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Electron Transfer Quenching of Excited States by Europium(III) in Acetonitrile Solutions

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The electron transfer processes have always been the object of extensive investigations because of theoretical and practical reasons [1]. In the past few years much interest has been focused on *light induced* electron transfer reactions because they are most promising for solar energy conversion [2] and can also allow testing the validity of the various electron transfer theories over a wide ΔG range [2c, 3].

The original Marcus theory [1, 4] is based on the assumption that outer sphere electron transfer reactions in fluid solution are adiabatic. This assumption, however, does not seem plausible [5] in the case of reactions involving the transfer of *f* electrons. Evidence of nonadiabatic behavior has in fact been recently discussed for electron transfer reactions involving europium ions [6, 7]. It has also been shown that the analysis of the log k_q *vs.* ΔG plots (where k_q is the electron transfer rate constant and ΔG is the corresponding free energy change of the reaction) obtained for homogeneous families of electron transfer reactions can allow disentangling the effects of nonadiabaticity (electronic factors) and intrinsic barrier (nuclear factors) in determining the reaction rate [2c, 7, 8].

We have studied the electron transfer reactions between excited states of aromatic molecules and Eu(III) in acetonitrile (AN) solutions (eqn. 1) and we have found very peculiar behavior of log k_q *vs.* ΔG (Fig. 1).

$$A^* + Eu^{3+} \xrightarrow[AN]{k_q} A^+ + Eu^{2+} \qquad (1)$$

The experiments were carried out at room temperature using reagent grade organic molecules and $Eu(ClO_4)_3 \cdot 6H_2O$. The equipment and the experimental technique used have been previously described [9]. The rate constant k_q was obtained from fluorescence (intensity or lifetime) quenching measurements in the case of the singlet excited states and from the decay of the triplet–triplet absorption for the triplet excited states. In all cases flash photolysis experiments showed that the excited state quenching was accompanied by the appearance of the spectrum of the A^+ radical cation. Conversely, the quenching of naphthalene fluorescence was found to cause no sensitized emission by Eu^{3+}, showing that electronic energy transfer cannot be an important quenching process [10]. Thus, it seems safe to conclude that the dominant (if not the sole) quenching mechanism in these systems is electron transfer. The k_q values obtained are collected in the Table I, where other similar literature data [11, 12] are also shown. Fig. 1 shows the corresponding log k_q *vs.* ΔG plot.

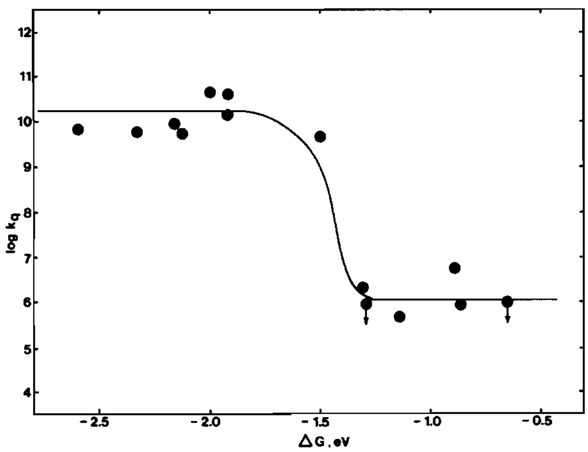

Fig. 1. Plot of the logarithm of the rate constants *vs.* ΔG for the quenching of aromatic molecules by $Eu(ClO_4)_3 \cdot 6H_2O$.

As one can see, the plot shows clear stepwise behavior. Such behavior is expected when, with increasing driving force, the rate constant of an outer sphere electron transfer reaction tends to a lower than diffusion plateau value because of nonadiabaticity reasons and, at the same time, other electronically more efficient reaction channels become thermodynamically allowed [2c, 7, 8]. A complete understanding of the behavior of these systems (particularly, of the nature of the reaction channel whose rate constant reaches the diffusion controlled value) must clearly wait other investigations. However, the only plausible reason for the low (and scattered) values of the rate constant up to ΔG values as negative as −1.3 eV lies in nonadiabatic behavior [2c, 7, 8] of Eu(III) in outer sphere electron transfer reactions. This result is in

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TABLE I. Bimolecular Quenching Rate Constants.

Donor, A*		k_q (M^{-1} s^{-1})	ΔG^a (eV)	$E_{0-0(A^*)}$ (eV)	ref.
Naphthalene	(S_1)	7.2×10^{9} [b]	−2.60	3.93	this work
Pyrene	(S_1)	6.3×10^{9} [b]	−2.33	3.34	this work
Perylene	(S_1)	8.3×10^{9} [b]	−2.15	2.82	[c]
9,10-Diphenilanthracene	(S_1)	5.8×10^{9} [d]	−2.13	3.16	this work
Tetracene	(S_1)	4.5×10^{10} [e]	−2.00	2.62	11
Coronene	(S_1)	4.0×10^{10} [e]	−1.92	3.03	11
Coronene	(S_1)	2.0×10^{10} [d]	−1.92	3.03	this work
Zn(TPP)[f]	(S_1)	1.6×10^{10} [e]	−1.50	2.06	12
Mg(TPP)	(T_1)	2.1×10^{6} [g]	−1.31	1.66	12
Coronene	(T_1)	$<10^{6}$ [g]	−1.29	2.37	this work, 12
Zn(TPP)	(T_1)	4.8×10^{5} [g]	−1.14	1.69	12
Anthracene	(T_1)	5.6×10^{6} [g]	−0.88	1.82	this work
$TPPh_2$	(T_1)	9.0×10^{5} [g]	−0.86	1.70	12
Tetracene	(T_1)	$<10^{6}$ [g]	−0.65	1.27	this work

[a] Free energy change of the electron transfer reaction calculated from the standard redox potentials of the reaction partners, *i.e.*, neglecting work terms. The standard potential used for Eu^{3+} ion is E^0 ($Eu^{3+/2+}$) = +0.15 V (I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc., 79,* 1852 (1957)). The redox potentials of the excited species have been obtained from the zero–zero spectroscopic energy of the excited state and the ground state redox potential. The values used have been taken from the following references: C. K. Mann and K. K. Barnes, 'Electrochemical Reactions in Non-aqueous Systems', Marcel Dekker, New York, 1970; W. Potter and G. Levin, *Photochem. and Photobiol., 30,* 225 (1979); J. B. Birks, 'Organic Molecular Photophysics', John Wiley and Sons, London, 1975; P. S. Engel and B. M. Monroe, in *'Adv. Photochem.', 8,* 245 (1971); R. O. Loufty and R. O. Loufty, *Can. J. Chem., 50,* 4052 (1972); G. D. Dorough, J. R. Miller and F. M. Huennekens, *J. Am. Chem. Soc., 73,* 4315 (1951).
[b] Obtained from emission decay measurements. [c] T. A. Shakhverdov, *Opt. Spectrosc., 29,* 166 (1970). [d] Obtained from emission intensity measurements. [e] Estimated value. [f] TPP: tetraphenylporphyrin. [g] Obtained from triplet–triplet absorption decay measurements.

agreement with a recent analysis of the Eu^{3+} electron transfer reactions in aqueous solutions as well as with theoretical expectations based on spectroscopic arguments [7].

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