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Substituent Effects on Intermolecular Electron Transfer: Coumarins in Electron-Donating Solvents

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Recently, intra- and intermolecular electron transfer (ET) reactions in solution have been studied extensively to investigate the roles of solvent dynamics and molecular vibrations.[1–11] One novel observation is ultrafast intermolecular ET from electron-donating solvents to electron-accepting dye molecules.[8–11] Some of these systems showed reaction rates much greater than the rate of solvent relaxation, indicating the importance of the intramolecular nuclear coordinate. For the study reported in this communication, we have chosen a variety of 7-aminocoumarin dyes as electron acceptors. A key observation of this work is a drastic change of the reaction rate as a function of the substituent groups of the coumarins.

Ultrafast fluorescence quenching of various coumarins, i.e., coumarin 151 (denoted C151 hereafter), C152, C481, C522, and C153 (Figure 1), in electron-donating solvents, i.e., aniline (AN) and *N,N*-dimethylaniline (DMA), was observed by means of the fluorescence up-conversion technique. The excited coumarins usually have lifetimes of a few nanoseconds in ordinary nonreacting solvents,[12,13] but in the present system, they are reduced down to a couple of hundred femtoseconds, as shown in Table I. We ascribe the quenching process to an intermolecular ET from the solvent to the excited dye by analogy with a similar type of reaction for Nile blue, where the reaction products, cations of the solvents, and a neutral radical of the dye were observed by subpicosecond transient absorption measurements.[9]

In the present series of measurements, several interesting features are observed. (1) The ET reaction ranges from a couple of hundred femtoseconds to several tens of picoseconds, which means that some of the reactions occur much faster than the solvation process, i.e., 6.7 ps in AN and 7.9 ps in DMA.[14] (2) The reaction dynamics give a nonexponential behavior for most cases. The results of analysis shown in Table I are tentatively made with a biexponential function, except the single exponential function (ca. 210 fs) for C151/DMA. (3) The reactions in DMA are always faster than those of the same coumarins in AN. (4) The reaction rate depends on the substituent group of the coumarin.[15] Extending the alkyl chain on the 7-amino group (C151, C152, and C481) and forming a hexagonal alkyl ring with the benzene moiety (C522 and C153) reduce the reaction rate.

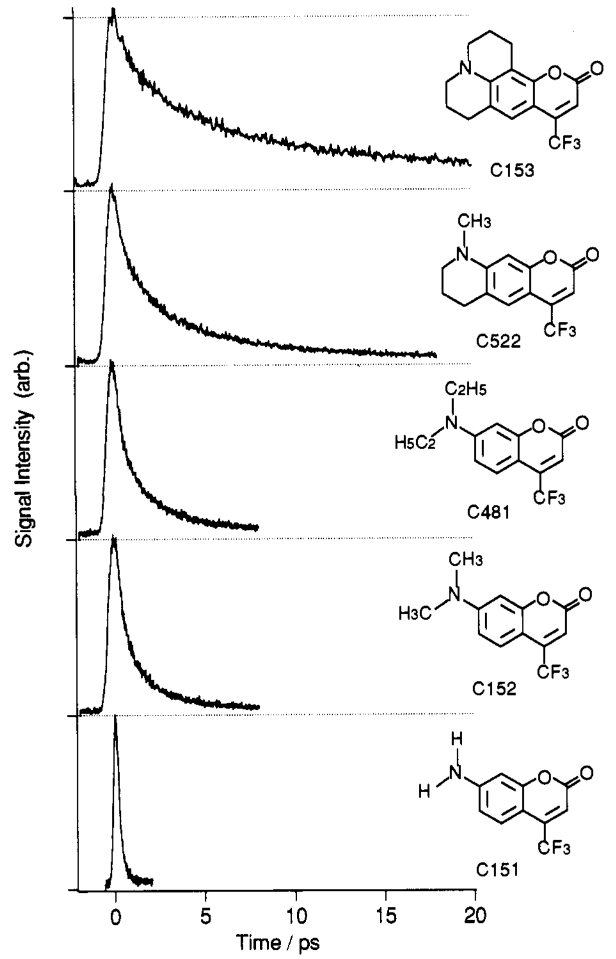

Figure 1. Up-conversion signals of the coumarins in DMA at fluorescence wavelength of 470 nm. Concentrations of the dyes were 1 × 10^{-3} M. The second harmonic generation (SHG) of a Ti:sapphire laser, at 395 nm, was used to excite the sample. The remaining fundamental at 790 nm was used to up-convert the fluorescence from the sample. The full width at half-maximum of the cross-correlation between SHG and fundamental was 250 fs for the experiments for the slower reactions and 100 fs for the faster reactions, which require better time resolution. All the up-converted signal was measured at the magic angle. The samples were circulated by micropump, and air in a sample reservoir was replaced by Ar gas during the measurements.

ET theory in solution usually treats outer-sphere and inner-sphere effects separately. The outer-sphere effect concerns the

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(1) Jortner, J.; Bixon, M. *J. Chem. Phys.* **1988**, *88*(1), 167.

(2) Sumi, H.; Marcus, R. A. *J. Chem. Phys.* **1986**, *84*, 4894.

(3) Sparpaglioni, M.; Mukamel, S. *J. Chem. Phys.* **1988**, *88*, 3265.

(4) Hynes, J. T. *J. Phys. Chem.* **1986**, *90*, 3701.

(5) Kosower, E. M.; Huppert, D. *Chem. Phys. Lett.* **1983**, *96*(4), 433.

(6) Kang, T. J.; Jarzeba, W.; Barbara, P. F.; Fonseca, T. *Chem. Phys.* **1990**, *149*, 81.

(7) Walker, G. C.; Akesson, E.; Johnson, A. E.; Levinger, N. E.; Barbara, P. F. *J. Phys. Chem.* **1992**, *96*, 3728.

(8) Kobayashi, T.; Takagi, Y.; Kandori, H.; Kemnitz, K.; Yoshihara, K. *Chem. Phys. Lett.* **1991**, *180*(5), 416.

(9) Kandori, H.; Kemnitz, K.; Yoshihara, K. *J. Phys. Chem.* **1992**, *96*, 8042.

(10) Yoshihara, K.; Yartsev, A.; Nagasawa, Y.; Kandori, H.; Douhal, A.; Kemnizt, K. In *Ultrafast Phenomena VIII*; Martin, J.-L., Migus, A., Mourou, G. A., Zewail, A. H., Eds.; Springer: Berlin, 1993; p 571.

(11) Yartsev, A.; Nagasawa, Y.; Douhal, A.; Yoshihara, K. *Chem. Phys. Lett.* **1993**, *207*(4,5,6), 546.

(12) Jones, G., II; Jackson, W. R.; Halpern, A. M. *Chem. Phys. Lett.* **1980**, *72*(2), 391.

(13) Jones, G., II; Jackson, W. R.; Choi, C.; Bergmark, W. R. *J. Phys. Chem.* **1985**, *89*, 294.

(14) These values are the fastest components obtained from dynamic fluorescence Stokes shift measurements using coumarin 102 (C102) as a probe molecule. The ET of C102 in AN and DMA are of the order of nanoseconds. Detailed analysis will be reported elsewhere.

(15) In this communication, we focused on the amino group in the 7-position, but substituents in the 4-position also affect the ET reaction. We observed ET reactions for coumarins with a 4-CF_3 group (C481), with a 4-H group (C466), and with a 4-CH_3 group (C47), and the quenched fluorescence lifetimes were 1.0 (average), 50, and 90 ps, respectively, in aniline. C466 and C47 show single exponential behavior. It seems that electrophilic substitution at the 4-position enhances ET reaction.

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Table I. Absorption (λ_{abs}) and Fluorescence (λ_{fl}) Maxima, Reduction Potential ($E_{red}(\text{dye}^{0/-})$), Relative Energy Gap ($\Delta G_{rel}$), and Fluorescence Lifetimes (τ_{ET}) of Coumarins

	in AN					in DMA				
coumarin	λ_{abs} (nm)	λ_{fl} (nm)	$E_{red}(\text{dye}^{0/-})^a$ (V)	$\Delta G_{rel}{}^b$ (eV)	$\tau_{ET}{}^c$ (ps)	λ_{abs} (nm)	$\lambda_{fl}{}^d$ (nm)	$E_{red}(\text{dye}^{0/-})^a$ (V)	$\Delta G_{rel}{}^b$ (eV)	$\tau_{ET}{}^c$ (ps)
C153	435	526	–1.76	0.00	17 {59%} 285 {41%} [127]	416	504	–2.4	0.00	3.1 {67%} 19.4 {33%} [8.5]
C522	422	512	–1.72	–0.13	10 {39%} 34 {61%} [25]	408	(460)	–2.2	–0.26	0.8 {69%} 4.0 {31%} [1.8]
C481	413	505	–1.69	–0.22	4.1 {37%} 15.2 {63%} [11]	400	(440)	–2.2	–0.32	0.57 {80%} 2.9 {20%} [1.0]
C152	408	504	–1.68	–0.27	3.7 {41%} 12.4 {59%} [8.8]	397	(470)	–2.1	–0.44	0.46 {89%} 2.7 {11%} [0.71]
C151	376	450	–1.75	–0.46	0.59 {50%} 1.9 {50%} [1.2]	370	(440)	–2.1	–0.67	0.21 {100%}

[a] Reduction (peak) potentials from irreversible waves measured by cyclic voltammetry. [b] Relative values of energy gap. [c] Values in brackets are the average lifetimes; $\langle\tau\rangle = A_1\tau_1 + A_2\tau_2$. [d] Values in parentheses are not accurate because of very weak intensity and disturbance from Raman bands of the solvent.

reorientation of solvent molecules on the solvent coordinate, and the inner-sphere effect concerns the intra-molecular relaxation on the nuclear coordinate, which is usually much faster than the solvation dynamics.[1,2] One of the solvation processes which could be very fast is the "inertial" component of solvation, which has recently been observed in acetonitrile.[16] This inertial component occurred within 100 fs. However, the solvation process we observed was 6.7 ps for AN and 7.9 ps for DMA.[14] Most of the ET reactions we observed are faster than these solvation process which are consistent with our previous conclusions; diffusive solvation does not necessarily limit ET in weakly polar solvents.[8–11] On the other hand, intermolecular ET removes an electron from the HOMO of donor to the LUMO of acceptor, which means that the nuclear bond length or bond angle of these molecules rearranges during the reaction. In the present system, longer alkyl chains and hexagonal alkyl rings will restrict the flexibility of the amino group. Some vibrational motions of the amino group may be treated as the nuclear coordinate involved in the reaction. The rotation of the amino group is often discussed in studies of the so-called twisted intramolecular charge-transfer (TICT) reactions, as represented by *N,N*-dimethylaminobenzonitrile (DMABN).[17–19] DMABN has a planar configuration between the amino group and the benzene moiety in the initially excited state but is considered to become perpendicular in the charge-transferred state in polar solutions.

The effect of substituent can also be discussed in terms of the free energy gap dependence of reaction. From the steady-state spectroscopic and cyclic voltammetric measurements, we estimate a free energy gap between the reactant and the product by using the following equation:[20]

$$\Delta G_0 = -E_{00} + E_{ox}(\text{solv}^{0/+}) - E_{red}(\text{dye}^{0/-}) - E_{IPS} \quad (1)$$

Here E_{00} is the transition energy from the S_0 state to the S_1 state of coumarin, $E_{ox}(\text{solv}^{0/+})$ is the oxidation potential of the solvent, $E_{red}(\text{dye}^{0/-})$ is the reduction potential of the coumarin, and E_{IPS} is the ion pair stabilization energy. The first and third terms are estimated from the absorption maxima and cyclic voltammetries of coumarins, respectively, but the second and fourth terms cannot be reliably estimated. For $E_{ox}(\text{solv}^{0/+})$, the values in the gas phase are known, 7.12 eV for DMA and 7.69 eV for AN,[21] which indicates that DMA is a better electron donor than AN. We think that this difference is the major reason for the faster reaction in DMA than that in AN. But the oxidation potential of neat solvent cannot be measured experimentally by cyclic voltammetry. Only relative values (ΔG_{rel}) are obtained at present on the assumption that the second and fourth terms do not depend on solute molecules. The results are given in Table I. Systematic changes of ΔG_{rel} are seen, which show good correlation with the change of the reaction rate; as the value of ΔG_{rel} becomes negative, the reaction becomes faster. This tendency is reasonable if we consider the reactions to be in the so-called Marcus "normal" region and not in the "inverted" region.[22]

The present research gives the first example for ultrafast intermolecular ET, which shows a systematic change of the reaction rate as a function of the molecular structure. Detailed analyses of the energy gap dependence on the molecular structure and of the nonequilibrium ET dynamics are under progress.

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(16) Rosenthal, S. J.; Xie, X.; Du, M.; Fleming, G. R. *J. Chem. Phys.* **1991**, *95*(6); 15; 4715.

(17) Grabowski, Z. R.; Rotkiewicz, K.; Siemiarczuk, A.; Cowly, D. J.; Baumann, W. *Nouv. J. Chem.* **1979**, *3*, 443.

(18) Lippert, E.; Rettig, W.; Bonacic-Koutecky, V.; Heisel, F.; Miehe, J. A. *Adv. Chem. Phys.* **1987**, *68*, 1.

(19) Kato, S.; Amatatsu, Y. *J. Chem. Phys.* **1990**, *92*(12), 15, 7241.

(20) Rehm, D.; Weller, A. *Z. Phys. Chem. N. F.* **1970**, *69*, 183.

(21) Castella, M.; Millie, P.; Piuzzi, F.; Caillet, J.; Langlet, J.; Claverie, P.; Tramer, A. *J. Phys. Chem.* **1989**, *93*, 3949.

(22) Marcus, R. A. *Discuss. Faraday soc.* **1960**, *29*, 21.