Cyanoanthracene-sensitized Photooxidations of *N*,*N*-Dibenzylhydroxylamine and its Derivatives; Observation of the Marcus 'Inverted Region' in Back Electron Transfer within Geminate Radical Ion Pairs

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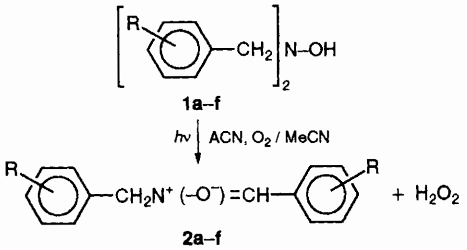
Back electron transfer within geminate radical ion pairs formed by electron transfer from the title hydroxylamines to singlet 9-cyano- and 9,10-dicyano-anthracenes in acetonitrile is shown to occur in the Marcus 'inverted region' and 'normal region', respectively.

The efficiency of the 9,10-dicyanoanthracene (DCA)-sensitized photooxidation of *N*,*N*-dibenzylhydroxylamine (DBH) in polar solvents has been shown to be determined by the rate of back electron transfer (BET) within the photochemically-generated geminate radical ion pair (GIP), relative to the rate of diffusive separation to free radical ions.[1] Recent experimental verification of the so-called Marcus 'inverted region'[2–8] stimulated us to investigate the free-energy dependence of BET rates within GIPs produced by electron transfer (ET) from the ground-state DBH **1a** and its derivatives **1b–f** to the excited-state 9-cyanoanthracene (CA) or DCA in MeCN at room temperature (Scheme 1).

An O_2-saturated MeCN solution of **1a–f** ($1.5–40 \times 10^{-3}$ mol dm^{-3}) containing CA or DCA (1.0×10^{-4} mol dm^{-3}), being irradiated with 366 nm light, exhibited UV absorption spectral changes very similar to those previously observed for the DCA-**1a** system. The same spectrophotometric method as before[1] was employed for determination of the quantum yield for appearance of **2** (Φ_2) at low conversions ($\leqslant 1\%$) of **1** (Scheme 1). We observed a good linear relationship between $1/\Phi_2$ and the reciprocal concentration (1/[**1**]), as well as efficient ET quenching of CA or DCA fluorescence by **1a–f** (quenching constant, $K_{SV} = 110–220$ mol^{-1} dm^3 for DCA and 6.7–28 mol^{-1} dm^3 for CA in MeCN),† suggesting the



2a–f
a; R = H
b; R = *p*-Cl
c; R = *m*-Cl
d; R = *p*-F
e; R = *p*-CF$_3$
f; R = *p*-Me
ACN = DCA or CA

Scheme 1

$$\mathrm{ACN} \xrightarrow{h\nu} {}^1\mathrm{ACN}$$

$${}^1\mathrm{ACN} \xrightarrow{k_d} \mathrm{ACN}$$

$${}^1\mathrm{ACN} + \mathrm{O_2} \xrightarrow{k_o} \mathrm{ACN} + \mathrm{O_2}$$

$${}^1\mathrm{ACN} + \mathbf{1} \xrightarrow{k_{et}} {}^1[\mathrm{ACN}^{\cdot -}\ \mathbf{1}^{\cdot +}]$$

$${}^1[\mathrm{ACN}^{\cdot -}\ \mathbf{1}^{\cdot +}] \xrightarrow{k_{-et}} \mathrm{ACN} + \mathbf{1}$$

$${}^1[\mathrm{ACN}^{\cdot -}\ \mathbf{1}^{\cdot +}] \xrightarrow{k_D} \mathrm{ACN}^{\cdot -} + \mathbf{1}^{\cdot +}$$

$$\mathrm{ACN}^{\cdot -} + \mathrm{O_2} \xrightarrow{k_{et'}} \mathrm{ACN} + \mathrm{O_2}^{\cdot -}$$

$$\mathbf{1}^{\cdot +} + \mathrm{O_2}^{\cdot -} \xrightarrow{k_r} \mathbf{2} + \mathrm{H_2O_2}$$

Scheme 2

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† Fluorescence of ACN (1.0×10^{-4} mol dm^{-3}) was quenched by **1a–f** ($1.5–40 \times 10^{-3}$ mol dm^{-3}) in N_2-purged MeCN according to the Stern-Volmer equation: $I_o/I = 1 + K_{SV}[\mathbf{1a–f}]$, where I and I_o refer to the fluorescence intensities of ACN with and without **1a–f**, respectively. Fluorescence from the ACN-**1** singlet exciplex could not be detected under the present experimental conditions.

Table 1 Limiting quantum yields for formation of **2a–f** ($\Phi_{2,\ \mathrm{lim}}$), rate constants for BET within geminate radical ion pairs ($k_{-\mathrm{et}}$), oxidation potentials of **1a–f** (E_{ox}) and free energy changes for BET ($-\Delta G_{-\mathrm{et}}$) at 24 ± 3 °C

		1a		**1b**		**1c**		**1d**		**1e**		**1f**	
	Solvent	DCA	CA	DCA	CA	DCA	CA	DCA	CA	DCA	CA	DCA	CA
$\Phi_{2,\ \mathrm{lim}}$	MeCN	0.21	0.59	0.20	0.50	0.12	0.63	0.18	0.59	0.14	0.83	0.27	0.67
$\Phi_{2,\ \mathrm{lim}}$	MeOH	0.37	0.56	0.30	0.31	—[c]	—[c]	0.31	0.50	0.34	0.83	0.63	0.07
$k_{-\mathrm{et}}/10^8\ \mathrm{s}^{-1}$	MeCN	19	3.5	20	5.0	36	3.0	23	3.5	31	1.0	14	2.5
$E_{\mathrm{ox}}/\mathrm{V}$[a]	MeCN	0.76		0.76		0.85		0.88		1.00		0.67	
$-\Delta G_{-\mathrm{et}}/\mathrm{kJ\ mol^{-1}}$[b]	MeCN	168	226	168	226	177	234	180	237	191	249	159	217

[a] Potential *vs.* saturated calomel electrode (SCE). Reduction potentials of DCA and CA (E_{red}) are reported to be −0.98 and −1.58 V *vs.* SCE in MeCN, respectively (J. Eriksen and C. S. Foote, *J. Phys. Chem.*, 1978, **82**, 2659). [b] $-\Delta G_{-\mathrm{et}}$ (kJ mol^{-1}) = 96.5 ($E_{\mathrm{ox}} - E_{\mathrm{red}}$). [c] Not determined.

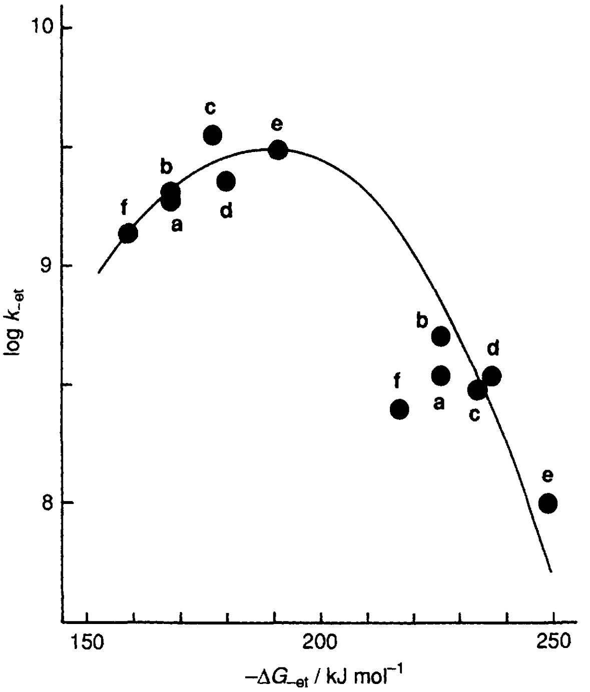

Fig. 1 Rates of back electron transfer for **1a–f** as a function of the free-energy change $-\Delta G_{-\mathrm{et}}$ in MeCN

preferential operation of a superoxide ($O_2^{\cdot -}$) mechanism at high concentrations of **1a–f** (Scheme 2).

By applying the steady-state approximation to Scheme 2, we obtain eqn. (1).

$$1/\Phi_2 = (1 + k_{-\mathrm{et}}/k_{\mathrm{D}})\{1 + (k_{\mathrm{d}} + k_{\mathrm{o}}\,[\mathrm{O_2}])/k_{\mathrm{et}}[\mathbf{1}]\} \quad (1)$$

The use of the limiting quantum yields, *i.e.* the quantum yields extrapolated to infinite concentration of **1a–f**, for formation of **2a–f** ($\Phi_{2\mathrm{a\text{–}f,lim}}$) makes it possible to neglect the contribution of a singlet oxygen mechanism, since **1a–f** at infinite concentration are assumed to quench the ACN fluorescence *via* ET in 100% efficiencies. Based on eqn. (2), where $k_{\mathrm{D}} = 5 \times 10^8\ \mathrm{s}^{-1}$

$$1/\Phi_{2,\ \mathrm{lim}} = 1 + k_{-\mathrm{et}}/k_{\mathrm{D}} \quad (2)$$

in MeCN at room temperature,[9] we estimate the rates of BET ($k_{-\mathrm{et}}$) within the GIP[1] [ACN$^{\cdot -}$ **1**$^{\cdot +}$] given in Table 1 along with the values of $\Phi_{2,\ \mathrm{lim}}$, oxidation potentials of **1** (E_{ox}), and free-energy changes in BET ($-\Delta G_{-\mathrm{et}}$). In Table 1 are also listed $\Phi_{2,\ \mathrm{lim}}$ values obtained in methanol (MeOH) under the same reaction conditions. As depicted in Fig. 1, the rate of BET increases first and then decreases with increasing exothermicity for this process ($-\Delta G_{-\mathrm{et}}$). Thus, the BET in the singlet cages ^{1}[DCA$^{\cdot -}$ **1**$^{\cdot +}$] and ^{1}[CA$^{\cdot -}$ **1**$^{\cdot +}$] is concluded to occur in the 'normal region' and 'inverted region', respectively.

The greater $\Phi_{2,\ \mathrm{lim}}$ value in MeOH than in MeCN in the DCA-sensitized oxidation of **1a** was previously shown to be a strong indication of the existence of the solvent-separated radical ion pair (SSIP) ^{1}[DCA$^{\cdot -}$/**1a**$^{\cdot +}$], which undergoes additional stabilization by hydrogen bonding between the radical ions and MeOH molecules to result in the much slower rate of BET in this ion pair.[1] The observation of higher DCA-sensitized oxidation efficiency ($\Phi_{2,\ \mathrm{lim}}$) of any starting hydroxylamine in MeOH than in MeCN is thus consistent with the occurrence of BET through a SSIP in the 'normal region'. On the other hand, the efficiency of the CA-sensitized oxidation is subject to the hydrogen-bonding effect to only a small extent except in the CA-**1f** system, allowing us to propose the contact radical ion pair (CIP) ^{1}[CA$^{\cdot -}$·**1**$^{\cdot +}$] as an intermediate from which BET takes place in the 'inverted region' giving CA and **1a–e**.‡ The non-fluorescent exciplex derived from singlet CA and **1a–e** should be responsible for formation of the ground-state CIP.[3]

The large downward deviation of the CA-**1f** system from the curve shown in Fig. 1 may be explained by assuming that BET proceeds *via* the SSIP ^{1}[CA$^{\cdot -}$/**1f**$^{\cdot +}$] which possesses much lower electronic coupling, compared to the CIP ^{1}[CA$^{\cdot -}$·**1f**$^{\cdot +}$], resulting in the much slower BET as observed.[3,4] Additional stabilization of this SSIP by hydrogen bonding mentioned above in the 'inverted region' should increase the rate of BET and thus lower the sensitized oxidation efficiency of **1f** to a great extent, being in agreement with the obtained result ($\Phi_{2f,\ \mathrm{lim}} = 0.07$).

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‡ We assume that the CIP ^{1}[CA$^{\cdot -}$·**1**$^{\cdot +}$] is isoenergetic with the SSIP ^{1}[CA$^{\cdot -}$/**1**$^{\cdot +}$] as already suggested for related systems by Gould *et al*[3] and Weller.[10] In the case that BET takes place from this CIP we use the equation: $1/\Phi_{2,\ \mathrm{lim}} = 1 + k_{-\mathrm{et}}/k_{\mathrm{solv}}$, where k_{solv} is the rate constant ($0.5\text{–}1.0 \times 10^9\ \mathrm{s}^{-1}$)[11] for the solvation of a CIP to form a SSIP. Calculation of $k_{-\mathrm{et}}$ using k_{solv} instead of k_{D} ($0.5 \times 10^9\ \mathrm{s}^{-1}$)[9] alter the Marcus plot to only a slight extent.