

Comparison of the Kinetics of Electron Transfer in the Diffusion Limit for the Singlet and Triplet Quenching of Eosin Y by Quinones

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ABSTRACT

Electron transfer (ET) rate constants were determined by means of lifetime measurements for the fluorescence quenching and by laser flash photolysis for the triplet quenching of the dye eosin Y by benzoquinones in acetonitrile. The results represent a new aspect of the dependence of the rate constants with the driving force in the diffusion limit region. That is, the rate constants for singlet quenching in the highly negative region of ΔG_{et} do not decrease as predicted by Marcus theory, but rather show a small positive dependence on the driving force. However, it is found that, in the same free energy range, the triplet rate constants are lower than those for the singlet process. They also increase with the exergonicity of the reaction, but the dependence with ΔG_{et} is less marked than that found for the singlet reaction. Even at a Gibbs energy change of -1.0 eV the triplet quenching rate constants do not reach the theoretical diffusion limit. The results are analyzed using the current theories for diffusion-mediated ET reactions.

INTRODUCTION

The kinetics of photoinduced electron transfer (ET) processes is an issue of current interest. The correlation of rate constants with the Gibbs energy change (ΔG_{et}) for intermolecular ET quenching of excited states is amply documented. Since the pioneering work of Rehm and Weller (1,2), it is generally accepted that ET fluorescence quenching rate constants reach a plateau in the exergonic region of ΔG_{et} (< -0.2 eV) and decrease when the driving force becomes positive. The value of the rate constant at the plateau is generally identified with the diffusion limit in the respective solvent. Two of the most employed solvents for photoinduced ET studies of organic molecules are methanol (MeOH) and acetonitrile (MeCN). Diffusional limits of $2.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ in MeCN and $1.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ in MeOH are commonly accepted for bimolecular rate constants at room temperature (3). These values are in agreement with the theoretical Smoluchowski–Stokes–Einstein approximation at 298 K. This is corroborated by numerous experimental studies, especially of bimolecular fluorescence quenching rate constants (4–9). Rehm and Weller results, and most of the fluorescence quenching rate constants in the literature, are derived from Stern–Volmer (SV) plots based on intensity measurements. Frequently SV plots present a positive deviation at high quencher concentration, and

several papers deal with the explanation of this curvature using diffusive models that yield a rate constant that depends on the quencher concentration (5,10–12). From this analysis, a distance-dependent rate constant in the highly exergonic region may be extracted. It is to be noted that this distance increase with $-\Delta G_{\text{et}}$, was previously proposed (13) as a possible explanation for the lack of inverted region in intermolecular rate constants for fluorescence quenching. One of the most used systems to investigate the region of large driving force is the quenching of cyanoanthracenes by electron donors. This system was investigated many years ago by Eriksen and Foote (14) and afterward by Jacques and Allonas (10) and Niwa *et al.* (11) by means of stationary fluorescence measurements. In these studies, curved SV plots at high quencher concentration were analyzed with a diffusional model, and intrinsic ET rate constants were derived. From the analysis the ET effective distance (R_{eff}), the mutual A/D diffusion coefficient (D) and the intrinsic rate constant for ET (k_{et}) can be extracted. These studies confirmed the apparent increase of R_{eff} with decreasing ΔG_{et} .

Less numerous are the studies on the diffusional limit in triplet quenching reactions (15). Kokubun *et al.* (16,17) studied the quenching of synthetic dyes triplet state by aromatic compounds in MeCN. When rate constants were determined directly from the triplet decay, values in the range 5.3×10^9 – $9.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ resulted for the quenching of triplet thionine for $-1.2 < \Delta G_{\text{et}} < -0.5$ eV. Das (18) measured bimolecular rate constants for the triplet-mediated ET from polycyclic aromatic hydrocarbons to methyl viologen in wet MeCN (10% water). The rate constants reach a limiting value between 7×10^9 and $9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ in the exergonic region. This is a factor of 2 lower than the normally accepted diffusion limit in MeCN and the effect cannot be ascribed to an increase in viscosity due to the presence of water. We have previously investigated (19) the singlet and triplet quenching of flavins and lumichrome by aromatic electron donors. The singlet quenching rate constants reach the diffusional limit at highly negative ΔG_{et} . However, for the triplet quenching, the limiting value of the rate constants is lower than the plateau of the singlet quenching.

In summary, ET singlet quenching in MeCN affords a diffusional limit for the rate constants in the order of 2 – $2.5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, whereas for the triplet state processes the limit seems to be below $10^{10} \text{ M}^{-1}\text{s}^{-1}$. In this study, we aim to explore this difference in the limiting value for singlet and triplet quenching in ET processes.

The lack of an inverted region at large negative ΔG_{et} , as predicted by Marcus free energy relation, was an intriguing feature

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of fluorescence quenching studies. Several explanations have been given, see refs (20–22) for a summary, and among them the dependence of the rate constants with the donor–acceptor separation distance was particularly successful in explaining the dependence on ΔG_{et} . Hug and Marciniak (20) analyzed the data of Rehm and Weller with different ET models coupled with a diffusion model developed by Tachiya and Murata (23). They found some difficulties in explaining the whole curve with a single set of parameters, specially the data at high exergonicity. However, an increase in the rate constants at high exergonicity was predicted by the model.

On the other hand, direct measurement of fluorescence quenching rate constants by means of time resolved experiments is much less frequent, in particular to investigate the dependence of the rate constant with ΔG_{et} in the region of high exergonicity (24–26). In a previous study (27), we presented a study of ET rate constants for the fluorescence quenching of 9,10-dicyanoanthracene by aromatic amines and methoxybenzenes as electron donors, and for the quenching of the synthetic dyes eosin Y and phenosafranin by a series of benzoquinones as electron acceptors in MeCN. The quenchers were chosen in order that the free energy change was in the region, $-1.8 \text{ eV} < \Delta G_{\text{et}} < -0.2 \text{ eV}$. The rate constants were determined by means of lifetime measurements and it was found that they increase linearly with the driving force of the ET reaction. At the same time Rosspeintner *et al.* (28) published a study of the fluorescence quenching of an electron donor by several electron acceptors in the region of the diffusion control. From an analysis of SV plots they find a similar distance dependence of the ET rate with ΔG_{et} .

To our knowledge, in the literature, there are no similar studies for the Gibbs energy dependence of triplet quenching rate constants in the region where the diffusion limit is expected. Here, we report a series of results on the quenching of singlet and triplet states of the same molecule by similar quenchers that clearly show that the limit at high exergonicity for the triplet state is lower than the diffusional limit. Moreover, an increase in the triplet rate constant is observed with the exergonicity. We extend the range of our previous study for the singlet quenching of eosin Y by benzoquinones by lifetime measurements and determine the triplet quenching by the same acceptors in the negative ΔG_{et} region. It is found that in the same free energy range, the triplet rate constants are lower than those for the singlet process. They also increase with the exergonicity of the reaction, but the dependence with ΔG_{et} is less marked than that found in the singlet reaction. The results are analyzed using the current theories for diffusion-mediated ET reactions.

MATERIALS AND METHODS

Eosin Y (Eos) was purchased from Aldrich and was used without further purification. It was checked that its Photophysical properties coincided with those reported in the literature. The quenchers 1,4-benzoquinone (BQ), chloro *p*-benzoquinone, *p*-toluquinone, 2,6-dimethylbenzoquinone, duroquinone, tetrachloro *p*-benzoquinone (chloranil, Cl_4Q) and tetrachloro 1,2-benzoquinone (*o*-chloranil, *o*- Cl_4Q) were obtained from Aldrich and were purified by sublimation. MeCN, HPLC grade, was from Sintorgan.

Absorption spectra were recorded using a HP8453 diode array spectrophotometer. Steady-state fluorescence experiments were carried out with a Spex Fluorolog spectrofluorometer. Fluorescence lifetime measurements were carried out with the time correlated single photon counting technique using an Edinburgh Instruments OB-900 equipment. The analysis of the decay was performed with the software provided by Edinburgh Instruments. All fluorescence measurements were carried out

in air-equilibrated MeCN solutions. The temperature was controlled at $25 \pm 0.1^\circ\text{C}$ by water circulation.

Transient absorption spectra and triplet quenching were determined by laser flash photolysis. A Spectron SL400 Nd:YAG laser generating 532 nm laser pulses (20 mJ per pulse, *ca* 18 ns FWHM) was the excitation source. The experiments were performed with rectangular quartz cells with right angle geometry. The laser beam was defocused to cover all the path length (10 mm) of the analyzing beam from a 150 W Xe lamp. The detection system comprises a photon technology international monochromator coupled to a Hamamatsu R666 PM tube. The signal was acquired by a digitizing scope (Hewlett-Packard 54504) where it was averaged and then transferred to a computer. All the triplet kinetics determinations were performed at $25 \pm 1^\circ\text{C}$. For the laser photolysis experiments, the solutions were deoxygenated by bubbling during 30 min with solvent saturated high purity argon.

RESULTS AND DISCUSSION

The fluorescence of Eos was effectively quenched by benzoquinones. The decay in the absence and in the presence of the quenchers could be adjusted with a single exponential. Bimolecular singlet quenching rate constants, $^1k_{\text{q}}$, were determined from fluorescence lifetime determinations according to Eq. (1)

$$\tau^{-1} = \tau_0^{-1} + ^1k_{\text{q}}[\text{Q}] \quad (1)$$

where τ^0 and τ stand for the fluorescence lifetime in the absence and in the presence of the quencher Q respectively. The lifetimes of Eos in air-equilibrated solution were $4.00 \pm 0.04 \text{ ns}$ in MeCN. The correlation coefficient of the linear plots was higher than 0.998.

The T–T transient absorption of Eos in MeCN presents two main positive bands at 400 and 580 nm and a strong bleaching at 520 nm (not shown). The triplet decays with a lifetime of the order of $100 \mu\text{s}$ mainly by self-quenching and is efficiently quenched by electron donors and acceptors (29). In the presence of benzoquinones, it decays with first-order kinetics. Bimolecular quenching rate constants, $^3k_{\text{q}}$, were obtained from a plot of the pseudo-first-order decay rate constants of the triplet state as a function of the quinone concentrations [Q], Eq. (2).

$$k_{\text{obs}} = k^0 + ^3k_{\text{q}}[\text{Q}] \quad (2)$$

A typical plot of the first-order rate constant as a function of [Q] is shown in Fig. 1. In the insets, the decay in the absence

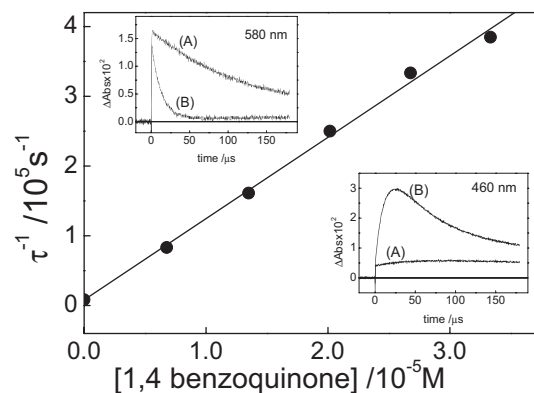


Figure 1. First-order triplet decay of eosin as a function of 1,4-benzoquinone (BQ) in acetonitrile measured at 580 nm at 25°C . Insets: time profiles at 580 and 460 nm in the absence (A) and in the presence (B) of BQ $6.8 \times 10^{-6} \text{ M}$.

and in the presence of BQ and the increase in absorption at 460 nm, where the semioxidized form of the dye absorbs (30), are illustrated. At the latter wavelength, there is also a small contribution from the absorption of the quinone-derived radical (31). The participation of an exciplex in the oxidative quenching of xanthene dyes by quinones was previously postulated (32). However, in the present case, at low quencher concentrations and in a low viscosity solvent, we did not find evidence of exciplex intermediacy in the triplet quenching. The participation of an excited state complex in the triplet quenching leads to a downward curvature in the plots of $1/\tau$ vs $[Q]$ (33–35). In our case, all kinetics plots were linear as shown in Fig. 1, without any evidence of this effect. Singlet and triplet quenching rate constants are collected in Table 1. The estimated errors are $\pm 5\%$ and $\pm 10\%$ for 1k_q and 3k_q respectively.

It is well established that the quenching of xanthene dyes by electron acceptors takes place through an ET mechanism (36,37). In Fig. 2, the time profiles at two wavelengths are presented. It can be seen that the decay of Eos triplet absorption at 580 nm, with a lifetime of 3.6 μs , matches the initial growth of the semioxidized dye at 460 nm. This confirms the oxidative process of the dye in the quenching reaction:



The Gibbs energy changes for the ET processes (ΔG_{et}) can be calculated according to the following equation:

$$\Delta G_{\text{et}} = E_{\text{Eos}^=/\text{Eos}^{-\bullet}} - E_{\text{Q}/\text{Q}^{\bullet-}} - E^* + w \quad (4)$$

where $w = z_1 z_2 e^2 / \epsilon R_{\text{AD}}$ represents the free energy gained by bringing the formed ions (with charges z_1 and z_2) from infinite to the contact distance R_{AD} in a medium of static dielectric constant ϵ . For the systems $\text{Eos}^=/\text{Q}$, with a mean value of $R_{\text{AD}} \sim 0.6$ nm and taking into account that the product $z_1 z_2$ is +1, the coulombic term in MeCN is 0.064 eV. ΔG_{et} for the singlet and triplet reaction were calculated with $E_{(\text{Eos}^=/\text{Eos}^{-\bullet})} = 0.80$ V and $E^* = 2.31$ eV for excited singlet and 1.91 eV for the triplet energy (38,39). The redox potentials of the quinones in MeCN vs SCE were obtained from the literature (40–42). The ΔG_{et} values are also collected in Table 1.

It can be observed in Table 1 that the rate constants become higher when ΔG_{et} becomes increasingly negative. In Fig. 3, the singlet and triplet rate constants are plotted as a function of ΔG_{et} . The singlet rate constants increase beyond the diffusional limit, k_D , whereas the triplet rate constants fall below this value for all the explored ΔG_{et} range, showing a moderate increment as the Gibbs energy becomes more negative.

This dependence of the rate constants on ΔG_{et} is contrary to the commonly accepted result for free energy correlations in ET reactions, in the sense that for driving forces larger than -0.2 eV a plateau should be reached. However, this effect was previously reported for singlet quenching (11,20,27,28). Even in the original data of Rehm and Weller, (1) an increase in the rate constant beyond this limit may be noted for $-\Delta G_{\text{et}} > 2$ eV.

Table 1. Singlet and triplet quenching of Eos by benzoquinones in acetonitrile at 298 K.

Quencher	ΔG_{et} (S)/eV	k_q (S)/ $10^{10} \text{ M}^{-1} \text{ s}^{-1}$	R_{eff} (S)/nm	ΔG_{et} (T)/eV	k_q (T)/ $10^{10} \text{ M}^{-1} \text{ s}^{-1}$
Duroquinone (0.84)*	-0.6	1.23	0.55	-0.21	0.57
2,6-Dimethylbenzoquinone (0.67)*	-0.77	1.54	0.68	-0.38	0.65
p-Toluquinone (0.58)*	-0.86	1.79	0.79	-0.47	0.76
p-Benzoquinone (0.50)*	-0.94	1.99	0.88	-0.55	1.2
Chloro p-benzoquinone (0.34)*	-1.1	2.37	1.05	—	—
Cl_2Q (0.17)*	-1.27	2.47	1.09	-0.88	1.3
o- Cl_4Q (0.15) [†]	-1.29	—	—	-0.90	1.1
Cl_4Q (-0.04)*	-1.44	2.70	1.19	-1.05	1.3

*Reduction potential in acetonitrile vs SCE from refs (40,41); [†]idem from ref. (42).

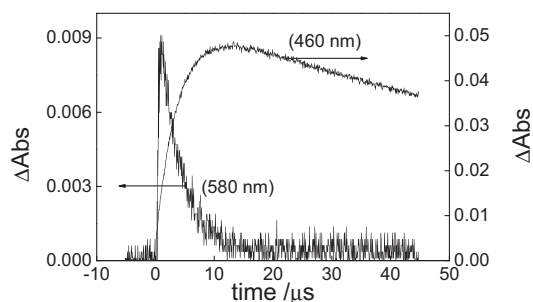


Figure 2. Transient absorption at 580 and 460 nm of Eos in the presence of o-chloranil 2.6×10^{-5} M.

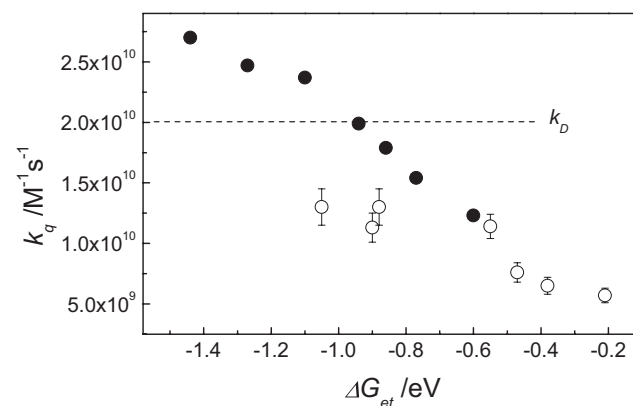


Figure 3. Rate constants as a function of the Gibbs energy for the electron transfer quenching of eosin Y by benzoquinones in acetonitrile. Singlet (●); triplet (○).

What is new is to find a ΔG_{et} dependence for the ET triplet quenching in the region $-0.2 > -1.1$ eV.

The other important point to be discussed is the difference in singlet and triplet rate constants in the same Gibbs energy range, where the diffusion limit is expected to be reached. This effect was formerly observed in the quenching of the dye safranin by anilines and phenols in MeOH (43) where the triplet rate constants clearly are lower than the singlet reaction for the same ΔG_{et} , although the effect went unnoticed in that moment. Later on, a similar effect was detected in the quenching of flavins and lumichrome by electron donors in MeOH (19). Nevertheless, the Gibbs energy dependence of the diffusion limit of the triplet quenching rate constant was not clearly apparent in those results. The results presented here clearly show that in MeCN the ET rate constants for both reactions increase in the Gibbs energy region where the diffusion limit is expected. This may be a consequence of the different molecular structure of the solvent. The available data for singlet quenching in MeOH (19,43) seem to indicate that such effect is absent in this solvent. The importance of the solvent effect on the kinetics in the diffusional regime was already pointed out by Rosspeintner *et al.* (28).

The free energy dependence of the diffusion-limited quenching rate constants in photoinduced ET processes was previously reported by us for the singlet quenching of cyanoanthracene as electron acceptor, and eosin Y and phenosafranin as electron donors in MeCN (27). Different theoretical models were tried to explain the observed trend in the rate constants. The underlying idea is that there is a distance dependence of the intrinsic ET rate. ET reactions can produce diverse ionic species that differ in their degree of solvation such as contact radical ion pairs (CRIP) and solvent separated radical ion pairs (SSRIP). CRIP arise from neutral A/D precursors that have diffused to the contact distance ($R_{\text{AD}} = R_{\text{A}} + R_{\text{D}}$), while SSRIP can be formed (through a solvent-mediated superexchange coupling mechanism) from a wide distribution of A/D pairs in which the reactants are at variable distances (R) (44). In Marcus theory (45), the largest rate for an ET reaction is attained when: $\Delta G_{\text{et}} + \lambda = 0$. Hence, for an ET reaction falling in the inverted region (i.e. $\Delta G_{\text{et}} + \lambda < 0$) there is a significant probability for the process to take place from the solvent separated A/D pairs; species characterized by a larger A/D separation and therefore, by a larger solvent reorganization energy. Another consequence of this interpretation is that the effective A/D separation distance (R_{eff}) at which the ET reaction takes place should increase with decreasing ΔG_{et} .

The analysis of the singlet quenching data in our previous work (27) is summarized here. The theoretical limit for a diffusional controlled rate constant for the reaction $A + Q$ is given by the following equation:

$$k_{\text{D}} = 4\pi DR_{\text{AQ}} \quad (5)$$

here R_{AQ} is the acceptor–donor encounter distance and D is the mutual diffusion coefficient $D_{\text{A}} + D_{\text{Q}}$. This is Smoluchovsky's result (46) for the longtime limit solution of the diffusion equation

$$\frac{\partial \rho}{\partial t} = D\nabla^2 \rho \quad (6)$$

where $\rho(r, t) = \frac{Q}{Q_0}$ is the density distribution of Q about A .

For a diffusional process in which one reactant can transfer an electron to the acceptor over a distance larger than the encounter

separation, Eq. (6) is modified to (47)

$$\frac{\partial \rho}{\partial t} = D\nabla^2 \rho - k(r)\rho(r, t) \quad (7)$$

here $k(r)$ is the distance-dependent ET rate constant that, in a simple formulation, may be written as

$$k(r) = k_0 \exp[-\beta(r - R_{\text{AQ}})] \quad (8)$$

with $k_0 \approx 10^{13} \text{ s}^{-1}$ and $\beta \approx 3\text{--}10 \text{ nm}^{-1}$ (45).

From an integration of Eqs. (7) with (8) for $k(r)$ the rate constant for simultaneous diffusion and long-distance ET is

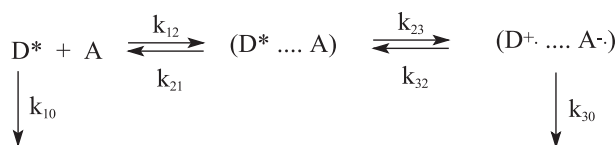
$$k_{\text{D}}(t) = 4\pi DR_{\text{eff}} \left[1 + \frac{R_{\text{eff}}}{(\pi Dt)^{1/2}} \right] \quad (9)$$

and the longtime limit ($t > 1 \text{ ns}$)

$$k_{\text{D}}(t) = 4\pi DR_{\text{eff}} \quad (10)$$

where R_{eff} is an effective distance for the ET process that depends on $k(r)$. Since in our experimental conditions the decay may be fitted with a single exponential, the results may be analyzed with the aid of Eq. (10). With a constant value of $3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for D (10,20) the effective quenching distances given in Table 1 were calculated with Eq. (10). They are in the range of the values obtained from an analysis of SV plots by Jacques and Allonas (10) and Niwa *et al.* (11).

In the case of triplet quenching, if a similar analysis is carried out, the values R_{eff} are in the range of 0.2–0.5 nm, smaller than that estimated for $R_{\text{A}} + R_{\text{D}}$. Therefore, a diverse mechanism other than simple diffusion must be operating in the triplet quenching. A feasible explanation was given (19) in terms of the Rehm–Weller mechanism (Scheme 1) for the quenching of an excited donor (D) by an acceptor (A)



Scheme 1

According to the mechanism, the stationary state rate constant is

$$ptk_{\text{q}} = \frac{k_{12}}{1 + \frac{k_{21}}{k_{23}} \left(\frac{k_{32}}{k_{30}} + 1 \right)} \quad (11)$$

introducing the Gibbs energy change for the ET process

$$\frac{k_{23}}{k_{32}} = \exp(-\Delta G_{\text{et}}/RT) \quad (12)$$

and $k_{23} = k_{23}^0 \exp(-\Delta G^*/RT)$, where ΔG^* is the Gibbs activation energy for the ET step, Eq. (11) becomes

$$k_{\text{q}} = \frac{k_{12}}{1 + \frac{k_{21}}{k_{23}^0} \exp(\Delta G^*/RT) + \frac{k_{21}}{k_{30}} \exp(\Delta G_{\text{et}}/RT)} \quad (13)$$

The limit of Eq. (13) for very exergonic processes, when $\Delta G^* \rightarrow 0$ according to Rehm and Weller (1) is

$$k_q = \frac{k_{12}}{1 + \frac{k_{21}}{k_{23}^0}} \quad (14)$$

According to Eq. (14), a limiting value of $k_q = k_{12} = k_D$ is expected for the quenching rate constant if k_{23}^0 is much larger than k_{21} . This is the case commonly observed in singlet quenching by an ET process. However, a value lower than k_{12} results if k_{23}^0 is of the order of k_{21} . That this could be the case was explained on the grounds of a lower value for the electronic coupling matrix element $H_{TP} = \langle \Psi_R^0 | \hat{H}_{el} | \Psi_P^0 \rangle$. For a triplet reaction, the contribution of states of differing multiplicity to the wave function of products may lead to a value of k_{23}^0 comparable to k_{21} . What remains to be explained is the increase in the rate constant with the Gibbs energy for the triplet ET. Burshtein (48) presented a theoretical analysis of the ET quenching of singlet and triplet states based on the integral encounter theory. He analyzed our experimental data (19) and basically concludes that there is a kinetic control of the rate at ${}^3k_q = 0.5 k_D$. However, it is not clear in the model the origin of the increase of 3k_q with ΔG_{et} .

In summary, in the ET quenching of eosin by benzoquinones, in the region of high exergonicity, $\Delta G_{et} < -0.5$ eV the singlet quenching rate constants do not reach a plateau at the commonly accepted value for a diffusion-controlled process in this solvent, but they increase steadily. This is interpreted as an ET taking place at a variable distance generating a solvent separated ion pair (SSIP). On the other hand, for the triplet quenching rate constants fall below the diffusion limit. They also increase as ΔG_{et} becomes more negative but in a less noticeable way than the singlet quenching rate constants.

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