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Comment on "A comparative study on electron transfer fluorescence quenching by aliphatic and aromatic amines" from Inada et al., J. Photochem. Photobiol. A 137 (2000) 93–97

P. Jacques*, X. Allonas, M. Dossot

Department of Photochemistry, Université de Haute Alsace, 3, rue Alfred Werner, 68093 Mulhouse Cedex, France

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Abstract

This comment draws attention to the fact that a biased set of electron donor/acceptor couples can lead to an unorthodox vision of fluorescence quenching mechanism. It is shown that the results reported by Inada et al. can be adequately explained by resorting to adiabaticity and stereo-electronic effects. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electron transfer; Exciplex; Adiabaticity; Aliphatic amines

1. Introduction

Earlier work on photoinduced electron transfer (PET) from our laboratory has evidenced that for a given electron acceptor, π- and n-type electron donors lead to distinct Rehm–Weller plots due to different Coulomb terms C_π and C_n, respectively [1,2]. Among others, the influence of the donor chemical structure on the fluorescence quenching of anthracene carbonitriles was evidenced on the following two items: (i) aliphatic amines are by far more efficient quenchers than aromatics, the two Rehm–Weller plots being separated by about 0.6 eV when using in abscissa the adiabatic ionization potential (aIP) as the electron donor ability; (ii) the effective electron transfer distance r_Q increases linearly when the exergonicity ΔG_{et} of the reaction becomes more negative, but the correlation is also divided in π- and n-donor class. Namely, r_Q for the n-class is always shorter than that for the π-class at a given ΔG_{et}. Very recently in this journal, Inada et al. have addressed the difference in PET between aromatic and aliphatic amines as quenchers of aromatic acceptors [3]. They have reported results totally at variance with our proposal, which has deserved the following comment. For sake of clarity let us discuss the items separately.

2. Item 1: are aliphatic amines really less efficient quenchers than aromatic donors?

Fig. 1 of the paper of Inada et al. shows that n-donors are *less* efficient quenchers than π-ones by nearly 0.5 eV, a result both qualitatively and quantitatively at the opposite of our measurements [1,2]. In fact, we intend to show that this strong discrepancy originates from an unfortunate choice of electron donor/acceptor couples which constitutes a clear example of how an inadequate set of donors can be misleading. Secondly, these authors do not take into consideration the role of adiabaticity in PET which we reported in [4], although this paper has mentioned the same (Ref. [14] in their work). Here, Fig. 1 reports the data contained in Table 1, namely those of Inada's study involved in this discussion completed by an additional point measured for this comment (phenanthrene/diazabicyclo-[2,2,2]-octane, DABCO), and the data for the fluorescence quenching of anthracene by a representative set of aliphatic amines [4]. This set is truly representative since it ranges from exergonic to endergonic region with homogeneous chemical structure [4]. Fig. 1 also shows the original Rehm–Weller curve to mark the position of aromatic donors [5]. For consistency, we have calculated ΔG_{et} by the usual Rehm–Weller equation [5] with our own measurements of oxidation potentials [6], hence minor changes with the ΔG_{et} values reported in Table 1 of Inada's paper. However, these small changes do not affect the trend

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* Corresponding author. Tel.: +33-3-89-33-68-28.
E-mail address: p.jacques@uha.fr (P. Jacques).

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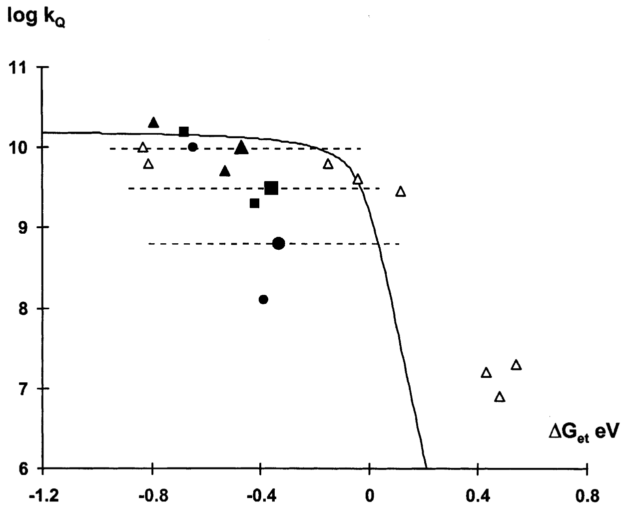

Fig. 1. Plots of log k_Q vs. ΔG_{et}. (△): Anthracene/aliphatic amines. Filled symbols: quenching data obtained with the sequence DABCO, TEA and ABCO for anthracene (▲), perylene (■) and phenanthrene (●) as electron acceptors. Solid line: the original Rehm–Weller curve. Dashed lines: the position of the adiabatic plateau for the three acceptors estimated on the quenching data with TEA.

of the data. It can be seen from Fig. 1 that the quenching of anthracene by aliphatic amines follows a Rehm–Weller behavior but with a significant shift of 0.4 eV towards *more positive* driving force ΔG_{et}. The shift is slightly shorter than that obtained by using aIP but clearly inconsistent with the data reported by Inada. It is well known that for most of the aliphatic amines, the oxidation potential wave is irreversible. However, our work brings about reliable values of E_{ox} with uncertainty estimated at ±0.1 eV [6]. Moreover, the use of these potentials to evaluate ΔG_{et} can in no way explain the strong discrepancy of about 0.9 eV with the results of Inada. It is then essential to note that we neither challenge the quenching data obtained in their paper (our measurements for anthracene are in perfect agreement) nor the values of ΔG_{et} they have calculated. This comment rather proposes a different explanation of their results which directly ensues from previous work on adiabaticity [4] and which is compatible with the π/n classification of electron donors.

It has been shown that the fluorescence quenching of three-ring aromatic acceptors by aliphatic amines gives rise to the observation of different plateau values in the exergonic region [4]. This effect was evidenced for true unimolecular electron transfer rate constant k_{et} by resorting to the finite sink model [4]. However, the plot in Fig. 1 of bimolecular rate constants k_Q for anthracene/amines indicates that the plateau value is also appreciably inferior to the diffusion limit in acetonitrile ($\log k_d = 10.3$). We then claim that the phenomenon unveiled with k_{et} is still valid in k_Q, depending on the structure of the acceptor. Since triethylamine (TEA) is a pure non-bridged aliphatic amine and its reaction with the aromatic acceptors used by Inada is always markedly exergonic, its quenching rate constant gives a good idea of the plateau value for the different acceptors. The observation of such plateaus for pure aliphatic amines lies in a low value of the electronic coupling matrix element H_{el} between wide π orbitals of the acceptor and the more localized lone pair orbital of the amine involved in the PET. Therefore, if H_{el} becomes so small that the maximum electron transfer rate constant k_{et} is lower than the diffusion rate constant k_d, the quenching mechanism is going from diffusion controlled to

Table 1
Fluorescence quenching data for three-ring aromatic acceptors and aliphatic amine electron donors in acetonitrile: (a) measured in the same conditions as Ref. [6]; (b) taken from S.L. Murov, I. Carmichael, G.L. Hug, Handbook of Photochemistry, 2nd Edition, Marcel Dekker, Basel; (c) S.G. Lias, J.E. Bartmess, J.F. Lieman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (Suppl. 1) (1988); (d) taken from Ref. [6]; (e) calculated by the usual Rehm–Weller equation with a Coulombic term $C = -0.06$ eV; (f) our measurements extracted from Ref. [2] excepting phenanthrene/DABCO measured for this comment; (g) Inada et al.'s data extracted from Ref. [3]; (h) extrapolated by the use of the relation $E_{ox} = 0.83 \times \text{aIP} - 5.34$ [6]

Fluorescer	E_{red} (V/SCE)	$E_{0,0}$ (eV) (b)	Quencher	aIP (eV) (c)	E_{ox} (V/SCE) (d)	ΔG_{et} (eV) (e)	log k_Q (f)	log k_Q (g)
Anthracene	−2.02 (a)	3.31	Triisobutylamine	7.14	0.54 (h)	−0.81	9.8	
			Tripropylamine	7.18	0.52	−0.83	10	
			Di-*n*-propylamine	7.84	1.2	−0.15	9.8	
			Diethylamine	8.01	1.31 (h)	−0.04	9.6	
			Dimethylethanolamine	8.2	1.47 (h)	0.12	9.45	
			Cyclohexylamine	8.62	1.78	0.43	7.2	
			tert-Butylamine	8.64	1.83 (h)	0.48	6.9	
			n-Butylamine	8.71	1.89 (h)	0.54	7.3	
Anthracene	−2.02 (a)	3.31	DABCO	7.2	0.56	−0.79		10.3
			Triethylamine	7.5	0.88	−0.47	10	10
			ABCO	7.4	0.82	−0.53	9.7	9.7
Perylene	−1.65 [3]	2.83	DABCO	7.2	0.56	−0.68		10.2
			Triethylamine	7.5	0.88	−0.36		9.5
			ABCO	7.4	0.82	−0.42		9.3
Phenanthrene	−2.44 (a)	3.59	DABCO	7.2	0.56	−0.65	10	
			Triethylamine	7.5	0.88	−0.33		8.8
			ABCO	7.4	0.82	−0.39		8.1

only diffusion influenced regime. Consequently, the plateau value observed does not reach the diffusion limit.

In addition to the adiabatic effect, the sequence DABCO, TEA, ABCO (azabicyclo-[2,2,2]-octane) reveals to have a bias. Indeed, DABCO and ABCO are bridged amines, whereas TEA is freely subject to the umbrella-like motion (ULM). As aliphatic amines donate their electron through the localized n orbital, and as the nitrogen center is pyramidal, the probability of sufficient orbital coupling between the acceptor and the donor is reduced if compared with aromatic donors. In fact, ULM allows an increase of this probability since the inversion is very fast and makes the n orbital swing between the two semi-spaces defined by the plane of the three N–C bonds at the planar transition state. Nevertheless, if ULM is hindered by bridging the amine as in ABCO, only the semi-space containing the n orbital is subject to orbital coupling, and the efficiency of electron transfer is reduced. By contrast, in DABCO the two nitrogen atoms are frozen by methylene bridges in a configuration which increases the probability of orbital coupling. Indeed, DABCO can be viewed as two TEA attached together by the base of their pyramid, and thus it mimics the two opposite enantiomers involved in ULM, but in a permanent pattern. Moreover, the through-space interaction of the two n orbitals of the nitrogen atoms stabilized the DABCO cation, a factor which probably favors the electron transfer. These effects are clearly evidenced by using the three acceptors reported in Table 1. The PET rate constants for a given acceptor always decrease in the following sequence: DABCO, TEA and ABCO (see Fig. 1). As the adiabatic plateau goes further from the diffusion limit, the quenching rate constant k_Q reflects more closely k_{et} and the gap between DABCO, TEA and ABCO increases. This is perfectly clear with the data obtained with phenanthrene, the acceptor which possesses the lower adiabatic plateau in Fig. 1. The driving force changes only by about 0.25 eV, but the log k_Q values differs by nearly 2, despite the fact that these data belong to the exergonic region. Thus, the position of these three amines does not draw a single falling off due to a fluorescence quenching mechanism different from outer-sphere PET, as proposed by Inada, but has to be related to stereo-electronic effects coupled to the role of adiabaticity which affects the H_{el} value, soon revealed in paper [4].

3. Item 2: is the effective electron transfer distance really the same for aliphatic amines and aromatic donors?

It is now well accepted that the effective electron transfer distance r_Q increases as ΔG_{et} becomes more negative. However, we have shown that this increase is quantitatively different for π- and n-donors. Note that this difference remains when using ΔG_{et} instead of aIP as in our previous work [2]. Inada reports results at variance since aromatic and aliphatic amines follow the same dependence of r_Q towards ΔG_{et}. This disagreement results from the use of completely different methods. Inada have determined r_Q from the modified Stern–Volmer equation [7]. It is presently known that this rather crude model overestimates the electron transfer distance, mainly due to the fact that the electron transfer rate is considered to be infinite [8]. This approximation *essentially* cannot take into account the difference in two families of electron donors, and thus it is expected that the results are the same for aromatic and aliphatic amines. Our measurements of r_Q have been derived from the finite sink model approximation, which defines a finite electron transfer rate, and then is more reliable in the parameterization of diffusion-limited electron transfer quenching [9].

4. Item 3: a biased set of acceptor/donor couples can lead to an unorthodox vision of fluorescence quenching mechanism

The results of Inada seem puzzling at first glance. The falling off observed for the aliphatic amine donors near $\Delta G_{et} = -0.5$ eV is interpreted by the authors as an indication of a switch-over in fluorescence quenching mechanism from pure outer-sphere electron transfer to exciplex formation. This switch-over has been proposed from a network of subtle proofs by Kikuchi [10] in the case of aromatic quenchers, where π–π sandwich-like exciplexes can occur. However, using the same argumentation for aliphatic amines is an extrapolation which brings about very unusual consequences. First, Inada established the involvement of an exciplex with aliphatic amines on the basis of a heavy atom effect on triplet and radical ions quantum yields. However, this effect was exclusively evidenced for aromatic donors. Suggesting that the effect remains with aliphatic amines, the authors stated that the quenching mechanism occurs through an exciplex as soon as $\Delta G_{et} > -0.5$ eV. To explain the difference between aromatic and aliphatic amines in this range of driving force, Inada et al. invoked a difference in the stabilization energy of exciplex due to the impossibility to form face-to-face π complex. Accordingly, the exciplex is considered to be loose and can dissociate before the excitation deactivation takes place: the quenching does not occur, hence the falling off was observed around $\Delta G_{et} = -0.5$ eV. Note that the authors have to invoke a difference in the nature of the exciplex when the amine is aromatic or aliphatic, whereas they have just stated before that these exciplexes undergo the same heavy atom effect. It thus underlines the weakness of this argument. Moreover, considering that exciplex mechanism is the fluorescence quenching mechanism in the range $\Delta G_{et} > -0.5$ eV is clearly not in accord with virtually all previous work in electron transfer. This proposal does not explain why the plot of log k_Q towards ΔG_{et} falls off when ΔG_{et}, the free energy change for pure outer-sphere electron transfer, is about 0 eV, whereas the driving force should be governed by the exciplex formation (even though the latter can be linked to the former). It is also not consistent with the data obtained with anthracene acceptor and aliphatic amines.

5. Conclusion

As a conclusion, this comment explains the results of Inada by resorting to adiabatic and stereo-electronic effects in total consistency with the literature on fluorescence quenching by PET published for more than 30 years.

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