



ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 119 (1998) 85–91

Journal of  
Photochemistry  
and  
Photobiology  
A: Chemistry

## Water induced electron transfer from hematoporphyrin triplet state to metronidazole

Serguei V. Kuznetsov, Marc Bazin, René Santus\*

Muséum National d'Histoire Naturelle, Laboratoire de Photobiologie INSERM U 312, Paris, France

Received 9 July 1998; received in revised form 3 September 1998; accepted 11 September 1998

### Abstract

The electron transfer from an optically excited donor (hematoporphyrin) to an acceptor (metronidazole) has been investigated by 532 nm laser flash photolysis in water, in organic solvents (alcohols, acetonitrile, formamide, *N*-methylformamide, *N,N*-dimethylformamide and dimethylsulfoxide) and in binary mixtures of these solvents with water. The electron transfer is characterized by the quenching of the donor triplet–triplet transient absorption by metronidazole. The quenching constant has a maximum value of  $2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in water. This constant decreases according to an exponential function as the water content of the binary water–cosolvent mixtures decreases. In neat organic solvents, the electron transfer has only been observed in methanol and formamide, but at a rate three orders of magnitude lower than that in water. The changes in the rate constants and activation parameters of the electron transfer in going from water to neat solvents are not compatible with Marcus' theory. The water-induced electron transfer is analyzed in terms of specific solute–water interactions. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Hematoporphyrin; Metronidazole; Triplet state; Electron transfer; Solvent effect

### 1. Introduction

Photoinduced electron transfer (ET) is one of the most important primary processes encountered in many chemical and biochemical reactions and is the subject of a large body of experimental and theoretical investigations [1–3].

The most extensive researches in this area deal with the ET theory for systems of donors and acceptors which are randomly distributed in space and in fixed positions [4–6]. This theory has also been extended to solid liquids to include diffusion of the reactants [7,8]. However, because of the complexity of the problem of forward and back transfers in systems undergoing molecular diffusion, there are serious difficulties in applying this theory to liquid solutions [9,10]. In particular, the forward transfer parameters obtained from the solid and liquid samples are virtually identical, while the back transfer parameters obtained from solid solutions are able to reproduce the liquid solution's back-transfer data

only when the high-frequency dielectric constant is used. Existing ET theories describing diffusion-controlled reactions in liquid solutions are generally based on dielectric continuum of medium [1,11,12]. They are in good agreement with experimental data when the influence of nonelectrostatic terms and effects of specific solute–solvent interaction on the rate of reactions or quantum yields are negligible [1,13,14]. In the case of photochemical reactions accompanied by extensive structural reorganization within the reactive species [15] or directly induced by solvent molecules [16–18] experimental data, as a rule, are opposite to those predicted by standard dielectric continuum theories. There is, thus, considerable current interest in the search and study of ET systems showing pronounced structural effects to better understand the application limits of existing theories. In addition, new experimental data about these type of reactions and their mechanisms should help to improve the ET theory.

In this work, we have investigated the solvent effects on the kinetic and activation parameters of the electron transfer from the hematoporphyrin triplet state ( $^3\text{HP}^*$ ) to metronidazole (METRO) a nitroimidazole derivative. To this end, the quenching of the  $^3\text{HP}^*$  transient absorption by METRO was studied in water, various organic solvents and their binary water–cosolvent mixtures.

**Abbreviations:** HP, hematoporphyrin;  $^3\text{HP}^*$ , first excited triplet state of hematoporphyrin; METRO, metronidazole

\*Corresponding author: Tel.: +33-1-40793726; fax: +33-1-40793716; e-mail: santus@mnhn.fr

## 2. Experimental details

### 2.1. Materials

Hematoporphyrin (HP) and metronidazole (METRO) were obtained, respectively, from the Sigma and Janssen Chimica (Beerse, Belgium). Alcohols of the purest available grade were provided by Merck or by Fluka. Formamide, *N*-methylformamide (NMF), *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO) were purchased from Merck whereas Janssen Chimica provided acetonitrile. All these solvents were used without further purification. Water was bidistilled in a quartz still from Quartex (Paris, France). Aqueous solutions were buffered with sodium phosphate (100 mM, pH 7.4).

### 2.2. Measurements

Flash photolysis experiments were carried out with a Quantel YG44 Nd : YAG laser using 532 nm as the excitation wavelength. The optical cell, the excitation path-length and analyzing light conditions are the same as those used by Bazin et al. [19]. Transient species generated by absorption of light from the 6 ns duration pulses were monitored at  $\lambda_{\text{max}} = 440$  nm (corresponding to the maximum of the HP triplet–triplet absorption [20]) or at  $\lambda_{\text{max}} = 690$  nm (corresponding to the maximum of the HP radical–cation absorption [21]). Five to ten shots were taken into account for each measurement, depending on the signal/noise ratio. Kinetics were then averaged and analyzed by means of computerized least square fitting procedures using the Hewlett-Packard 98820 statistical library. The temperature of the cell holder was adjusted with a thermostated bath (Huber, Germany). Temperature measurements were carried out with a YSI-401 thermistor (Yellow Springs Instrument, USA) attached to the optical cell (accuracy:  $\pm 0.5^\circ\text{C}$ ). All the experiments were carried out in argon-saturated solutions.

## 3. Results and discussion

### 3.1. Solvent effect on the quenching of $^3\text{HP}^*$ by metronidazole

Table 1 shows that in argon-saturated water and a variety of neat solvents, the hematoporphyrin triplet state ( $^3\text{HP}^*$ ) formed upon 532 nm laser flash photolysis decays by first-order kinetics with a rate constant  $k_{\text{T}}^0 \leq 5 \pm 2 \times 10^4 \text{ s}^{-1}$ . In the presence of metronidazole (METRO), in water and in binary water–cosolvent mixtures, a slow decay corresponding to a transient absorption with a maximum in the 690 nm region follows the initial and fast  $^3\text{HP}^*$  transient decay. Fig. 1 shows typical kinetics observed at 440 nm (Fig. 1(A); transient 1) and at 690 nm (Fig. 1(A); transient 2) in a *n*-propanol–water mixture. Transient 2 (Fig. 1) can be attributed to the formation of the HP radical-cation ( $\text{HP}^{\cdot+}$ ) by electron transfer from  $^3\text{HP}^*$  to METRO [21]. The METRO radical-anion transient ( $\text{METRO}^{\cdot-}$ ) has a maximum in the 500 nm region, but it also weakly contributes to the transient absorption at 440 nm [22]. Furthermore, in the presence of a constant METRO concentration, the rate constant of the  $^3\text{HP}^*$  triplet decay ( $k_{\text{T}}$ ) and the rate constant ( $k_{\text{R}}$ ) of the  $\text{HP}^{\cdot+}$  formation decreases as the water content of the binary water–cosolvent mixture decreases. However  $k_{\text{T}}$  and  $k_{\text{R}}$  remain correlated (Fig. 1(B)). Furthermore, the decay rate of the  $^3\text{HP}^*$  depends, as expected, on the METRO concentration (Fig. 2), according to the relationship:

$$k_{\text{T}} = k_{\text{T}}^0 + k_{\text{Q}}[\text{METRO}] \quad (1)$$

where  $k_{\text{Q}}$  is the quenching constant. The quenching of  $^3\text{HP}^*$  by METRO is clearly a dynamic process. However, the value of  $k_{\text{Q}}$  is dramatically decreased in neat solvents as compared to that in water. Thus, among the neat solvents investigated, the dynamic quenching by METRO was observed only with methanol and formamide (Fig. 2; Inset) with  $k_{\text{Q}}$  values three orders of magnitude less than that in water (Table 1).

Table 1

Rate constant ( $k_{\text{T}}^0$ ) of the  $^3\text{HP}^*$  deactivation, bimolecular rate constant ( $k_{\text{Q}}$ ) for the quenching of the  $^3\text{HP}^*$  by  $\text{ArNO}_2$  in water and neat solvents, and  $\gamma$  value corresponding to solvents used in binary water–cosolvent mixtures (see Eq. (2))

Solvent	$\epsilon_{\text{T}}^{\text{a}}$	$k_{\text{T}}^0$ ( $\text{s}^{-1}$ )	$k_{\text{Q}}$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$\gamma$
Water <sup>b</sup>	78.5	$1 \times 10^4$	$2.1 \times 10^9$	–
Methanol	32.6	$5 \times 10^4$	$1.2 \times 10^6$	7.87
Ethanol	24.3	–	no	19.7
1-Propanol	20.1	–	no	39.3
1-Butanol	17.1	–	no	74.1
Formamide	109	$3 \times 10^4$	$1.9 \times 10^6$	6.03
NMF	182	$2 \times 10^4$	no	17.8
DMF	36.7	$3 \times 10^4$	no	36.6
Acetonitrile	35.9	$3 \times 10^4$	no	16.2
DMSO	46.5	$3 \times 10^4$	no	32.6

<sup>a</sup> Dielectric constant of neat solvents at 25°C.

<sup>b</sup> 0.01 M sodium phosphate buffer (pH 7.4).

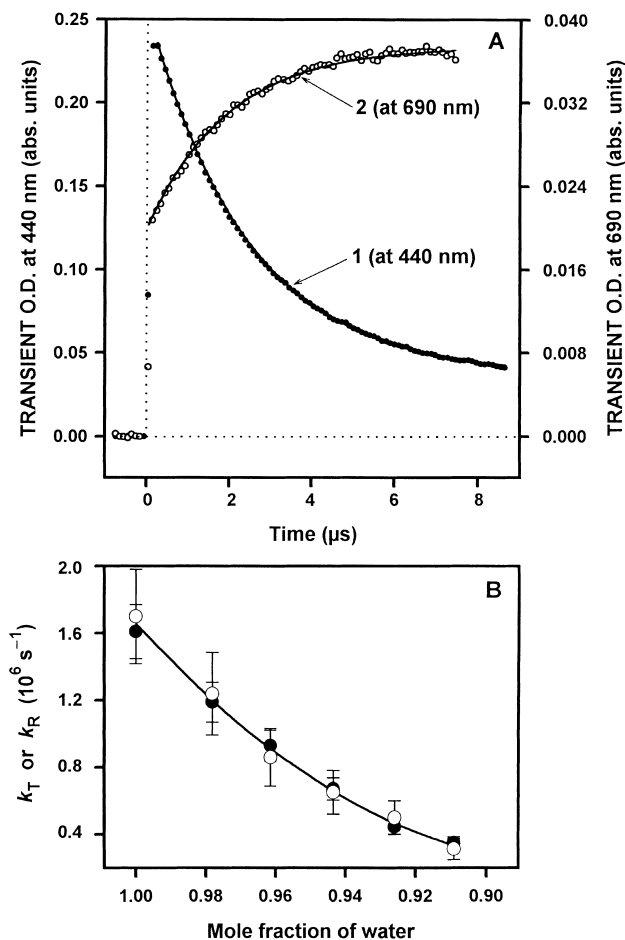


Fig. 1. (A) Decay kinetics of the  $^3\text{HP}^*$  transient and kinetics of  $\text{HP}'^+$  transient formation observed at 440 nm and 690 nm, respectively, after 532 nm laser flash excitation in the presence of 0.63 mM metronidazole in argon-saturated 1-propanol-water 30% v/v mixture. Solid lines are exponential fit of the kinetics. (B) Rate constants of the  $^3\text{HP}^*$  decay ( $k_T$ ; ●) and  $\text{HP}'^+$  formation ( $k_R$ ; ○) in the presence of 0.85 mM of METRO as a function of the mole fraction of water in 1-propanol-water mixtures.

Fig. 3 depicts for two examples the dependence of  $k_Q$  with the mole fraction of water ( $\text{MF}_{\text{water}}$ ) in the mixture. These curves can clearly be approximated as exponentials. They are described by the following equation:

$$k_Q = \frac{k_T - k_T^0}{[\text{METRO}]} = k_Q^w \exp\{-\gamma(1 - \text{MF}_{\text{water}})\} \quad (2)$$

where  $\gamma$  is a proportionality coefficient depending on the kind of solvent in the mixture. The  $\gamma$  values listed in Table 1 have been calculated as the slope of  $\ln k_Q$  as a function of  $\text{MF}_{\text{water}}$  (Fig. 3; Inset). In all cases the regression coefficient was  $r^2 > 0.97$ .

All these experimental data strongly suggest that water plays a key role in the electron transfer between  $^3\text{HP}^*$  and METRO. It may be proposed that the including effect of water on the ET reaction implies that the water molecule(s) directly participate(s) in the reorganization of the collision complex into a configuration which allows the irreversible electron transfer through the formation of an activated

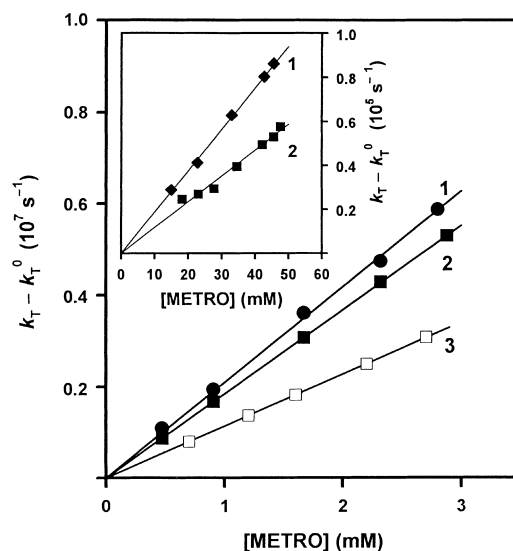


Fig. 2. Stern-Volmer plots for the quenching of  $^3\text{HP}^*$  by METRO in 0.01 M sodium phosphate buffer, pH 7.4 (1), in methanol-water 20% v/v mixture. Inset: Stern-Volmer plots in formamide (1) and methanol (2).

complex (exciplex). In neat solvents, with the exception of methanol and formamide, the electron transfer either does not occur or is completely reversible, i.e. the collision complex dissociates into  $^3\text{HP}^*$  and METRO since, in the presence of METRO, the natural lifetime of  $^3\text{HP}^*$  ( $\tau_T = 1/k_T^0$ ) is about the same in neat solvents as it is in water in the absence of METRO (Table 1). It must be noted that in methanol and formamide, where the electron transfer takes place, the inducing effect of these two solvents is much weaker than that of water.

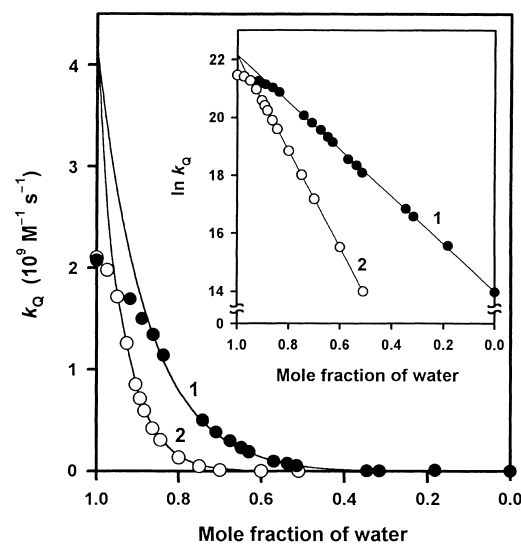
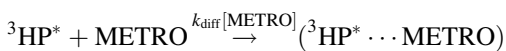
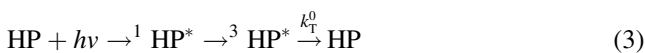


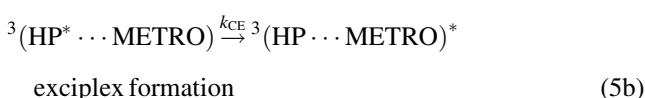
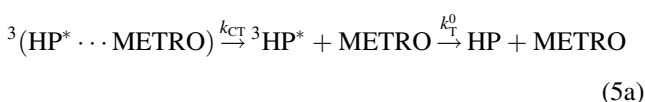
Fig. 3. Variation of the quenching constant ( $k_Q$ ) of  $^3\text{HP}^*$  by METRO as a function of the mole fraction of water in methanol-water mixtures (1; ●) and acetonitrile-water mixtures (2; ●). Inset: Variation of  $\ln k_Q$  as a function of the mole fraction of water in methanol-water mixtures (1; ●) and acetonitrile-water mixtures (2; ○).

### 3.2. Kinetic analysis of the quenching of $^3\text{HP}^*$ by metronidazole

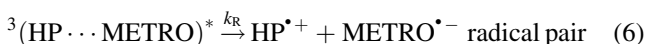
On the basis of the above data, the electron transfer from  $^3\text{HP}^*$  to METRO can be described by the following scheme (Eqs. (3)–(5a) and (6)):



collision complex



exciplex formation



The kinetic analysis of reactions Eqs. (3)–(5a) and (6) leads to the following expression for  $k_{\text{T}}$

$$k_{\text{T}} = k_{\text{T}}^0 + k_{\text{diff}} p [\text{METRO}] \quad (7)$$

where  $p = k_{\text{CE}} / (k_{\text{CE}} + k_{\text{CT}})$  is a probability factor for the transition from the collision complex state to the exciplex state,  $k_{\text{CE}}$  and  $k_{\text{CT}}$  are the rate constants characterizing the number of transitions per time unit resulting from the evolution of the collision complex state to the exciplex state and triplet state, respectively.  $k_{\text{diff}}$  is the diffusion-controlled rate constant.

The extent to which  $k_{\text{Q}}$  is affected by changes in  $k_{\text{diff}}$  (Eq. (7)) in going from water to neat solvents was studied in water–methanol mixtures for two reasons. First, among neat solvents, the electron transfer only takes place in neat methanol and formamide (Table 1) and, secondly, the physico-chemical properties of methanol are very close to those of water. To calculate  $k_{\text{diff}}$ , we used Debye's equation [23].

$$k_{\text{diff}} = \frac{2}{3\eta} RT \frac{(a_1 + a_2)^2}{a_1 a_2} 10^6 (\text{M}^{-1} \text{s}^{-1}) \quad (8)$$

where  $\eta$  (cP) is the viscosity,  $R$  ( $8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ ) is the gas constant,  $T$  is the absolute temperature (293 K, under our experimental conditions),  $a_1$  and  $a_2$  are the hydrodynamic radius of solutes. It is evident that the hydration of reactants by molecules of a given liquid increases their radius and leads to a change in their density to values closer to that of the liquid. The average hydrodynamic radius of HP and METRO in solution may be expressed as

$$a = \sqrt[3]{\frac{3M_0}{4\pi N\rho}} \times 10^8 \text{ \AA} \quad (9)$$

where  $M_0$  ( $\text{g mol}^{-1}$ ) is the mole weight of the solute,  $\rho$  ( $\text{g cm}^{-3}$ ) is the density of the liquid, and  $N$  is Avogadro's number. Indeed, the hydrodynamic radius determination by this way seems to be as correct as calculation of density of reactants from X-ray crystallography data [24]. For example, using a value of  $1.23 \text{ g cm}^{-3}$  as the density determined by three-dimensional X-ray diffraction of tetrapyrrols [25,26], the average radius of HP is found to be  $5.8 \text{ \AA}$  as compared to  $6.2 \text{ \AA}$  obtained by Eq. (9). In water using both radius values, the calculated  $k_{\text{diff}}$  differ by no more than 2%. It can therefore be deduced that this formula allows the calculation of reasonable values of the hydrodynamic radius of solutes in going from water to methanol. As a consequence, values ranging from  $4.1$  to  $4.4 \text{ \AA}$  and from  $6.2$  to  $6.7 \text{ \AA}$  were used as hydrodynamic radius of METRO and HP, respectively, for the calculation of  $k_{\text{diff}}$  listed in Table 2.

As can be seen from Table 2, in water,  $k_{\text{Q}}$  is nearly three times less than  $k_{\text{diff}}$ , i.e. one third of the collisions only lead to electron transfer. In neat methanol  $k_{\text{diff}}$  is twice greater than it is in water, but  $k_{\text{Q}}$  is a thousand-fold smaller. In methanol, the limiting factor governing the 'preparation' of the optimal configuration of the collision complex for ET is, probably, the lifetime of  $^3\text{HP}^*$ . Thus, practically, changes in  $k_{\text{diff}}$  have virtually no influence on the linear character of  $\ln k_{\text{Q}}$  plots as function of  $\text{MF}_{\text{water}}$  (Fig. 3).

Table 2  
Rate constants and activation parameters of the quenching of  $^3\text{HP}^*$  by metronidazole in binary water–methanol mixtures

Mole fraction of methanol in water	$k_{\text{Q}}$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$k_{\text{diff}}$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$k_{\text{act}}$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$E_{\text{a}}$ ( $10^3 \text{ J mol}^{-1}$ )	$\Delta S_{\text{ws}}^* - \Delta S_{\text{w}}^*$ ( $\text{J mol}^{-1} \text{ K}^{-1}$ )	$\Delta F_{\text{ws}}^* - \Delta F_{\text{w}}^*$ ( $10^3 \text{ J mol}^{-1}$ )	$\lambda$ ( $10^3 \text{ J mol}^{-1}$ )
0.00	$2.1 \times 10^9$	$6.8 \times 10^9$	$3.0 \times 10^9$	29	0	0	81
0.04	$1.6 \times 10^9$	$5.6 \times 10^9$	$2.2 \times 10^9$	24	-20	0.8	80
0.10	$9.6 \times 10^8$	$4.5 \times 10^9$	$1.2 \times 10^9$	23	-30	2	79
0.16	$6.0 \times 10^8$	$4.0 \times 10^9$	$7.0 \times 10^8$	17	-52	4	79
0.23	$3.5 \times 10^8$	$3.7 \times 10^9$	$3.9 \times 10^8$	12	-75	5	78
0.40	$9.1 \times 10^7$	$3.9 \times 10^9$	$9.3 \times 10^7$	5	-108	9	76
0.51	$3.9 \times 10^7$	$4.4 \times 10^9$	$3.9 \times 10^7$	7	-109	11	75
0.64	$1.4 \times 10^7$	$5.4 \times 10^9$	$1.4 \times 10^7$	2	-133	13	75
1.00	$1.2 \times 10^6$	$11.6 \times 10^9$	$1.2 \times 10^6$	0.8	-159	19	73

### 3.3. Activation parameters of the quenching of $^3\text{HP}^*$ by metronidazole

The activation energies ( $E_a$ ) of the quenching of  $^3\text{HP}^*$  by METRO in methanol–water mixtures and in various water–cosolvent mixtures listed in Tables 2 and 3 were calculated from Arrhenius plots:  $\ln k_Q$  versus  $1/T$ . In water, the value of  $E_a$  is about  $30 \text{ kJ mol}^{-1}$  and is close to the value expected for diffusion-controlled processes. However, in binary mixtures, as  $k_Q$  is decreased the activation barrier of the quenching is not increased (Fig. 4; curve 1), but, on the contrary, it is decreased. In neat methanol, where  $k_Q$  is a thousand-fold smaller than it is in water, the activation barrier of the quenching is about  $1 \text{ kJ mol}^{-1}$ . According to the activated complex theory [27] this situation can take place when the rate of reaction is not governed by the heat of activation but rather by the change in the free energy of activation. More specifically, if the solvent effect is accompanied by a large decrease in entropy then, in spite of the low barrier of activation, the rate is small.

Tables 2 and 3 report the values of the changes in entropy of activation ( $\Delta\Delta S^*$ ) for water–methanol mixtures and various water–cosolvent mixtures. The  $\Delta\Delta S^*$  values were calculated from the relationship [15,27]

$$\Delta\Delta S^* = \Delta S_{\text{ws}}^* - \Delta S_{\text{w}}^* = R[(\ln k_{\text{Q}}^{\text{ws}} + E_a^{\text{ws}}/RT) - (\ln k_{\text{Q}}^{\text{w}} + E_a^{\text{w}}/RT)] \quad (10)$$

Subscripts ‘w’ and ‘ws’ correspond to water and water–cosolvent mixtures, respectively. Curve 2 in Fig. 4 suggests that the decrease in  $k_Q$  correlates with the decrease in the entropy of activation in binary water–cosolvent mixtures.

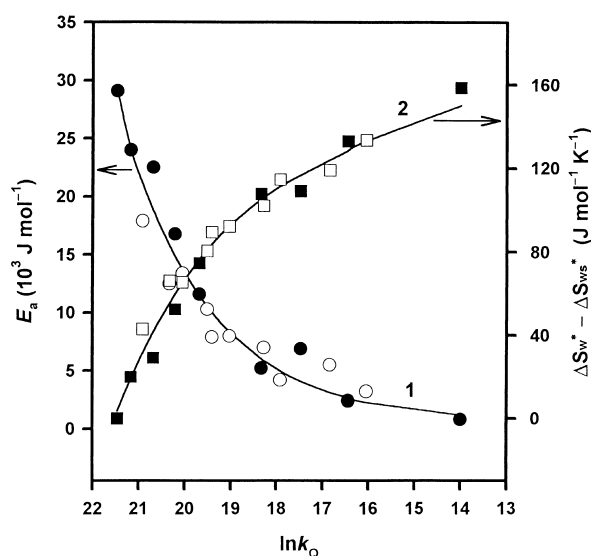


Fig. 4. Activation energies ( $E_a$ ; curve 1) and changes in entropy of activation ( $\Delta S_{\text{w}}^* - \Delta S_{\text{ws}}^*$ ; curve 2) as a function of logarithm of the quenching constant ( $\ln k_Q$ ): ● and ■, correspond to the values in methanol water mixtures listed in Table 2; ○ and □ correspond to the values in various cosolvent–water mixtures listed in Table 3.

Moreover, the contribution of the changes in  $E_a$  to Eq. (8) is practically negligible. These data support the view that it is the reorganization processes within the collision complex and/or the activated complex that affect the quenching rate in going from water to neat solvents.

According to Marcus' theory [1,11] the changes in dielectric properties are expected to affect the reorganization of solvent molecules around the reactant and activated complex. While the macroscopic dielectric properties of water and methanol are not very different, the water–methanol mixtures exhibit marked structural and dielectric changes [28,29] which are probably related to the thousand-fold decrease in the  $k_Q$  values observed in going from water to methanol. Accordingly it may be supposed that the microscopic properties of water and other alcohols as well as their mixtures are essentially different. Consequently, depending on the solvent under consideration, the organization of solvent molecules around the reacting species may differ.

Classically, the thermodynamics of the outer-sphere reorganization processes during the electron transfer can be estimated from the Marcus theory. It is therefore interesting to study whether, in the  $^3\text{HP}^*$ –METRO system, the kinetics and activation parameters are relevant to Marcus' theory. According to this theory, for water–methanol mixtures the changes of the free energy of activation ( $\Delta\Delta F^*$ ) can be calculated (Table 2) from the relationship [1]

$$\Delta\Delta F^* = \Delta F_{\text{ws}}^* - \Delta F_{\text{w}}^* = RT(\ln k_{\text{act}}^{\text{w}} - \ln k_{\text{act}}^{\text{ws}}) \quad (11)$$

where  $k_{\text{act}}$  is the constant of activation. Here, we suppose that the number of collisions in the solutions does not practically change in going from water to methanol. The value of  $k_{\text{act}}$  listed in Table 2 can be obtained from the relationship [1]

$$1/k_{\text{obs}} = 1/k_{\text{diff}} + 1/k_{\text{act}} \quad (12)$$

In our case,  $k_{\text{obs}}$  corresponds to  $k_Q$ . From Marcus' theory it follows that  $\Delta F^*$  is related to  $\lambda$ , the outer-sphere reorganization energy, to  $\Delta F^0$ , the standard free energy of reaction in the prevailing medium, and to  $W$ , the difference in work of bringing together the reactants and separating the products of reaction [1]

$$\Delta F^* = W + \frac{\lambda}{4} \left( 1 + \frac{\Delta F^0}{\lambda} \right)^2 \quad (13)$$

The value of  $W$  can be neglected in comparison with  $\lambda$  and  $\Delta F^0$  since METRO is uncharged. The outer-sphere reorganization energy  $\lambda$  can be expressed as [1]:

$$\lambda = \left[ \frac{1}{2a_{\text{D}}} + \frac{1}{2a_{\text{A}}} - \frac{1}{a_{\text{DA}}} \right] \left[ \frac{1}{D_{\text{op}}} - \frac{1}{D_{\text{s}}} \right] k(\Delta z)^2 e^2 \quad (14)$$

where  $D_{\text{s}}$  and  $D_{\text{op}}$  are the static and optical (square of refractive index) dielectric constants of the liquid,  $a_{\text{D}}$  and  $a_{\text{A}}$  are the radii of electron donor and electron acceptor molecules,  $a_{\text{DA}}$  is the effective radius of the reaction,  $\Delta z$  is the number of electrons transferred, and  $k = N/4\pi\epsilon_0$

Table 3  
Value of  $k_Q$  and activation parameters of the quenching of  $^3\text{HP}^*$  by metronidazole in various binary water–cosolvent mixtures

Cosolvent in water	$k_Q$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$E_a$ ( $10^3 \text{ J mol}^{-1}$ )	$\Delta S_{\text{ws}}^* - \Delta S_{\text{w}}^*$ ( $\text{J mol}^{-1} \text{ K}^{-1}$ )
DMF 6% v/v	$1.21 \times 10^9$	17.9	–43
DMF 12% v/v	$6.75 \times 10^8$	12.5	–66
1-Butanol 9% v/v	$5.10 \times 10^8$	13.4	–65
DMSO 20% v/v	$2.97 \times 10^8$	10.3	–80
Acetonitrile 30% v/v	$2.68 \times 10^8$	7.9	–89
Formamide 60% v/v	$1.83 \times 10^8$	8.0	–92
DMSO 30% v/v	$8.60 \times 10^7$	7.0	–102
DMF 32% v/v	$6.03 \times 10^7$	4.2	–114
Ethanol 50% v/v	$2.05 \times 10^7$	5.5	–119
1-Propanol 40% v/v	$9.27 \times 10^6$	3.2	–133

( $\epsilon_0 = 8.85 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$  is the vacuum permittivity). The values of  $\lambda$  for water–methanol mixtures were calculated using the values of  $a_D$ ,  $a_A$  whereas  $a_{\text{DA}} = a_D + a_A$  was used for calculation of  $k_{\text{diff}}$ . From Eqs. (11) and (13) it follows that the  $k_{\text{act}}$  must increase with decreasing  $\lambda$  in going from water to methanol. However, the changes in the  $k_{\text{act}}$  value (Table 2) are in disagreement with this prediction. As a consequence, the lack of correlation between the macroscopic polarization properties of the medium and the parameters characterizing the solvent effect rather suggests that the change in the microscopic properties in the vicinity of the reacting species plays a key role in determining the irreversibility or the reversibility of the electron transfer (reactions Eqs. (5a) and (5b)).

From our experiment data it is evident that the electron transfer becomes practically irreversible only when water molecules are present within the collision complex. Thus, in the solvent reorganization preceding the electron transfer, the specific solvation of the collision complex by water may become the determining factor of the irreversibility of the electron transfer. Studies on organic molecules in aqueous solutions indicate that they are surrounded by solvent molecules sequestered by hydrogen bonds [2]. For methanol–water mixtures, it is known that hydrogen bond formation is stronger in water than in methanol because it takes more energy to break the structure of water than that of methanol. Moreover, even if the mole ratio in the bulk is the same as in the solvent shell, hydrogen bonding with the solute preferentially occurs with methanol [30]. Thus, the decrease in the activation barrier is going from water to methanol (Fig. 4) takes probably place because the breaking of the medium structure facilitates the transition of reactants from the collision complex to the activated complex state. On the other hand, the preferential solvation of the collision complex by methanol hinders the access of water molecules to the collision complex and also decreases the rate of reaction. In this regard it is interesting to note that an increase in the size of the solvent molecules in the alcohol and formamide families leads to an increase in the  $\gamma$  parameter (Table 1) which is linked to  $k_Q$  via Eq. (2). Furthermore, the tendency of  $E_a$  to decrease in parallel to  $k_Q$  observed in water–

methanol mixtures (Fig. 4) is also found for other binary water–cosolvent mixtures (Table 3). We can therefore suggest that the mechanism we propose here on the effect of methanol on the kinetics and activation parameters of the water-induced electron transfer from  $^3\text{HP}^*$  to METRO is the same for all the solvents investigated. The study of a possible general correlation linking  $\gamma$  to the empirical parameters characterizing solvents [31] such as  $\alpha$ ,  $\beta$  and  $\pi^*$  is under way.

### Acknowledgements

We are grateful to Paul Mathis from CEA (Saclay) for very helpful comments. S.K. is pleased to acknowledge a travel grant from Museum National d'Histoire Naturelle.

### References

- [1] R.A. Marcus, N. Sutin, *Biochim. Biophys. Acta* 811 (1985) 265.
- [2] C. Reichardt, *Solvent Effects in Organic Chemistry*, VCH, Weinheim, 1988.
- [3] E. Kohen, R. Santus, J.G. Hirschberg, *Photobiology*, Academic Press, Orlando, 1995.
- [4] J.R. Miller, *Chem. Phys. Lett.* 22 (1973) 180.
- [5] M. Tachiya, A. Mozumder, *Chem. Phys. Lett.* 28 (1974) 87.
- [6] R.K. Huddleston, J.R. Miller, *J. Phys. Chem.* 86 (1982) 200.
- [7] R.C. Dorfman, Y. Lin, M.B. Zimmt, J. Baumann, R.P. Domingue, M.D. Fayer, *J. Phys. Chem.* 92 (1988) 4258.
- [8] R.C. Dorfman, Y. Lin, M.D. Fayer, *J. Phys. Chem.* 94 (1990) 8007.
- [9] L. Song, R.C. Dorfman, S.F. Swallen, M.D. Fayer, *J. Phys. Chem.* 95 (1991) 3454.
- [10] L. Song, S.F. Swallen, R.C. Dorfman, K. Weidemaier, M.D. Fayer, *J. Phys. Chem.* 97 (1993) 1374.
- [11] R.A. Marcus, *J. Chem. Phys.* 43 (1965) 3477.
- [12] E.S. Amis, *Solvent Effects on Reaction Rates and Mechanisms*, Academic Press, New York, 1966.
- [13] M. Hoebeke, A. van de Vorst, *Photochem. Photobiol.* 61 (1995) 347.
- [14] S. Murata, S.Y. Matsuzaki, M. Tachiya, *J. Phys. Chem.* 99 (1995) 5354.
- [15] O.I. Micic, B. Cereck, *J. Phys. Chem.* 78 (1974) 285.
- [16] A. Wakisaka, T.W. Ebbesen, H. Sacuragi, K. Tokumaru, *J. Phys. Chem.* 91 (1985) 6547.
- [17] T.W. Ebbesen, C.A. Ghiron, *J. Phys. Chem.* 93 (1989) 7139.

- [18] S.V. Kuznetsov, M. Bazin, R. Santus, J. Photochem. Photobiol. A: Chem. 103 (1997) 57.
- [19] M. Bazin, L.K. Patterson, J.C. Ronfard-Haret, R. Santus, Photochem. Photobiol. 48 (1998) 177.
- [20] E. Reddi, G. Jori, M.A.J. Rodgers, J.D. Spikes, Photochem. Photobiol. 38 (1983) 639.
- [21] R. Bonnett, C. Lambert, E.J. Land, P.A. Scourides, R.S. Sinclair, T.G. Truscott, Photochem. Photobiol. 38 (1983) 1.
- [22] M. Bazin, R. Santus, Photochem. Photobiol. 43 (1986) 235.
- [23] P.W. Atkins, Physical Chemistry, 5th ed., Oxford University Press, Oxford, 1995.
- [24] T.M. Cotton, R.L. Heald, J. Phys. Chem. 91 (1987) 3891.
- [25] K.M. Barkigia, J. Fajer, L.D. Spaulding, G.J.B. Williams, J. Am. Chem. Soc. 103 (1981) 176.
- [26] K.M. Barkigia, J. Fajer, K.M. Smith, G.J.B. Williams, J. Am. Chem. Soc. 103 (1981) 589.
- [27] G.M. Pantchenkov, V.P. Lebedev, Chemical Kinetics and Catalysis, Chemistry, Moscow, 1974.
- [28] CRC Handbook of Chemistry and Physics, 53rd ed., R.C. Weast (Ed.), CRC, Cleveland, 1972.
- [29] N. Nishi, S. Takahashi, M. Matsumoto, A. Tanaka, K. Murays, T. Takamuku, T. Yamaguchi, J. Phys. Chem. 99 (1995) 462.
- [30] C. Lurf, P. Suppan, J. Chem. Soc. Faraday Trans. 88 (1992) 963.
- [31] Y. Marcus, Chem. Soc. Rev. 65 (1993) 409.