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The interplay between steric hindrance and exergonicity in the rates of excited state quenching

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Abstract

The quenching rate constants of excited states by two closely related electron donors (hexamethylbenzene and hexaethylbenzene) are very different. This is explained by the combined effects of steric hindrance, increase in the electron transfer distance and the exergonicity of the reaction.

Keywords: Electron transfer rate; Steric hindrance

1. Introduction

The quenching rate constants k_q of excited states by electron acceptors or donors are well documented [1,2], and are usually assumed to depend on the reaction free energy ΔG_{et} expressed as

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

where $E_{ox}(D)$ and $E_{red}(A)$ are the oxidation potential of the donor (D) and the reduction potential of the acceptor (A) respectively, E^* is the excited state energy and C corresponds to the electrostatic interaction between the ions resulting from electron transfer.

However, the reality is more complex than represented by Eq. (1). For example, the electronic delocalization of D can significantly affect k_q [3–7]. Obviously, steric hindrance is another interesting parameter, since the electron transfer efficiency depends on the A–D distance. Moreover, the transfer distance, which normally corresponds to the contact of the partners, can be increased with increasing exergonicity [8–11]. Interestingly, these two effects have opposite influences on the quenching rate. This paper provides an example of the combination of both influences using the well-known electron acceptors, 9-cyanoanthracene (CNA), 9,10-dicyanoanthracene (DCA) and triplet benzophenone (^{3}BP), and two closely related electron donors, hexamethylbenzene (HMB) and hexaethylbenzene (HEB).

2. Results and discussion

The quenching rate constants k_q of the singlet states were obtained from the linear Stern–Volmer plots. Those of the triplet states were derived from flash spectroscopy.

From Table 1, it can be seen that both donor compounds have similar ionization and oxidation potentials. In principle, changing the substituents from methyl to ethyl should increase slightly the propensity of HEB to donate an electron compared with HMB, as reflected in the vertical ionization potentials. In agreement with this, the reversible oxidation potentials are identical.

In view of the above-mentioned observations, it is remarkable to find that the quenching rate constants for HEB are considerably lower than expected in the case of CNA and ^{3}BP, whereas with DCA the diffusional rate constant is observed. This can be explained by considering the combined effects of the steric hindrance and reaction exergonicity on k_q.

2.1. Steric hindrance

HEB is the prototype of a class of sterically crowded, homo-substituted hexaalkylbenzenes, for which the lowest energy stereoisomer has an "up–down" alternation of the alkyl groups [15]. It should be noted that this isomer is significantly more stable (by 18.9 kJ mol^{-1}) than its nearest analogue [16]. Moreover, the geometries of HEB and HMB were optimized by the AM1 procedure and the molecular

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Table 1

Quenching rate constants and energetics in acetonitrile

	vIP (eV) [12]	E_{ox} (V) [12]	log k_q ($M^{-1}s^{-1}$)		
			CNA ($E_{red} = -1.58$ V, $E_s^* = 3.04$ eV)	DCA ($E_{red} = -0.98$ V, $E_s^* = 2.90$ eV)	^{3}BP ($E_{red} = -1.68$ V, $E_t^* = 3.0$ eV)
HMB	7.85	1.62	9.16	10.23 [5]	9.14
HEB	7.71	1.59	≤6.50	10.03	6.70
ΔG_{et} (eV)			~ −0.17	~ −0.63	~ −0.03

ΔG_{et} from Eq. (1) with $C = -0.3$ eV, an intermediate value between $C = -0.06$ eV [13] and $C = -0.5$ eV [14].

Table 2

Quenching rate constants k_q ($M^{-1}s^{-1}$) in benzene

	^{1}CNA*			^{1}DCA*			^{3}BP*
	log k_q	Exciplex	$h\nu_{exc}^{max}$ (eV)	log k_q	Exciplex	$h\nu_{exc}^{max}$ (eV)	log k_q
HMB	8.04	Yes	2.75	9.9	Yes	2.39	9.10
HEB	≤6.5	No	–	≤6.5	No	–	≤6.5

radii were derived from the van der Waals' volumes; they were found to be 4.85 Å and 3.43 Å for HEB and HMB respectively. This leads to steric hindrance for HEB and thus to a lower k_q value than for HMB.

2.2. Exergonicity

Further information tends to indicate that the transfer distance can increase significantly with the exergonicity of the reaction. It should be kept in mind that this effect has an opposite influence on k_q to that related to steric hindrance.

This explains why, in the case of DCA as acceptor, the diffusional limit is still observed. The decrease in k_q due to steric hindrance, which evidently occurs, is overcome by the increase in k_q due to the significantly higher exergonicity of the reaction for DCA compared with CNA and ^{3}BP.

This interpretation is substantiated by the fact that, in benzene, a low quenching rate constant is observed for the three acceptors when HEB is used as donor (Table 2). In this solvent, the deactivation probably proceeds via an exciplex mechanism. Further experiments will shed more light on the emission decay of the exciplex. Current evidence indicates that exciplexes are extremely dependent on the mutual arrangement of the partners and, in particular, on their separation distance [17,18]. From the van der Waals' radii, it is clear that the aromatic ring of HEB is less available for exciplex formation than that of HMB. This is in agreement with the observations that exciplex emission is not observed and the quenching rate constants are very low with HEB as donor, even in the case of DCA.

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