

Quenching of triplet benzophenone by methyl and methoxy benzenes: are triplet exciplexes involved?

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Abstract

The quenching of triplet benzophenone by methyl and methoxy substituted benzenes in acetonitrile was investigated. For both series of donors the quenching rate constants are considerably higher than expected from the Rehm–Weller relationship, which could be explained by a mechanism involving a (triplet) exciplex intermediate. Two corresponding models from the literature were chosen for simulating the experimental data. The results are in accord with the exciplex proposal. For a given driving force the quenching rate constants differ substantially for the two kinds of donor employed. Together with the free ion yields, obtained by transient photoconductivity measurements, this confirms the important role of the chemical structure of the donors which determines the stability of the exciplexes. © 1997 Elsevier Science S.A.

Keywords: Benzophenone; Triplet exciplex; Quenching

1. Introduction

In most models used for the description of photoinduced electron transfer (PET) reactions, a key point is the correlation between the rate constant k_{q} and the free energy change ΔG_{et} , the latter being given by the Rehm–Weller equation:

$$\Delta G_{\text{et}} = E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A}) - E^* + C \quad (1)$$

where E_{ox} is the oxidation potential of the donor D, E_{red} the reduction potential of the acceptor A, E^* the energy of the excited state to be quenched, and C the Coulomb energy of the incipient ion pair formed after electron transfer.

It was shown that the electronic structure of D plays an important role in determining k_{q} , 'π'-donors being far less efficient quenchers than 'n'-donors as evidenced by so-called 'multiple Rehm–Weller plots' [1–4]. This phenomenon is thought to result from the greater delocalization of the positive hole in the former than in the latter donor cations generated after ET, which leads via a smaller (attractive) C-term to a smaller driving force ΔG_{et} .

However, A/D systems which show full ET are rather scarce, and in many cases there must be only partial charge

transfer occurring between the partners. This is clearly indicated for those quenching reactions for which the driving force Eq. (1) is positive. Hence, for the intermediates ensuing from such endergonic ET quenching processes the notion of 'ion pair' is inappropriate and is replaced by 'exciplex'.

Until recently it was believed that such exciplexes can be observed only in non-polar solvents, since in polar solvents they will dissociate efficiently into free solvated ions. Recent reports, however, have shown that exciplexes exist also in polar media such as acetonitrile (MeCN) [5–7].

The quenching of triplet benzophenone (³BP) by electron donors is a well known reaction which involves charge transfer [8–11] and exhibits multiple Rehm–Weller plots [12]. Quenching by amines, a class of strong D, is documented in [13]. We have now studied this reaction employing methyl and methoxy substituted benzenes (D ≡ MeB or MeOB respectively) in order to obtain insight into the degree of ET for these much weaker donors and to obtain at least indirect evidence about the role of (triplet) exciplexes.

2. Experimental part

A nanosecond flash photolysis apparatus was used for the determination of the quenching rate constants k_{q} , the ketyl

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Table 1
Quenching of ³BP by MeOB and MeB in MeCN

Donor	Number	iP_{e} (eV) ^a	E_{ox} (V vs. SCE) ^b	ΔG_{et} (eV) ^c	$\log k_{\text{q}}$	$\log k_{\text{et}}$ ^d	ϕ_{BPH}	ϕ_{ion} ^e
MeOB								
1,2,4-	1	7.35	1.13	-0.11	9.88	9.88	0.0	0.67
1,4-	2	7.53	1.30	0.06	9.04	9.04	0.0	<0.01
1,2,3-	3	7.7	1.42	0.18	8.33	—	—	<0.01
1,2-	4	7.8	1.45	0.21	8.58	—	—	<0.01
1,3,5-	5	7.8	1.49	0.25	8.37	8.37	0.0	nm
1,3-	6	7.53	1.51	0.27	8.10	8.10	0.0	<0.01
1-	7	8.21	1.75	0.51	6.66	6.66	0.0	nm
MeB								
per-	8	7.85	1.59	0.35	9.14	9.04	0.19	<0.01
1,2,4,5-	9	8.04	1.82	0.58	7.74	7.66	0.18	nm
1,2,4-	10	8.27	1.87	0.63	7.06	6.89	0.33	nm
1,4-	11	8.44	2.00	0.76	6.50	6.20	0.5	nm
1,3,5-	12	8.41	2.07	0.83	7.21	7.15	0.12	nm
1,3-	13	8.56	2.14	0.90	6.45	6.30	0.27	nm
1-	14	8.82	2.40	1.16	5.67	5.12	0.66	nm

Adiabatic ionization potentials (iP_{e}), oxidation potentials (E_{ox}), overall quenching rate constants (k_{q}), isolated ET quenching rate constants (k_{et}), ketyl radical yields (ϕ_{BPH}), and free ion yields (ϕ_{ion}). Solvent is MeCN. For further explanations see text.

^a See [16].

^b See [17].

^c From Eq. (1) with $E_{\text{red}}(\text{BP}) = -1.76$ V vs. SCE, $E^*(\text{BP}) = 3$ eV. The C -term is neglected in view of the solvent MeCN.

^d See text.

^e nm: Quenching of ³BP with 100% efficiency was not possible owing to solubility problems. Nevertheless, it can safely be assumed that $\phi_{\text{ion}} < 0.01$.

radical (BPH) yields (ϕ_{BPH}) and the free ion yields (ϕ_{ion}). The excitation sources were a frequency tripled Q-switched Nd:YAG laser (JK lasers 2000) generating 19 ns pulses of 6 mJ, and a nitrogen laser (PRA NL 100) yielding pulses of 0.6 ns at 0.1 mJ. Both lasers were operated at a repetition rate of 10 Hz.

All the solutions were made with neat MeCN, the concentration of BP being 5 mM. The absorbance of these solutions then came to 0.5 at 355 nm and to 0.78 at 337 nm. They were deoxygenated by bubbling Ar for 15 min. The values of the quenching rate constant k_{q} were obtained from the measurements of the ³BP phosphorescence lifetime, applying the usual Stern–Volmer treatment. The ketyl radical yields ϕ_{BPH} were determined via the corresponding transient absorption signal at 540 nm, the standard being the BP/benzhydrol system for which $\phi_{\text{BPH}} = 2$ and $k_{\text{q}} = 4.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ [14]. The ion yields ϕ_{ion} were measured by the transient photoconductivity technique, the standard being the system BP/DABCO in MeCN for which $\phi_{\text{ion}} = 1$ [15]. BP (Aldrich Gold Label) and DABCO were sublimed before use. MeCN (Fluka, UV grade) was employed as received. The other compounds were purified by standard procedures.

3. Results and discussion

Inspection of the k_{q} -values reported in Table 1 shows that MeOB are significantly less efficient quenchers than MeB

(for example, compare the couple of donors 1,3-MeOB and per-MeB with about equal ET driving force). This behaviour, which is unexpected within the framework of the Rehm–Weller or Marcus models, also appears clearly in the plot of $\log k_{\text{q}}$ vs. ΔG_{et} (Fig. 1).

It is well known that the quenching of ³BP by MeB leads to the formation of ketyl radicals (BPH), whereas MeOB do not yield significant hydrogen abstraction when benzene is used as solvent. These observations are presently confirmed with acetonitrile as solvent. The relative contributions of hydrogen abstraction and of electron transfer can be derived from Scheme 1 [18]:

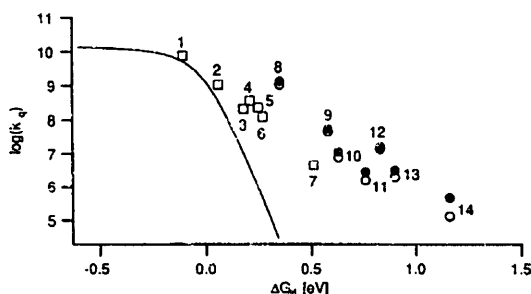
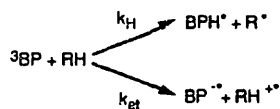


Fig. 1. Theoretical Rehm–Weller curve and observed quenching rate constants for MeOB (□) and MeB (●) in MeCN. (○) Quenching rate constants corrected for H-abstraction (i.e. k_{et}) according to Scheme 1.



with $k_{\text{ct}} = (1 - \phi_{\text{BPH}})k_{\text{q}}$, where $\phi_{\text{BPH}} = k_{\text{H}} / (k_{\text{H}} + k_{\text{ct}})$ and $k_{\text{q}} = k_{\text{H}} + k_{\text{ct}}$.

However, even with the contribution of k_{H} taken into account, the rate constants of electron transfer k_{ct} are still higher for MeB than for MeOB. It is not reasonable to trace this effect to the C-term in Eq. (1) since for both benzenoid donor-cations the positive hole is similarly delocalized. The following remarks can then be made on the basis of Fig. 1.

(i) The slopes for MeB and MeOB are different (-3.5 eV^{-1} and -5.5 eV^{-1} respectively) and significantly less than -17 eV^{-1} which according to the Rehm-Weller model corresponds to full ET.

(ii) The quenching rate constants remain high even for apparently strongly endergonic processes.

We submit that these two observations may indicate the intermediacy of a (triplet) exciplex in the quenching process. Singlet exciplexes are well characterized by their spectroscopic properties, but this is not the case for triplet exciplexes which have proven so far rather elusive. It is therefore of interest to consider the modifications which must be applied to the classical scheme for full ET to account for exciplex intermediates. Three different approaches to this question have been proposed so far in the literature:

In the simplest model 1 it is assumed that the ET or, equivalently, the charge transfer (CT) character of the exciplex is independent of the reaction free energy ΔG_{ct} [19]. Two other models 2 [20] and 3 [5] introduce an algebraic dependence of the CT character from the driving force, but differ in accounting for the Marcus reorganization energy. Specifically, they differ in accounting for the influence of the medium being polarized in the course of ET, and in implications resulting from the definition of the reaction coordinate. A further notable difference concerns the relationship between $\log k_{\text{q}}$ and the driving force ΔG_{ct} in the endergonic regime: model 1 supposes proportionality between these quantities, whereas in models 2 and 3 $\log k_{\text{q}}$ approaches $-\log \Delta G_{\text{ct}}$. We decided to simulate our experimental data to models 1 and 3 in view of their minimal parameter space. The underlying algebraic equations are not repeated here as they can be found in the cited literature. For better comparison, our results are given in terms of the symbols used therein.

From Figs. 2 and 3 and Tables 2 and 3 it appears that both models fit the data quite well, although the exciplex lifetimes in the ms-time scale for model 3 (τ in Table 3) seem very large indeed. Specifically, the optimized parameters for model 1 are quite reasonable and lie within the hitherto observed range. Note that the CT-degree is higher for MeOB than for MeB (b^2 in Table 2). This agrees with the expectation that positive charge is better accommodated in the former compounds which are iso-conjugated to the corresponding benzyl systems.

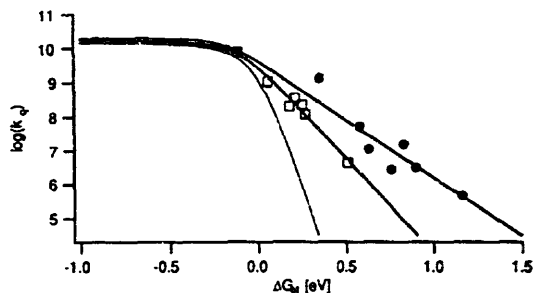


Fig. 2. Fits according to model 1 [19]: MeOB (□) and MeB (●), see text.

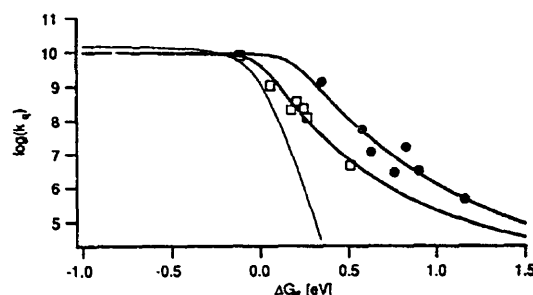


Fig. 3. Fits according to model 3 [5]: MeOB (□) and MeB (●), see text.

Table 2
Optimal fitting parameters according to model 1 (see text): symbols are those of the original publication [19]

Donor	$k_1 \text{ (s}^{-1}\text{)}^a$	b^2	$\Delta G_1(0) \text{ (kJ mol}^{-1}\text{)}$	$\Delta G_{\text{ct}}(0) \text{ (kJ mol}^{-1}\text{)}^b$	χ^2
MeOB	5.89×10^9	0.33	3.4	10.0	0.15
MeB	5.72×10^9	0.20	0.85	10.0	1.19

^a k_1 corresponds to the sum of k_2 and k_3 in [19].

^b Kept constant for all fitting runs.

Table 3
Optimal fitting parameters according to model 3 (see text): symbols are those of the original publication [5]

Donor	$\beta \text{ (eV)}$	$\tau \text{ (s)}$	χ^2
MeOB	0.33	0.0012	0.268
MeB	0.59	0.014	0.760

We also mention that convergence was found for all curve fitting runs. This may be taken as further support for the key assumption in both models, i.e. the intermediacy of an exciplex in equilibrium with reactants and final products as initially suggested in [21]. Clearly, successful simulations do not constitute a proof for an assumed mechanism but, together with other observations, they can support a proposal.

We are aware of the fact that the use of ΔG_{ct} in these plots may be questioned in case of an exciplex being involved. However, the more reasonable driving forces for exciplex

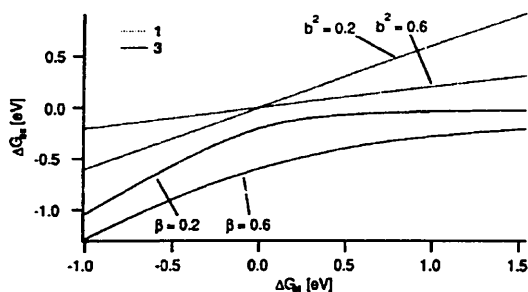
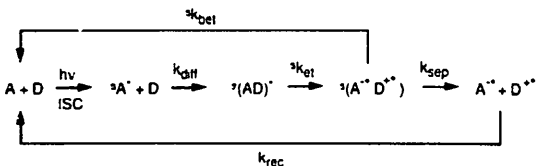


Fig. 4. Relationship between the driving forces for ET (ΔG_{et}) and for exciplex formation (ΔG_{ex}) according to the two models 1 [19] and 3 [5] employed. For model 1 two values for the CT character (b^2) and for model 3 two different resonance integrals (β) were considered.

formation ΔG_{ex} are closely related to ΔG_{et} within both models 1 and 3, as shown in Fig. 4. The conversion of the ΔG_{et} to a ΔG_{ex} axis is therefore quite simple, but it must be noted that a reaction may then be described, depending on the chosen variant, as endergonic or exergonic respectively.

Finally, these simulations tend to confirm that MeB and MeOB show intrinsically different behaviour on quenching 3BP in MeCN. The inclusion of both types of quencher in one single Rehm–Weller or Marcus plot is therefore inappropriate and even misleading.

We now turn to the discussion of the free ion yields ϕ_{ion} reported in Table 1. Based on Scheme 2 below they allow calculation of the back ET (BET) rate constants $k_{bet} = k_{sep}[(1 - \phi_{ion}) / \phi_{ion}]$ where the additional index s in Scheme 2 denotes the spin multiplicity ($s = 1$ or $s = 3$) of A^* being quenched by D.



In the case of $^1A^*$ the values of k_{bet} vary considerably with $\Delta G_{bet} = E_{red}(A) - E_{ox}(D)$ (neglecting the C -term in the polar solvent MeCN), and the plot of $\log k_{bet}$ vs. ΔG_{bet} shows the Marcus inverted region. Obviously, ϕ_{ion} depends greatly on $E_{ox}(D)$.

However, if as in this study $^3A^*$ is employed, the situation is not so clear because BET is subject to spin restrictions and ϕ_{ion} can therefore be especially high. For example $\phi_{ion} = 1$ has been obtained for the couple $^3BP/DABCO$ [15]. Other large free ion yields for triplet quenching reactions have been reported in [22].

However, the values of ϕ_{ion} shown in Table 1 are at variance with the above cited results. The highest value is 0.67 for the sole negative ΔG_{et} -value quoted. They then decrease sharply with increasing ΔG_{et} , eventually vanishing for clearly endergonic ET. This could be rationalized on the basis of the exciplex model. In the case of MeOB two parallel quenching mechanisms are operative which involve either full ET or

exciplex formation. As ΔG_{et} increases the exciplex route becomes predominant and ϕ_{ion} consequently decreases.

On the other hand, for MeB we can safely assume that only the exciplex mechanism is operative in view of the following observations:

- (i) even with per-MeB which is the best donor in this series, no ions could be detected;
- (ii) a higher quenching rate constant is observed for per-MeB than for 1,3-MeOB;
- (iii) the trend of ϕ_{ion} indicates a switchover in the quenching mechanism, as reported for example in the fluorescence quenching of cyananthracenes by butadienes [23].

Finally, we underline the role of the chemical constitution of the employed D. For a given driving force MeOB give more ions than MeB. This may be related to the stability of the exciplexes which depends greatly on the electron distribution of the constituent partners.

4. Conclusions

We have investigated the quenching of triplet benzophenone by methyl and methoxy substituted benzenes in acetonitrile. For both series of donors the quenching rate constants are considerably higher than expected from the Rehm–Weller relationship, which could be explained by a mechanism involving a (triplet) exciplex intermediate. Two corresponding models from the literature were chosen for simulating the experimental data. The results are in accord with the exciplex proposal. For a given driving force the quenching rate constants differ substantially for the two kinds of donor employed. Together with the free ion yields, obtained by transient photoconductivity measurements, this confirms the important role of the chemical structure of the donors which determines the stability of the exciplexes.

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