Femtosecond intermolecular electron transfer between dyes and electron-donating solvents

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Abstract. Ultrafast intermolecular electron transfer (ET) is discussed for the system of various xanthene dyes in diffusionless weakly polar electron donating solvents. ET was observed by fluorescence quenching dynamics. It gives a non-exponential process in case of dyes in aniline. ET rate is determined by mutual displacement of the reactants and by the solvent relaxation. In case of dyes in N,N-dimethylaniline, ET quenching gives very different dynamics and shows a single exponential decay with a rate constant as fast as 10^{13} s^{-1}. Ultrafast ET, which is much faster than solvent relaxation time, requires a new mechanism for a cause of ET.and its rate constant may be determined by nuclear motion, rather than controlled by solvent dynamics.

1. INTRODUCTION

Intermolecular electron transfer (ET) reaction is one of the most important chemical reaction because of their universality in chemistry and biology. Adiabatic and non-adiabatic ET process were examined theoretically [1,2], and numerous investigations were made experimentally. We have reported ultrafast ET (as fast as 10^{13} s^{-1}) between excited dye and weakly polar electron-donating solvent molecules [3]. This system has several specific features. (1)The electron donor and acceptor are in contact and there is no translational diffusion in order to induce ET. (2)The weakly polar solvent system gives less dielectric friction to ET. (3)There is no change of the net charge before and after the reaction. The time scale of ET in these systems falls into the time scale of solvent relaxation time and of nuclear motion and the reaction will be severely influenced by these dynamics. It is also the aim of present study to investigate the role of intermolecular interaction, namely solvent effect to the reaction as well as the effects of intramolecular dynamics such as vibrational relaxation and nuclear motion.

2. EXPERIMENTAL

Ultrafast intermolecular ET (forward ET) between the excited dye molecule and solvent was investigated by probing femtosecond fluorescence quenching. Synchronously pumped hybridly mode-locked dye laser with group velocity dispersion (GVD) control by a prism pair was used to generate optical pulses at different wavelengths at 76 MHz. Using usual combination of Rh-6G and DODCI/DQOCI and spatial filters between the second prism and high reflecting mirror, 70 fs pulses were generated at 583, 605, and 615 nm with output power of ca. 100 mW. With sulforhodamine 101 and DQTCI generation of 50 fs pulses at 675 nm was achieved.

The fluorescence decay was measured at the magic angle by a conventional fluorescence up-conversion system using a 0.3 mm BBO crystal. A quartz flow-cell of 1 mm optical path length was used to minimized thermal effects on the fluorescence decay. In order to avoid long term instabilities of the dye laser, fluorescence decay was measured many times to increase accumulation time to several minutes at each delay position. The transient absorption of reaction products, which provides a direct evidence of ET was investigated with time resolution of 0.7 ps. The reverse ET was observed by both the decay of the reaction products and the ground-state recovery.

Nile blue perchlorate (NB) and oxazine 1 perchlorate (OX1) (Figure 1) were obtained from Exiton and used without purification. Aniline (AN) and N,N-dimethylaniline (DMA) were vacuum distilled. The concentration of NB and OX1 in electron-donating solvent was varied from 0.5×10^{-4} to 2×10^{-4} M. Dye solutions were bubbled by N_2 to eliminate a possible effect of solvent oxidation.
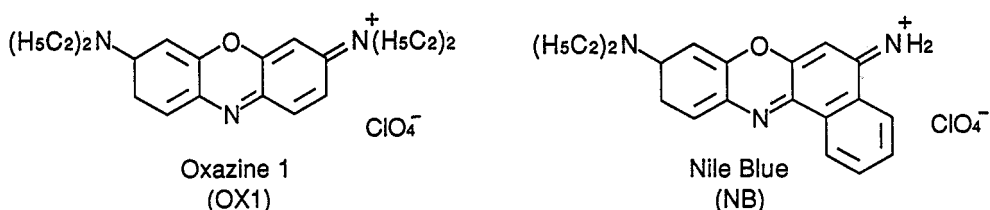

Figure 1. Structures of Nile blue A perchlorate and oxazine 1 perchlorate.

3. RESULTS

In Figure 2(a) fluorescence decays are shown for OX1 dissolved in AN excited at 605 nm (blue side of the absorption spectra). Non-exponential character of the decay is obvious. Very similar non-exponential time behavior at all measured fluorescence wavelengths (at 680, 700, 725, 775, and 830 nm) was observed for NB in AN as shown in Figure 2. A decay curve of OX1 in DMA upon excitation at 605 nm is presented in Figure 3(b). Decay was well fitted by a single exponential dependency with the time constant of 280 fs for OX1/DMA and 160 fs for NB/DMA. To analyze the influence of the excess vibrational energy in the excited state, fluorescence decays were measured upon excitation at 675 nm which corresponds to the red slope (close to 0-0 transition) of the absorption spectra for both dyes in AN and DMA. In AN non-exponential decays were observed and almost the same multi-exponential decay components were obtained by deconvolution as in the case of excitation at 605 nm. The fluorescence of OX1 in DMA also gives a similar single exponential decay to that obtained at 605 nm excitation.

The ultrafast quenching due to intermolecular ET resulted in formation of solvent cation and neutral radical of dye. The reaction takes place in the following manner, taking Nile blue in DMA as an example.

$$NB^+ClO_4^- + DMA \underset{}{\overset{h\nu}{\rightleftarrows}} NB\ ClO_4^- + DMA^+$$
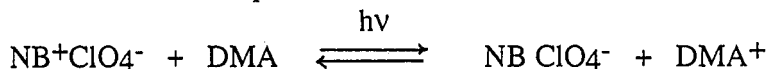
To get a separate experimental evidence, we measured sub-picosecond transient absorption of NB/DMA and found a spectrum which coincides well with that of DMA$^+$ [4]. This provides a direct proof of ET reaction. The transient species appear rapidly and decrease exponentially with a decay time constant of 3.7 ps, indicating that the reverse ET occurs with this time. In the present system, the both forward and reverse ET occur very rapidly and it performs a full cycle of charge separation and recombination in less than a few picoseconds.
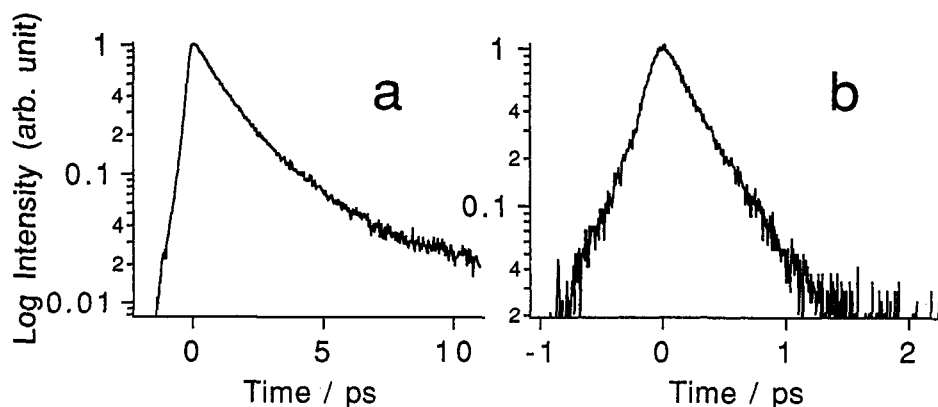
Figure 2. Non-exponential fluorescence decay of OX1 in AN (a). Single exponential fluorescence decay of OX1 in DMA (b).
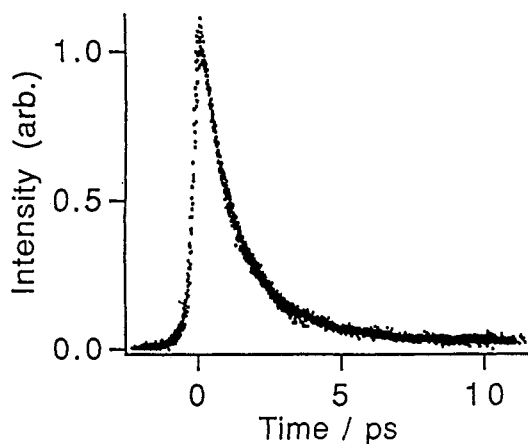

Figure 3. Superposition of fluorescence decays of OX1 observed at 680, 700, 725, and 830 nm. The intensities are normalized to the 0.5 ps delay. Excitation wavelength is 605 nm.

4. DISCUSSION

There are two main results on the wavelength dependence of the present fluorescence decay measurements. 1) Fluorescence decays for NB/AN and OX1/AN showed the same time behavior in a wide spectral region from 670 to 830 nm (Figure 2). 2) The time behavior of fluorescence signal upon excitation at 605 nm with much excess of vibrational energy and at 675 nm close to 0-0 transition gave very similar decay kinetics (data not shown). These observations indicate that ET takes place from the bottom of the excited state potential after ultrafast intramolecular vibrational relaxation. One of the important consequence of this result is the possibility to eliminate the influence of vibrational relaxation on the ET dynamics. Excited state relaxation faster than 100 fs, which should provide the present result, can be inferred from the measured two exponentials with 70 fs and 410 fs time constants with 70 fs resolution [5]. The fluorescence of NB and OX1 in methanol gave instantaneous rise times at different wavelengths with 55 fs resolution [6]. The thermalization of ground and excited states was reported as fast as 50 fs for the same oxazine dye, cresyl violet, in transient spectroscopy with 60 fs pulse excitation and 10 fs pulse probing [7]. Since the vibrational relaxation is very fast (<<100 fs), we now concern only ET dynamics on our present measurements.

The non-exponential fluorescence decays measured for NB and OX1 in AN have to be related with the nature of ET itself. This non-exponentiality can be caused by static
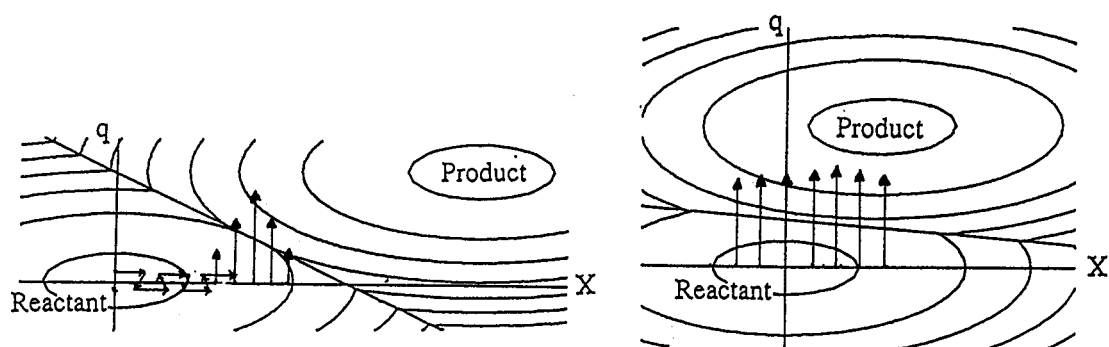
Figure 4. Two dimensional description of potentials of electron transfer reaction with solvent configurational axis (X) and nuclear configurational axis (q). The left figure shows a typical narrow window case and right figure wide window case. The different length of the vertical arrows schematically indicate rates of ET by different donor-acceptor relative orientations (see text).

and dynamic effects both based on the assumption of the strong interaction between donor-acceptor orientation and ET rate. Such a view could be explained by a two-dimensional potential energy surface as shown in Figure 4(a). Here the abscissa represents the solvent configurational coordinate (X). A slow diffusive (Brownian) motion of the solvent takes place along this coordinate. The ordinate represents nuclear configurational coordinate (q). An ultrafast molecular vibrational motion takes place along this coordinate. The particle moves along X and jumps to the product surface at the region of minimum potential barrier along q (narrow window case [1]). In practice, the present case does not belong to the narrow window case, but to "intermediate window case", since both inner and outer reorganization energies happen to have similar values (about 0.3 eV) [3]. The typical narrow window case will be realized when the former is much greater than the latter [1]. Static effect occurs when ET takes place for the different solvent-solute mutual orientation, where the different magnitude of electronic interaction gives different ET rate. In the all ensemble of the molecules ET will give interaction gives different ET rate.   In the all ensemble of the molecules ET will give non-exponential decay. Dynamic non-exponenti-ality realizes if the donor-acceptor orientation changes during ET and disturbs its single exponential character. As the measured signal is the sum of all these different disturbed exponential processes for each separated orientation, it becomes non-exponential. To explain observed experimental time behavior we suggest the effect of molecular reorient-ation with the rate in the order of ET (dynamic non-exponentiality).   AN has two values of longitudinal reorientation times, which were calculated from Debye relaxation time [8] as 1.2 ps and 15 ps and this also contributes the actual non-linearity.

ET in the order of 100 fs observed for NB/DMA and OX1/DMA is due to strong interaction between donor and acceptor molecules. Almost single exponential ultrafast fluorescence decays obtained in these cases can be explained in two aspects. A single exponential ET can be realized if the ET rates are close for different molecular orientations ("wide window" case [1]) and/or if the molecular reorientation takes place much faster than ET occurs, as shown in Figure 4(b). The assumption of "wide window" means that ET is determined mainly by nuclear motion and is not much affected by solvent reorientation. Nuclear motion in this strongly coupled donor-acceptor system can also reorient the interacting molecules. Generally, molecular vibrations (intramolecular vibration and/or some inter-molecular vibrational motion) induce ultrafast ET. One particular motion named libration was recently found to be as fast as 60 fs in a light polar solvent [9]. It is also important to emphasize that for realization of ET with such a fast rate, some

mechanism of ET stabilization process is required. It means that relaxation of the ET products dissipates the excess energy above the bottom of the products energy surface to eliminate the back ET reaction. This relaxation is as fast as ET, when the ET rate is determined by stabilization process.

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