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FRONTIER ORBITAL SYMMETRY CONTROL OF INTERMOLECULAR ELECTRON TRANSFER

PROGRESS REPORT

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1. Fluorescence Quenching by Electron Transfer. The modification of Quenching Dynamics by Solvent Properties and Net Free Energy Change (David N. McKeithan, Ph.D. 1990).

Electron transfer quenching rate constants k_Q obtained from the variation in relative fluorescence quantum yield of acceptor 9,10-dicyano anthracene with concentration of selected donor quenchers have been measured as a function of donor oxidation potential in high dielectric solvents at temperatures of 0°C, 25°C and 50°C. The data are analysed in terms of the finite sink (nearest neighbour quenching) model expression

$$k_Q = 4\pi ND\rho k^\circ/(4\pi ND\rho + k^\circ[1-(2\pi NC)^{1/3}\rho]) \qquad \mathrm{I}$$

to obtain the intrinsic rate constant k° for electron transfer between the encountered donor/acceptor pair. Two dynamical situations are recognized:-

a) if $k^\circ << 4\pi ND\rho$ (the diffusional encounter rate constant k_D), $k_Q = k^\circ$ is independent of quencher concentration C, linear Stern-Volmer behaviour is observed and quenching is reaction-limited;

b) if $4\pi ND\rho = k_D < k^\circ$, k_Q^{-1} exhibits a linear dependence on $C^{1/3}$, quenching is diffusion-influenced and Stern-Volmer plots are non-linear. In this case the diffusion coefficient D, encounter diameter ρ and intrinsic rate constant k° may be recovered from measurements of $k_Q(C)$ at different temperatures.

Accordingly linear S-V behaviour (reaction-limited) quenching dynamics should become non-linear as k° is increased by an increase in the (negative) change in free energy ΔG, or reduction in quencher oxidation potential. This is confirmed by the following data for DCNA fluorescence quenching in methanol at 25 °C:-

Quencher(D)	pyridine	aniline	triethylamine	DABCO[c]
$E(D/D^+)$ eV	> 2.2	1.02	0.76	0.57
ΔG(kcal)	> 0	-24	-30	-34.3
$10^{-10}k^\circ$ ($M^{-1}s^{-1}$)	0.09[a]	23[b]	7[b]	1.0[a]
ρ	—	0.7 nm	0.49 nm	—

[a] reaction-limited quenching ($k_Q{}^{\ddagger}f(c)$

[b] diffusion-influenced quenching ($k_Q = f(c)$

[c] diazabicyclooctane

Thus reduction in the quencher oxidation potential from 2.2 eV(pyridine) to 1.02 eV(aniline) introduces a dependence of k_Q on quencher concentration C due to an increase in k° by a factor of ~ 200. However a further reduction in oxidation potential (with concomitant increase in $-\Delta G$) leads to a reduction in k° (symptomatic of the Marcus inverted region) by factors of 3(TEA) and 20(DABCO) such that at the lowest oxidation potential (DABCO) quenching again becomes reaction-limited. It is also interesting to note that the recovered encounter diameter ρ differs by ~40% for the quenchers aniline and triethylamine (TEA).

Under reaction-limited conditions ($k_Q \approx k^\circ << k_D$) it is expected that k_Q is independent of relative diffusion coefficient D or solvent viscosity η. The data obtained for benzylamine quenching of DCNA in the following solvents at 3 different temperatures support this prediction:-

Solvent	T°C	η^a(cP)	ϵ^a	$10^{-9}k_Q(=k^\circ)M^{-1}s^{-1}$
	0	0.909	37.8	1.5_4
methanol	25	0.612	32.9	2.5_3
	50	0.434	28.7	4.1_7
	0	2.13	28.9	1.6_6
ethanol	25	1.26	24.8	2.3_1
	50	0.851	23.7	3.6_7
	0	6.11	23.2	1.2_5
butanol	25	3.20	16.5	2.0_5
	50	1.79	8.3	3.6_9

[a] measured in this laboratory by Brendan Murphy (undergraduate).

This is consistent with the Weller expression

$$k_Q = \frac{4\pi N D \rho}{1 + A[\exp(\Delta G^{\ddagger}/RT + \exp(\Delta G/RT)]}$$

if the second term in the denominator is >> 1 (for reaction-limited quenching) and A is a linear function of the diffusion coefficient D (Weller). Moreover the increase in k_Q with temperature is that predicted by the exponential term although recovered values of $\Delta G^\ddagger$ ($>>\Delta G$) are also temperature-dependent possibly due to the temperature-dependence of dielectric constant ϵ.

2. <u>Transient Absorption Measurements Following Selective Excitation of 1:1 EDA Complex Isomers</u> (Prof. Da-Chang Yuan, Research Associate).

The strong CT absorption bands with maxima at 450 nm and 560 nm exhibited by solutions of naphthalene and TCNE in either $CHC\ell_3$ or $CH_2C\ell_2$ are predicted (Stevens 1986) to originate in different isomers of 1:1 EDA complexes. Accordingly the naphthalene positive ion produced by selective excitation in these bands is expected to undergo geminate and homogenous recombination on different time scales. Following ps excitation with second harmonic pulses (at 532 nm) from a Quantel YG402 mode-locked Nd:YAG laser (at CFKR, Texas) with ps probing at 693.1 nm it is found that

a) relaxation of the naphthalene cation is purely exponential over 4 half-lives with a rate constant of $4.5 \pm 1.1 \times 10^{10} s^{-1}$ with no indication of a second order component at longer times consistent with a negligible homogeneous recombination component;

b) the absorption has a finite rise time of ~15 ps consistent with reorientation of the initially-excited complex configuration as prerequisite for electron transfer.

No transient absorption was observed following excitation of this system by third harmonic pulses at 355 nm possibly because this wavelength coincides with a low OD of the shortwave CT band.

A proton NMR spectrum of solutions of naphthalene and TCNE in perdeuterated solvents at ambient temperature (Brooker AMx 360 MHz) provided no evidence of naphthalene complexation under these conditions.

3. <u>Selective Quenching (and Enhancement) of Dual Fluorescence from Linked EDA Systems</u> (Mr. Carl Biver).

The substitution of electron acceptor ($-NO_2$) and donor ($-NH_2$) groups at the terminal positions of p-terphenyl introduces additional long wave absorption and fluorescence bands in dioxane solution. Selective quenching of the long-wave fluorescence band by water and other polar compounds has been shown to be a dynamic (diffusion-influenced) process contrary to its expected origin in a TICT state.

On the other hand $CC\ell_4$ is found to both quench the short wave fluorescence component and increase the intensity of the long wave fluorescence band with no detectable change in the absorption spectrum over the $CC\ell_4$ concentration range employed. This behaviour is not presently understood although simultaneous quenching and enhancement of the two fluorescent components is consistent with a system of coupled excited states, in support of which the fluorescence response functions following ps excitation (carried out at CFKR) are essentially biexponential ($1.0 < X^2 < 1.2$) for both fluorescent bands. Initial measurements show that the spectroscopic behaviour of 9-NO_2, 10'-NH_2 bianthryl in dioxane is qualitatively similar.

4. <u>Electron-Transfer Sensitized Cycloreversion of Rubrene Endoperoxide</u> (Tie-Yu Liu, Ph.D. May 1990).

The photosensitized reaction

$^1S^* + RO_2 \longrightarrow {}^1(S^-..., RO_2^+) \longrightarrow {}^3(S^-...RO_2^+) \longrightarrow S + {}^3RO_2 \longrightarrow R + {}^3O_2$

(S=DCNA sensitiser, R=rubrene) provided a well-characterized sequence to test the effect of a magnetic field on the overall quantum yield by enhancing the rate of spin-rephasing of the singlet to triplet geminate radical-ion pair $^{1,3}(S^-...RO_2^+)$. A magnetic field of 600 gauss (provided by 2 bar magnets) was found to increase the cycloreversion yield by 50% for the singlet sensitizer indicated, but had no effect in the case of a triplet (chloranil) sensitizer. Publication expected in 11/90.

5. <u>Vibronic Modification of Adiabatic Requirements for Intermolecular Electron Transfer</u> (Dr. B. Stevens, P.I.)

Following an examination of the symmetry species of transient intermolecular vibrational modes and their effect on transformation properties of reaction surfaces (with W.A. Glauser, in press) attention has been focussed on the similar role of in-plane <u>intra</u>molecular modes selectively excited in either aromatic electron donors or acceptors. Specifically the electron transfer sequence

$$D^* + A \longrightarrow (D^*A) \longrightarrow (D^+A^-) \longrightarrow D^+ + A^-$$

will be adiabatic if the locally-excited state (D^*A) transforms as the charge-transfer configuration (D^+A^-), via an exciplex intermediate $(DA)^*$. In complexes of C_{2v} symmetry, in-plane vibrations of the aromatic donor subjuce to each representation of the point group. Thus an adiabatic channel between B_1(LE) and B_2(CT) configurations could be promoted by exciting an A_2 mode in D^* by excitation at shorter wavelengths. This is supported by the results of Lim et al. who find that excitation of the S_2 state of TCNB increases the efficiency of exciplex formation with p-xylene as compared with excitation of its S_1 state. In this case the S_2 and S_1 states of TCNB transform as B_2 and B_1 whereas the CT state belongs to B_2 symmetry; internal conversion of the initially-excited S_2 state to S_1 with one quantum of an A_2 mode should therefore promote exciplex formation.

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