Letter

From Rehm–Weller to exciplex mechanisms by a structural effect: fluorescence quenching of a thioxanthone derivative by methoxy- and methyl-substituted benzenes in acetonitrile†

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The fluorescence quenching of a thioxanthone derivative was found to follow either a Rehm–Weller behavior with methoxy-substituted benzenes or a sigmoidal curve due to an exciplex quenching mechanism with analogous methyl-substituted compounds.

The observation of multiple Rehm–Weller plots[1–3] has evidenced the possibility of tuning the photoinduced electron transfer efficiency in polar solvents by altering the coulombic stabilization energy *C* of the created ion-pair *via* the use of "n-donors" (such as aliphatic amines) rather than "π-donors" (such as aromatics).[4] In addition to this energetic control of the reaction, a *structural* effect within the π-donor class has been previously reported in triplet state quenching: namely, methyl-substituted benzenes (MeB) quench triplet benzophenone with larger quenching rate constants k_Q than the analogous methoxy-substituted compounds (MeOB).[5] This fact has been interpreted as due to the involvement of triplet exciplexes with variable degrees of charge separation and orbital coupling, although their rather elusive nature has prevented them from being detected.[5] Furthermore, a previous study[6] has shown that fluorescence quenching of 3-carboxyethyl-7-methylthioxanthen-9-one (ETX) by MeB in acetonitrile gives rise to the formation of *emissive* singlet exciplexes. As fluorescence quenching is relevant to the Rehm–Weller framework[7] and avoids undesirable reactions such as hydrogen abstraction from the triplet state, the present paper reports a comparison of the quenching behavior of MeB and MeOB toward the singlet excited state of ETX in acetonitrile.

Singlet excited ETX interacts with MeB to form exciplexes that fluoresce with a red-shifted band, even in polar acetonitrile. In contrast, no exciplex emission was observed with MeOB quenchers for the most exergonic reactions; nevertheless, for 1,3-dimethoxybenzene and anisole a slightly red-shifted and weak emission band was detected. Table 1 collects the k_Q values and also mentions the presence of exciplex emission. The free enthalpy ΔG_{et} of the electron transfer reaction was calculated according to the Rehm–Weller relationship [eqn. (1)][7] in which E_{ox} is the oxidation potential of the donor D, E_{red} the reduction potential of the acceptor ETX (−1.37 V/SCE, obtained in this study by cyclic voltammetry), $E_{0,0}$ the energy of the singlet excited state of ETX (3.0 eV) and *C* the coulombic interaction energy of the ion-pair (taken as −0.06 eV[7]).

$$\Delta G_{et} = E_{ox} - E_{red} + E_{0,0} + C \qquad (1)$$

The driving-force dependence of log k_Q is shown in Fig. 1. The Rehm–Weller treatment, which considers full photoinduced electron transfer, should properly describe the fluorescence quenching of ETX in a polar solvent.[7] The kinetic scheme postulated by Rehm and Weller can be summarized as follows. The excited acceptor A* and the electron donor D diffuse together and form a weak precursor complex within

Table 1 Thermodynamic and kinetic parameters of the fluorescence quenching of ETX by methoxy- and methyl-substituted benzenes. E_{ox} is the oxidation potential of the donors *vs.* SCE

Donor	E_{ox}/V[8]	ΔG_{et}/eV	log k_Q
1,2,4-Trimethoxybenzene	1.13[a]	−0.56	10.3
1,4-Dimethoxybenzene	1.3	−0.39	10.15
1,2-Dimethoxybenzene	1.45	−0.24	9.9
1,3-Dimethoxybenzene	1.51	−0.18	9.6[b]
Anisole	1.75	0.06	8.0[b]
Hexamethylbenzene (HMB)	1.59	−0.1	10.0[b]
1,2,4,5-Tetramethylbenzene	1.82	0.13	9.2[b]
1,2,4-Trimethylbenzene	1.88[a]	0.19	8.6[b]
1,3-Dimethylbenzene	2.14	0.45	8.1[b]
Toluene	2.4	0.71	8.05[b]

[a] This study, using the procedure described in ref. 8. [b] Presence of emissive exciplex.

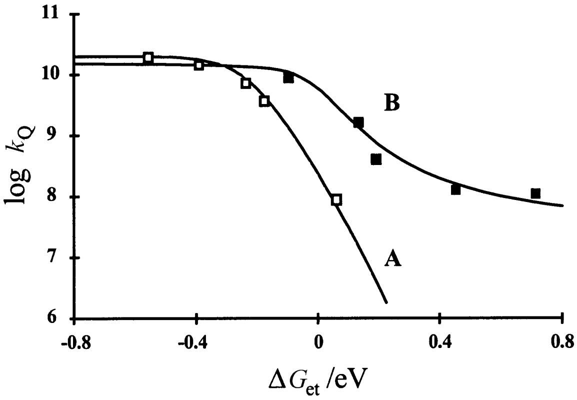

Fig. 1 Log k_Q *vs.* electron transfer driving force ΔG_{et} for fluorescence quenching of ETX by (■) methyl- and (□) methoxybenzenes. Solid lines: (A) Rehm–Weller curve with $\Delta G^{\neq}_{et}(0) = 0.15$ eV; (B) Simulation by the exciplex model [eqn. (4–8)] with $\beta = 0.17$ eV, $\tau_{exc} = 48$ ns and $\Delta G^{\neq}_{exc}(0) = 0.08$ eV.

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† *Non-SI unit employed*: 1 eV ≈ 1.6 × 10^{-19} J ≈ 96.5 kJ mol^{-1}.

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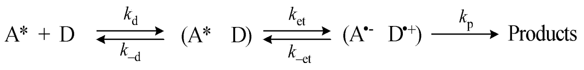


Scheme 1

which electron transfer occurs (Scheme 1). Then, the radical ion-pair undergoes subsequent reactions (ground state recombination, ion separation, *etc*. . . .).

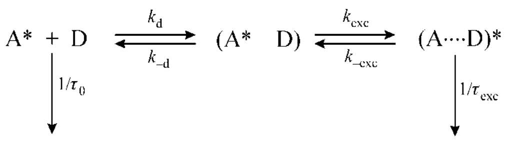
Assuming that the electron transfer step is an activated process and that k_{et} follows an Arrhenius-type law, a steady-state treatment leads to eqn. (2), in which $\Delta G^{\neq}_{et}$ is the activation energy of the reaction. In order to properly fit their data, Rehm and Weller related $\Delta G^{\neq}_{et}$ to ΔG_{et} by eqn. (3).[7]

$$k_Q = \frac{2 \times 10^{10}}{1 + 0.25\left[\exp\left(\frac{\Delta G^{\neq}_{et}}{RT}\right) + \exp\left(\frac{\Delta G_{et}}{RT}\right)\right]} \tag{2}$$

$$\Delta G^{\neq}_{et} = \frac{\Delta G_{et}}{2} + \sqrt{\left(\frac{\Delta G_{et}}{2}\right)^2 + \Delta G^{\neq}_{et}(0)^2} \tag{3}$$

The Rehm–Weller curve in Fig. 1 was obtained by setting $\Delta G^{\neq}_{et}(0)$ at 0.15 eV, a value slightly higher than the original one (0.1 eV[7]), but still reasonable. This model accurately fits the data for MeOBs, but it is clear from Fig. 1 that the MeBs do not follow it. The MeBs are more efficient quenchers than the MeOBs since their quenching rate constants are markedly higher for the same driving force. In addition, the curve for MeBs flattens out in the endergonic region instead of falling off as expected for a full electron transfer process.[7] In view of these results, the unusual discrepancy between methyl- and methoxy-substituted benzenes must be underlined. The divergence is clear if the quenching rate constants are compared at a similar driving force ΔG_{et} (*e.g.* 1,2,4,5-tetramethylbenzene and anisole). The sigmoïdal distribution of the MeBs results also strongly contrasts with the Rehm–Weller-like behavior of the MeOBs. Thus, the difference in quenching ability of MeBs and MeOBs is strengthened in the present singlet quenching case, compared to the benzophenone triplet quenching.[5] This behavior cannot be rationalized in terms of known full electron transfer theories.

As sigmoidal curves have already been reported in polar solvents[9–11] and tentatively explained by an alternative quenching mechanism involving the formation of exciplexes,[9,11–13] the applicability of such models can readily be tested. In this paper, our data are confronted with the exciplex model proposed by Kuzmin,[12,13] for the basic reason that it explicitly refers to the Rehm–Weller-type kinetic scheme. Indeed, the reversible formation of the exciplex is preceded by the encounter complex (see Scheme 2). Kuzmin's model offers a basic framework that gives some indications about the nature of the exciplexes. The purpose is to test if such a simple model is able to describe the unexpected behavior of MeB and to examine the physical meanings of the introduced parameters. Following kinetic Scheme 2, the steady-state approximation gives eqn. (4).[12,13] Exciplex formation is thought to be a reversible and activated process like the electron transfer step in the Rehm–Weller scheme, but in the present case the driving force is the free enthalpy change ΔG_{exc} of exciplex formation [eqn. (5)].[12,13] The forward step of exciplex formation is given by an Arrhenius-type law [eqn. (6)] with $\Delta G^{\neq}_{exc}$ being the activation energy.



Scheme 2

$$k_Q = \frac{k_d}{1 + (1 + k_{-exc}\tau_{exc})\frac{k_{-d}}{k_{exc}}} \tag{4}$$

$$K_{exc} = \frac{k_{exc}}{k_{-exc}} = \exp\left(\frac{-\Delta G_{exc}}{RT}\right) \tag{5}$$

$$k_{exc} = A \exp\left(\frac{-\Delta G^{\neq}_{exc}}{RT}\right) \tag{6}$$

ΔG_{exc} is related to ΔG_{et} as it describes the exciplex as a resonance between the locally excited state and the charge transfer state. A variational treatment leads to eqn. (7) in which β is the resonance integral between the two states. In a way similar to the empirical Rehm–Weller relationship (3), $\Delta G^{\neq}_{exc}$ is given by eqn. (8).[12,13]

$$\Delta G_{exc} = \frac{\Delta G_{et}}{2} - \sqrt{\left(\frac{\Delta G_{et}}{2}\right)^2 + \beta^2} \tag{7}$$

$$\Delta G^{\neq}_{exc} = \frac{\Delta G_{exc}}{2} + \sqrt{\left(\frac{\Delta G_{exc}}{2}\right)^2 + \Delta G^{\neq}_{exc}(0)^2} \tag{8}$$

Note that the term "exciplex" implicitly considers that $K_{exc} > 1$ and, thus, refers to a more stable complex than the precursor complex of Scheme 1. At large positive ΔG_{et} values, Kuzmin's model predicts that log k_Q levels off around $\log(1/\tau_{exc})$, due to the fact that K_{exc} is always greater than unity. This unrealistic behavior must be considered in more detail. At too high an endergonic driving force, there is no distinction between the "exciplex" and the encounter complex. This means that Scheme 2 no longer applies, which invalidates the use of eqn. (4). Moreover, the definition of τ_{exc} has no meaning under these conditions. Nevertheless, in the kinetic region around $\Delta G_{et} = 0$, the parameter τ_{exc} can be defined as representing all the deactivation processes of the exciplex. In addition, the parameter β, which governs the curvature in this region, becomes determinant and provides a good estimation of the stabilization of the exciplex.

Fig. 1 shows the adjustment of the exciplex quenching model to the MeB data. In the fitting procedure, A and $\Delta G^{\neq}_{exc}(0)$ were fixed at 10^{11} s^{-1} and 0.08 eV, respectively (10^{11} s^{-1} and 0.1 eV in ref. 12), whereas β and τ_{exc} were used as adjustable parameters. The best fit was obtained for $\beta = 0.17$ eV and $\tau_{exc} = 48$ ns. The value for β is physically realistic[9–13] and supports an efficient spatial interaction between donor and acceptor molecular orbitals. If care has been exercised in obtaining a reasonable value of β, the exciplex lifetime is surprisingly long (48 ns), considering the excited singlet lifetime of ETX (1.25 ns in acetonitrile[6]). This may be an outcome of the model, which only considers an average value of τ_{exc}. This assumption seems to be unrealistic since time-resolved fluorescence measurements have shown[14,15] that exciplex fluorescence lifetimes tend toward excited acceptor lifetimes in the very endergonic region. Moreover, previous work performed in this laboratory has yielded an exciplex lifetime of *ca.* 6 ns for the ETX–HMB system in acetonitrile,[6] a value markedly lower than 48 ns. Yet τ_{exc} represents nonradiative, radiative and intersystem-crossing deactivation pathways of the exciplex, the balance between them being possibly affected by the value of ΔG_{et}. This crude all-embracing vision implies that τ_{exc} cannot simply be related to the exciplex emission lifetime. Thus, the physical meaning of this parameter should be considered with caution. However, it is worthy of note that a relatively simple kinetic model makes it possible to describe the unexpected sigmoidal behavior of MeB and, therefore, points the way towards an alternative description of fluorescence quenching in polar solvents.

The Rehm–Weller curve in Fig. 1 accurately fits the MeOB data. Although such findings could be expected in acetonitrile,[7] this observation contrasts with the detection of exciplex fluorescence in the case of anisole and 1,3-dimethoxybenzene. Indeed, the observation of a Rehm–Weller curve in fluorescence quenching was believed, until recently, to support the electron transfer mechanism through an encounter complex with no strong interaction between the two molecules. Nevertheless, recent studies on triplet quenching have challenged this "outer-sphere" process by reporting exciplexes with $K_{\mathrm{exc}} \gg 1$ and quenching rate constants matched by the Rehm–Weller curve.[16,17] The electron transfer step can thus occur within the exciplex if its geometry is favorable. This process could be at work in the fluorescence quenching of ETX, all the more since the absence of an exciplex fluorescence cannot rule out its formation. This is particularly true if its main deactivation process becomes the subsequent electron transfer step in the exergonic region. However, the lack of exciplex emission from 1,2-, 1,4- and 1,2,4-MeOB could also find another explanation: a reversal in the quenching mechanism around $\Delta G_{\mathrm{et}} = -0.2$ eV. Such a mechanistic switchover has already been reported to occur at -0.4 eV in the case of anthracene-carbonitrile fluorescors quenched by aromatic compounds.[18,19] If the situation is still debatable for the MeOB class, the separation between MeBs and MeOBs cannot merely be due to such a switch-over in quenching mechanism since at the same driving force the quenching rate constants are higher for MeBs. For example, the exciplex quenching mechanism for 1,2,4,5-tetramethylbenzene is more efficient than for anisole (the exciplex emission being rather weak and less red-shifted in the latter case).

The above-mentioned results deserve clarification. A decade ago, we introduced the term "select donors" for MeBs,[2] mainly because these substances do not contain any oxygen atom, in contrast to MeOBs. Indeed, at that time, we had no inkling that these two families of electron donors could behave so differently. The present paper acknowledges the flaw in this suggestion and indicates that the outcome of searching such donors (operating through a full electron transfer) may be uncertain. In view of these findings there is some doubt as to the reliability of the Rehm–Weller curve when used to evidence the electron transfer mechanism in polar solvents. Accordingly, it appears difficult to define pure outer-sphere electron donors by only monitoring quenching rate constants. Ultimately, these data give an example of a marked *structural effect* on the thermodynamic dependence of k_{Q}. This has nothing to do with steric hindrance since methyl and methoxy groups have similar encumbrances. It is apparent that substituting a methyl for a methoxy group substantially modifies the ability of the donor to undergo orbital coupling with ETX and, therefore, the quenching mechanism. The coulombic term cannot be invoked here since both donor families belong to the "π-donor" class. The mechanism is not only governed by ΔG_{et} but also by more subtle parameters, which need to be elucidated and related to experimental data such as exciplex dipole moment or radical ion quantum yield.

Experimental

All MeBs and MeOBs were commercially available and subjected to further sublimation or distillation prior to use. Acetonitrile from Fluka (spectrophotometric grade) was employed without further purification. ETX was a gift from Ciba–Geigy and recrystallized from ethanol. The fluorescence quenching rate constants k_{Q} were determined at ambient temperature by steady-state fluorescence on a Fluoromax-2 spectrofluorimeter from Jobin–Yvon. It was checked that no ground state complex occurs in the presence of quenchers. When no exciplex emission was observed, the usual Stern–Volmer treatment was applied. On detection of a new emissive species, the residual fluorescence of ETX was determined by the subtraction method for increasing quencher amounts, as previously described in the literature.[6,15,18] Note that a few quenching rate constants reported in this note differ slightly from those reported in ref. 6, due to the higher signal/noise ratio obtainable with the present set-up.

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