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Bimolecular electron transfer reactions in coumarin–amine systems: Donor–acceptor orientational effect on diffusion-controlled reaction rates

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Abstract

Electron transfer (ET) reactions between excited coumarin dyes and different aliphatic amine (AlA) and aromatic amine (ArA) donors have been investigated in acetonitrile solution using steady-state (SS) and time-resolved (TR) fluorescence quenching measurements. No ground state complex or emissive exciplex formation has been indicated in these systems. SS and TR measurements give similar quenching constants (k_q) for each of the coumarin–amine pairs, suggesting dynamic nature of interaction in these systems. On correlating k_q values with the free energy changes (ΔG^0) of the ET reactions show the typical Rehm–Weller type of behavior as expected for bimolecular ET reactions under diffusive condition, where k_q increases with $-\Delta G^0$ at the lower exergonicity ($-\Delta G^0$) region but ultimately saturate to a diffusion-limited value (k_q^{DC}) at the higher exergonicity region. It is, however, interestingly observed that the k_q^{DC} values vary largely depending on the type of the amines used. Thus, k_q^{DC} is much higher with ArAs than AlAs. Similarly, the k_q^{DC} for cyclic monoamine 1-azabicyclo-[2,2,2]-octane (ABCO) is distinctly lower and that for cyclic diamine 1,4-diazabicyclo-[2,2,2]-octane (DABCO) is distinctly higher than the k_q^{DC} value obtained for other noncyclic AlAs. These differences in the k_q^{DC} values have been rationalized on the basis of the differences in the orientational restrictions involved in the ET reactions with different types of amines. As understood, n-type donors (AlAs) introduce large orientational restriction and thus significantly reduces the ET efficiency in comparison to the π-type donors (ArAs). Structural constrains are inferred to be the reason for the differences in the k_q^{DC} values involving ABCO, DABCO donors in comparison to other noncyclic AlAs. Supportive evidence for the orientational restrictions involving different types of amines donors has also been obtained from DFT based quantum chemical calculations on the molecular orbitals of representative acceptor and donor molecules.

Keywords: Electron transfer; Coumarins; Aliphatic and aromatic amines; Fluorescence quenching; Diffusion-controlled rates; Orientational effect

1. Introduction

Electron transfer (ET) is one of the interesting subjects that have experienced extensive experimental and theoretical research for last few decades [1–14]. Studies on ET reactions have immense importance from the viewpoint of both academic and applied implications, as these reactions are ubiquitous in chemistry and biology. Understanding various factors that control ET reactions is the main impetus in most of the research on ET processes. Photoinduced ET reaction, where either the acceptor or the donor is photoexcited to trigger the reaction, is the most suitable experimental scheme, and has been used quite extensively to investigate various factors that control the ET mechanisms and dynamics in various ET systems [1–14].

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Coumarin dyes are reported to be good electron acceptors in their excited (S_1) states [15–25]. Measurements with femtosecond time resolution have demonstrated that photoinduced ET from amine solvents to several coumarin dyes occurs under nondiffusive condition and with exceedingly fast rate, even faster than the solvent relaxation dynamics [15–21]. ET reactions between a number of excited coumarin dyes and different amine donors under diffusive conditions using acetonitrile (ACN) as a polar nonreactive solvent have also been investigated previously, where ET mechanism has been established unambiguously by characterizing the radical ion-pairs in these systems following picosecond transient absorption measurements [22–25]. In some of the earlier studies on bimolecular ET reactions [24,26–31], it has been observed that the quenching process is largely dependent on the aliphatic and aromatic nature of the quenchers involved. In the present study, bimolecular ET reactions in ACN solutions have been investigated under diffusive conditions following the fluorescence quenching for a series of coumarin dyes by different aliphatic amine (AlA) and aromatic amine (ArA) donors, aiming to understand how the nature of the amines affect the ET process. In the present study, in addition to the noncyclic AlAs, cyclic amines like 1-azabicyclo-[2,2,2]-octane (ABCO) and 1,4-diazabicyclo-[2,2,2]-octane (DABCO), have also been used to obtain better understanding and interpretation of the observed results. Chemical structures of different acceptors (A; coumarin dyes) and donors (D; amines) used in the present study are shown in Fig. 1 along with their abbreviations used in the present paper.

2. Materials and methods

Laser grade coumarin dyes were obtained from Exciton, and used without further purification. Amine samples were obtained either from E. Merck (Mumbai, India), SISCO Research Laboratories (India), Spectrochem (India), S.D. Fine Chemicals (India), or Fluka (Switzerland). Liquid amines were purified by vacuum distillation. Solid amines were purified by vacuum sublimation.

Absorption spectra were measured in a JASCO (Japan) model V-530 UV–vis spectrophotometer using 1 cm path length Suprasil quartz absorption cells. Steady-state (SS) fluorescence spectra were measured in a Hitachi (Japan) model F-4010 spectrofluorimeter using 1 cm × 1 cm Suprasil quartz cuvettes. All fluorescence spectra were recorded with corrections for the wavelength dependent instrument responses. Time-resolved (TR) fluorescence measurements were carried out using a time-correlated-single-photon-counting (TCSPC) spectrometer [32] from IBH, UK, where a TBX4 detection module (IBH) coupled with a special Hamamatsu PMT was used for fluorescence detection. For all the coumarin dyes except C120, a diode laser (408 nm, 1 MHz, 100 ps) was used as the excitation source, where the instrument response function (IRF) was estimated to be ~230 ps at FWHM. For C120, a 373 nano-LED (1 MHz, 1 ns) was used for sample excitation and in this case the instrument response function (IRF) was estimated to be ~1 ns at FWHM. A DAS-6 software obtained from IBH was used to analyze the observed fluorescence decays following a reconvolution procedure [32]. The IRF as required in the reconvolution analysis of the observed decays was obtained independently by replacing the sample cell with a light scatterer (suspended TiO_2) in the TCSPC measurement. For the present systems, the fluorescence decays were seen to fit well with a single-exponential function as,

$$I(t) = B\exp(-t/\tau) \tag{1}$$

where τ is the fluorescence lifetime and B is the pre-exponential factor. For all the accepted fits the reduced chi-square (χ^2) values were within 1.00–1.15 and the distributions of the weighted residuals were quite random among the data channels [32].

Reduction potentials of all the coumarin dyes in ACN solution against saturated calomel electrode (SCE) were estimated using cyclic voltammetry (Eco Chemie Potentiostat, AUTOLAB 100), where glassy carbon disc and platinum rod are used as the working and the counter electrode, respectively. The oxidation potentials of the amine donors in ACN solution against SCE were obtained from earlier works [22–24,26]. The redox potentials and the other relevant parameters of the donors and acceptors used in this study are listed in Table 1. In the present study, all the experimental measurements were carried out at ambient temperature (25 ± 1 °C).

DFT based quantum chemical calculations was carried out in the present work on some typical electron acceptor and electron donor molecules to obtain supportive evidences for the experimental results and their interpretations. In the calculations, full geometry optimization was carried out applying B3LYP hybrid functional adopting 6-31+G(d, p) basis function [33–35] to predict the ground state structure of the molecules. Excited state calculation on the lowest excited state (S_1) of the molecules was carried out following TDDFT procedure using the same set of basis function [33–38]. These calculations have been performed adopting GAMESS suite of program on a PC-based LINUX cluster [35].

3. Results and discussion

3.1. Steady-state and time-resolved fluorescence quenching studies

Ground state absorption spectra and steady-state (SS) fluorescence spectra of the coumarin dyes were recorded in acetonitrile (ACN) solutions. Table 1 lists the absorption maxima (λ_{abs}^{max}) and fluorescence maxima (λ_{fl}^{max}) of the coumarin dyes in ACN solution. SS fluorescence quenching measurements for the coumarin dyes by amine donors were carried out in ACN solutions. In these measurements, the samples were excited at the absorption maxima of the con-