

Long Distance Intramolecular Photoinduced Electron Transfer in Donor–Acceptor Systems: Effect of Exothermicity on Electron-transfer Rates

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Photoinduced intramolecular electron transfer in donor–acceptor systems separated by a long distance are studied by fluorescence quenching experiments; reduced rate constants for electron transfer are observed in highly exothermic reactions, which indicates the existence of an 'inverted region', in accord with Marcus' model.

Quenching of excited states by electron transfer is an area of great interest to photochemists and great efforts have been devoted to its theoretical study. Recently, new experimental schemes have been used to test the predictions of classical and nonclassical theories of electron transfer.^{1,2} Marcus' classical theory of electron transfer predicted the existence of an 'inverted region', but no experimental evidence was reported until quite recently.³ Thereafter, several groups have observed the inverted region for return electron transfer within photochemically generated radical ion pairs.⁴ Here, we report the synthesis and fluorescence quenching experiments of a new donor–acceptor system with anthracene (or its derivative 9,10-dimethoxyanthracene) linked with electron acceptors *via* a steroid (oestrone or oestradiol, ES) skeleton. The structures are illustrated in Fig. 1. Selective excitation of the electron donor in this system can lead to a long distance intramolecular electron transfer. The dependence of the photoinduced electron transfer rates on the exothermicity of the reaction is demonstrated.

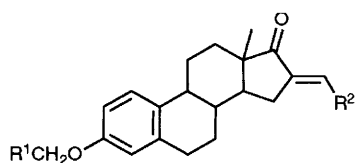
The average centre to centre distance between electron donors (anthracene = AN, 9,10-dimethoxyanthracene = DMAN) and electron acceptors is estimated on the basis of Corey–Pauling–Koltun models to be 17.5 Å, which approximates to the distance in the analogous indole–DMAN system (unpublished results).

The electron donor precursors used in the synthesis are 9-chloromethyl anthracene and 2-chloromethyl-9,10-dimethoxyanthracene. The former was synthesized according to a known method and the latter, as follows: bromination of 2-methylanthraquinone leads to 2-bromomethylanthraquinone followed by esterification, hydrolysis of the ester can give 2-hydroxymethylanthraquinone, which was reduced by

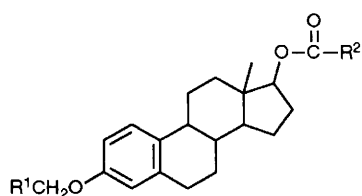
sodium dithionite and methylated by methyl iodide. The so-obtained 2-hydroxymethyl-9,10-dimethoxyanthracene was treated with thionyl chloride in chloroform at <5 °C to give 2-chloromethyl-9,10-dimethoxyanthracene in satisfactory yield.

The linking of electron donors and the steroid skeleton was performed in anhydrous dimethylformamide (DMF) catalysed by potassium carbonate. The linking of electron acceptors with steroid was realized in two ways: aldol condensation of the corresponding aldehyde and oestrone under standard conditions or the esterification of the corresponding benzoic acid and β -oestradiol in anhydrous pyridine with toluene-*p*-sulfonic acid (*p*-TSA) and dicyclohexylcarbodiimide (DCC) as catalysts. All the above experiments were carried out at room temperature to avoid the oxidation of electron donor. The compounds were purified by flash chromatography followed by recrystallization. The structures of all compounds obtained were consistent with their mass, ¹H NMR and IR spectra, and elemental analyses.

The intramolecular energy transfer in these systems can be eliminated because the overlap integral *J* may be assumed to be very small. Intermolecular interaction can also be excluded by employing a very dilute solution (<10⁻⁵ mol dm⁻³) in fluorescence quenching experiments. The free-energy changes for each of the electron-transfer reactions ($-\Delta G$) were obtained from the oxidation potentials of the donors and the reduction potentials of the acceptors recorded by cyclic



AN-ES-NO ₂	R ¹ = AN	R ² = 4-Nitrobenzene	A ₁
DMAN-ES-Cl ₂	R ¹ = DMAN	R ² = 2, 4-Dichlorobenzene	A ₂
DMAN-ES-NO ₂ (I)	R ¹ = DMAN	R ² = 4-Nitrobenzene	A ₁
DMAN-ES-NO ₂ Cl	R ¹ = DMAN	R ² = 4-Chloro-3-nitrobenzene	A ₃



AN-ES-(NO ₂) ₂	R ¹ = AN	R ² = 3, 5-Dinitrobenzene	A ₄
DMAN-ES-NO ₂ (II)	R ¹ = DMAN	R ² = 4-Nitrobenzene	A ₅
DMAN-ES-(NO ₂) ₂	R ¹ = DMAN	R ² = 3, 5-Dinitrobenzene	A ₄

Fig. 1 Structures of donor–acceptor compounds. A_{*n*} represents the model compounds of electron acceptors, which are used in Table 1.

Table 1 Energetics^a

	A ₁	A ₂	A ₃	A ₄	A ₅	AN	DMAN
<i>E_R</i> /V	-0.90	-1.40	-0.99	-0.65	-0.83	—	—
<i>E_{OX}</i> /V	—	—	—	—	—	1.4	0.9

^a Redox potentials (V vs. SCE) were measured by cyclic voltammetry at a Pt electrode. The measurements were performed in dimethylformamide (DMF) containing 0.1 mol dm⁻³ Et₄NClO₄ at room temperature. *E_s*(DMAN) = 2.95 eV and *E_s*(AN) = 3.10 eV. A_{*n*} is the model compound of electron acceptor shown in Fig. 1.

Table 2 Physical properties and rate constants of intramolecular electron transfer in donor–acceptor systems

Compound	$-\Delta G$ /eV ^a	τ_0 /ns ^b	τ /ns ^c	<i>k_{et}</i> /s ⁻¹ ^d
DMAN-ES-Cl ₂	0.65	15.0	13.0	1.1 × 10 ⁷
AN-ES-NO ₂	0.80	9.4	6.8	4.1 × 10 ⁷
DMAN-ES-NO ₂ Cl	1.05	15.0	7.5	6.7 × 10 ⁷
AN-ES-(NO ₂) ₂	1.05	9.4	5.7	6.9 × 10 ⁷
DMAN-ES-NO ₂ (I)	1.15	15.0	3.0	2.6 × 10 ⁸
DMAN-ES-NO ₂ (II)	1.22	15.0	8.0	5.8 × 10 ⁷
DMAN-ES-(NO ₂) ₂	1.40	15.0	11.5	2.0 × 10 ⁷

^a $-\Delta G$ is the free-energy change calculated using the Weller equation: $\Delta G = E_{OX(D)} - E_{R(A)} - E_{S(D)} - C$, *C* is the coulombic energy term, which can be eliminated in this case. ^b τ_0 is the fluorescence life time of model compound of electron donor, uncertainty is ± 0.2 ns. ^c τ is the fluorescence life time of electron donor in D–A system, uncertainty is ± 0.2 ns. ^d *k_{et}* is the rate constant of photoinduced intramolecular electron transfer which is calculated as: $k_{et} = 1/\tau - 1/\tau_0$, the uncertainty of *k_{et}* is less than $\pm 15\%$.

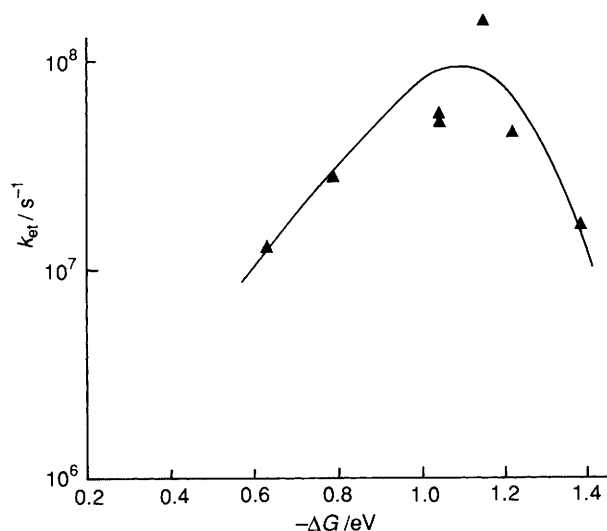


Fig. 2 Intramolecular electron transfer rate constants as a function of free-energy change in DMF at room temperature

voltammetry (Table 1). The rate constants of photoinduced electron transfer calculated from fluorescence lifetime measurements are listed in Table 2 and are plotted against the overall change of free energy in Fig. 2.

According to the classical theory, electron transfer requires orbital overlap between donor and acceptor. However, long distance intramolecular electron transfer occurs because of favourable nuclear factors and the optimisation of reaction energetics. From our results it is apparent that the rate constants of electron transfer first increase with the increasingly negative standard free energy and decline when at $-\Delta G > 1.15$ eV. We believe that our system is a promising one for demonstrating the existence of the inverted region in photo-induced electron transfer reactions.

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