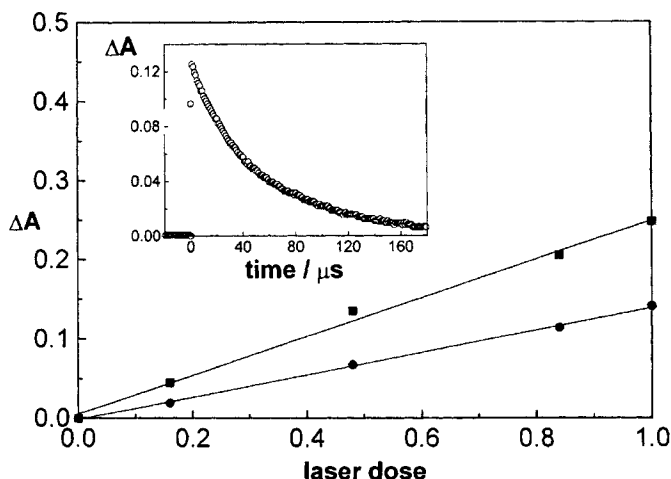


Figure 3. Absorbance changes monitored at 470 nm as a function of 337 nm laser dose for ZnTPP triplet in benzene. Ground-state absorbance (1 cm) at 337 nm: (●) 0.289; (■) 0.479. Inset: a decay trace for ZnTPP triplet monitored at 470 nm.

Ru(bpy)₃⁺ and from ground state to the triplet state of ZnTPP, respectively. Introducing the known extinction coefficients for both states of ZnTPP²¹ and both species of ruthenium¹⁸ we obtain values of 73 000 M⁻¹cm⁻¹ for ε_r at 470 nm and 13 800 M⁻¹cm⁻¹ for ε_{Ru(+)} at 510 nm, respectively. This extinction coefficient was assumed to be the same in all the methanol/water mixtures.

From equation 3 we calculated the quantum yields of formation of Ru(bpy)₃⁺, Φ_{Ru(+)}, which are summarized in Table 1. The experiments with ZnTPP and Ru(bpy)₃²⁺ DCP⁻ ion were repeated on three independent occasions and the Φ_{Ru(+)} values reported in Table 1 are the averages obtained from the individual experiments, and their scatter is within ±5%.

The yield of cage escape can be determined through the quantum yield of Ru(bpy)₃⁺ formation according to the following equation:

$$\Phi_{\text{Ru}(+)} = \Phi_{\text{CT}} Y_q Y_{\text{ce}} \quad (4)$$

where Φ_{CT} is the quantum yield for the formation of the excited state (³CT)Ru(bpy)₃²⁺; Y_q is the yield of quenching determined from the Stern–Volmer quenching constant and Y_{ce} is the cage escape yield, which represents the fraction of quenching that leads to solvent-separated products in the bulk. From equations (1) and (2) the Y_{ce} is defined by:

$$Y_{\text{ce}} = k_{-d} / (k_{-d} + k_{\text{bc}}) \quad (5)$$

The Y_{ce} values were calculated from equation (4), taking a value of one for Φ_{CT} in methanol or methanol/water mixtures. This value was reported in the literature from both photochemical and spectroscopic data in water and methanol.²² The obtained values for the cage escape yields are shown in Table 1. The Φ_{Ru(+)} and Y_{ce} values should be considered as upper bounds since they are based on the assumption that Ru(bpy)₃⁺ is the sole photoproduct that absorbed at 510 nm.

It is important to note that the Y_{ce} values obtained by flash photolysis in methanol for 2,6-DCP and 2,4-DCP (0.51 and 0.52, Table 1) are higher than the ones obtained in continuous photolysis (0.15 and 0.36 respectively, Ref. 7). The difference between both Y_{ce} values was higher for 2,6-DCP. This fact is also consistent with the results of reactive depletion quantum yield obtained in that paper,⁷ which indicate a lower reactivity for 2,6-DCP than for 2,4-DCP. Likewise, the difference between the Y_{ce} values obtained by both techniques for 2,4-DCP and 2,6-DCP can be explained by taking into account that, in the flash photolysis experiments, we are observing the electron-transfer products in bulk, before their significant decay takes place.

The change of Y_{ce} with the solvent composition in the methanol/water mixtures may be reflecting the behavior of the geminate pair produced by the electron-transfer quenching process in polar solvents. Moreover, the

measurement of Y_{ce} resulting from a photoinduced electron-transfer process is a valuable indirect way to determine the rate of back electron-transfer from the geminate pair (k_{bc}), provided that the rate of separation to free ions (k_{-d}) would be known.²³

The phenomenological theory of rate constants predicts²⁴ that a geminate ion pair produced in a solvent cage will diffuse apart to form dissociated ions with a rate constant k_{-d} that is proportional to the dielectric constant of the solvent and to the inverse of its viscosity. In general, due to the dependence of k_{-d} with the dielectric constant, the photoinduced bimolecular electron-transfer reactions are normally performed in polar solvents such as acetonitrile to facilitate the formation of separated radical ions in solution.²⁵

The rate constant calculated according to the Eigen diffusional equation can be considered fairly reliable for partners which are not held together by electrostatic forces. For the (³CT)Ru(bpy)₃²⁺/DCP⁻ quenching pair, one of the partners in the geminate pair is a radical and therefore there is not Coulombic interaction. Then, k_{-d} can be expressed as a function of the viscosity through the reduced form of the Eigen equation:

$$k_{-d} = 2kT / (\pi\eta r^3) \quad (6)$$

where η is the solvent viscosity and r is the radius of the solvent cage. From this equation, k_{-d} is computed by using the viscosity of methanol/water mixtures at 30 °C (Table 2) and by estimating that the solvent cage size is equal to that of the ion-radical pair with a radius of about 1 nm. The obtained k_{-d} values showed a little variation in the methanol/water mixtures and an important increase in methanol (Table 2). According to equation (5), this change of k_{-d} produces an increase in the yield of cage escape Y_{ce} on going from methanol/water mixtures to neat methanol.

The back electron-transfer rate constant from the geminate pair, k_{bc}, can be calculated from equation (5) together with the values of Y_{ce} and k_{-d}. Their values are also reported in Table 1 and range from 3.2 × 10⁹ to 1.3 × 10¹⁰ s⁻¹. The values for the decay to ground state are of the same order than those reported for solvent-separated ion pairs in the series of excited tetracyanoanthracene acceptor–alkylbenzene donor systems.^{19a}

Table 2. Cage escape rate constant from the ion-radical pair [Ru(bpy)₃⁺, DCP⁻] and solvent viscosity at 30 °C in methanol/water solutions (NaOH 0.01 M)

Methanol in water	% (v/v)			
	25	50	75	100
η [Cp] ^a	1.24	1.38	1.10	0.511
k _{-d} × 10 ⁻⁹ [s ⁻¹]	2.1	1.9	2.4	5.2

^a From Ref. 26.

The increase of Y_{ce} by the change of solvent from water to methanol may also be associated with the observed decrease of the rate constant k_{bc} (Table 1). The observed solvent effect on k_{bc} could be considered as a solvent cage effect. The solvent cage for the ion-radical pair is relatively weak in the less polar solvent, which shows weaker intermolecular hydrogen bonding, thus rendering a slower back electron-transfer to the ground-state process.

On the other hand, we must realize that an explanation of the solvent composition effect on the k_{bc} cannot be simple if the above discussion regarding the participation of CIP and SSIP intermediaries in the electron-transfer photo-induced reactions mechanism is taken into account.

However, from many experimental data reported in the literature,¹¹ the solvent motion appears to become the rate-limiting factor when alcohols are used as polar liquids. For some studied cases in Ref. 11a, the back electron-transfer reaction in alcohol solvents is clearly controlled by solvent relaxation. It was also remarked that other solvent properties such as hydrogen bonding in the alcohol solvents may be involved.

In summary, the increase of Y_{ce} from water to methanol and the effect of the second chloro atom on the oxidation reaction, and therefore on the k_q values for the quenching of emission of the $(^3CT)Ru(bpy)_3^{2+}$ by the dichlorophenols (2,4-DCP, 2,5-DCP and 2,6-DCP), are probably the most remarkable findings in this study. The increase in the cage escape yield from water to methanol for the $(^3CT)Ru(bpy)_3^{2+}/DCP^-$ quenching pair was discussed in terms of combined effects of solvent viscosity, which produces an increase in the k_{-d} value, and of a relatively weak solvent cage in the less polar solvent producing a decrease in the k_{bc} value.

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