

## Development of exciplex chemistry: Some fundamental aspects

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**Abstract.** Results of our picosecond and femtosecond laser spectroscopic studies on photoinduced electron transfer phenomena in solutions, which have aided the development of exciplex (EX) chemistry, are presented. Topics covered include the excited dipolar solute-polar solvent interactions, solvent and driving force effects on the electronic and geometrical structures of inter- and intra-molecular EX systems, energy gap dependences of charge separation (CS) in the fluorescence quenching reactions and charge recombination (CR) of product loose ion pairs (LIP's), non-Marcus type energy gap dependence of CR of compact ion pairs (CIP's) formed by excitation of ground state charge transfer (CT) complexes, photoinduced CS coupled with proton transfer or shift in benzophenone-amine and some hydrogen bonding EX systems, and extensions of EX studies to photosynthetic reaction center models. These results are summarized and discussed on the basis of theoretical arguments concerning the detailed relationships between fundamental mechanisms underlying these EX phenomena.

### INTRODUCTION

Photoexcitation of a solute molecule in solution causes changes in its electronic and geometrical structure, which also induces changes in its interactions with its environment and near-by molecules. Many photochemical reactions in solution start from such exciplex type interactions. "Exciplex chemistry" and/or "exciplex phenomena" here are considered as including: excited polar solute-solvent interactions; photoinduced hydrogen bonding interactions including proton shift or transfer coupled in some cases with ET (electron transfer) or CT via hydrogen bond; formation of excited CT complexes, various EX's, IP's (ion pairs or ion radical pairs) and subsequent chemical reactions. All these interactions and reactions are closely connected with photoinduced CT and ET processes. The most typical example of photoinduced ET is the fluorescence quenching reaction. The ET mechanism of the fluorescence quenching reaction was proposed more than 60 years ago (1) and has been studied for a long time. However, the most important investigations leading to the contemporary understanding of the mechanisms of the photoinduced ET and the exciplex chemistry in general were virtually started by pioneering studies on exciplex phenomena mainly during 1950-1970's and have been advanced greatly by more recent picosecond(ps) - femtosecond(fs) laser photolysis studies (2, 3). In this article, our studies on some fundamental problems of exciplex chemistry are summarized and discussed especially with regard to detailed relationships between fundamental mechanisms underlying various exciplex phenomena.

## I. EXCITED DIPOLAR SOLUTE - SOLVENT INTERACTIONS, AND SOLVENT AND DRIVING FORCE EFFECTS ON ELECTRONIC AND GEOMETRICAL STRUCTURES OF EXCIPLEX SYSTEMS

When a dipolar solute molecule has a much larger dipole moment in the excited state than the ground state, one observes a large fluorescence Stokes shift due to solvation in polar solvent which was expressed first in 1955 (3, 4) by Lippert-Mataga (L-M) equation assuming linear response for solute-solvent interaction and a dielectric continuum model for solvent. Based on the same approximation on the nature of solvent and solute-solvent interaction, classical Marcus equation for ET reaction was proposed in 1956 (5). In terms of the language of ET theory, the fluorescence transition in the above case of L-M equation corresponds to the process in the inverted region. Both of these equations are conceptually quite simple and widely used. However, they are no more than first approximations and actual systems seem to show a more complex behavior involving a kind of nonlinear effect depending on solvent polarity and driving force for ET, etc.

Thus, electronic and geometrical structures of excited donor(D) - acceptor(A) composite systems in solution are liable to change depending upon interaction with solvent and upon driving force ( $-\Delta G$ ) for ET between D and A, etc. For example, our ps-fs laser photolysis studies on the intramolecular exciplex (EX) of pyrene (A) and N,N-dimethylaniline(DMA) (D) linked by methylene chain,  $-(CH_2)_3-$ , in acetonitrile solution showed rapid formation (with time constant  $\tau_r = 11$ ps) of a loose EX with extended structure and with absorption spectrum very similar to the superposition of spectra of  $A^\cdot$  and  $D^+$  ion radicals. This compound also showed very slow formation ( $\tau_r \sim 4$ ns due to extensive conformational change) of a compact EX with sandwich structure and with absorption spectrum strongly broadened compared with superposition of spectra of  $A^\cdot$  and  $D^+$  ions due to the rather strong electronic interaction between them in compact configuration in hexane solution. In solvents of intermediate polarity such as butyronitrile and acetone,  $\tau_r$  was a little longer and absorption spectra of EX were a little broader than in acetonitrile due to a slight conformation change toward compact one necessary for EX formation. These results show clearly that the electronic and geometrical structures of EX can change depending upon solute-solvent interactions (2, 3, 6).

When sufficiently strong D and A chromophores are used in the intramolecular exciplex systems photoinduced charge separation (CS) is possible even in nonpolar solvent and in extended conformations due to the large driving force,  $-\Delta G$ , in Eq.1 (3), where  $V$  is the electron tunneling matrix element,

$$k_{ET} = (\pi \hbar^2 \lambda_s k_B T)^{1/2} V^2 \sum_n [e^{-S} (S^n/n!)] \exp\{-(\Delta G + \lambda_s + nh\langle w \rangle)^2 / 4 \lambda_s k_B T\} \quad (1)$$

$S = \lambda_s \hbar \langle w \rangle$  is the electron-vibrational coupling constant and  $\lambda_s$  is the reorganization energy due to the average intra-chromophore vibrational frequency  $\langle w \rangle$ , and  $\lambda_s$  is the solvent reorganization energy. Our ps-fs time-resolved absorption spectral measurements on a series of distance fixed porphyrin-quinone dyads in non-dipolar solvent benzene (Bz) showed transient IP state formation by complete photoinduced CS. Analysis of the observed  $-\Delta G$  dependences of  $k_{ET}$  in Bz as well as THF (tetrahydrofurane) and BuCN (butyronitrile) solutions by means of Eq.1 gave the following values of  $\lambda_s$ :  $\lambda_s(\text{Bz}) = 0.18\text{eV}$ ,  $\lambda_s(\text{THF}) = 0.87\text{eV}$ ,  $\lambda_s(\text{BuCN}) = 1.15\text{eV}$ (3, 7). However,  $\lambda_s(\text{Bz})$  calculated by classical Marcus equation based on simplified model as described above is almost zero, which indicates more complex actual solute-solvent interactions in the ET including some nonlinear effects.

The above results and discussions strongly suggest that, for photoinduced CT reactions in solution, formation of CT states having various electronic and geometrical structures depending upon solvent

polarity and energy gap for CT process ( $-\Delta G$ ) are possible and there may arise an ensemble of various EX's and IP's distributed over such CT states in solutions. This suggestion was supported by studies on EX fluorescence lifetimes and rise times of ps laser induced photoconductivity of typical EX systems in various polar solvents (2, 3, 8). We have elucidated that these results and discussions are closely related to the mechanism of the energy gap dependence of CS process in the fluorescence quenching reaction of unlinked D, A systems in polar solutions (3, 9).

## II. ENERGY GAP DEPENDENCES OF CS IN THE FLUORESCENCE QUENCHING REACTION AND CR (CHARGE RECOMBINATION) OF PRODUCT LIP'S (LOOSE IP'S) IN POLAR SOLUTIONS

It is well-known that no clear-cut inverted region predicted by Marcus theory has been observed for the CS in the fluorescence quenching reaction in polar solutions since the first demonstration of its absence in the CS rate constant,  $k_{CS}$ , vs.  $-\Delta G_{CS}$  relation in 1970 (10). Because the  $k_{CS}$  value for the favorable  $-\Delta G_{CS}$  region is masked by the diffusion - limit of the reaction, "true"  $k_{CS}$  values were estimated by analyzing transient effect in the fluorescence quenching process for a series of fluorescer - quencher pairs covering a wide energy gap range in 1991 (3, 11). Nevertheless, very broad and rather flat  $k_{CS}$  vs.  $-\Delta G_{CS}$  plots were obtained showing no inverted region (11). Contrary to this, for the CR of the LIP's produced by CS in the fluorescence quenching reaction, nearly bell-shaped  $k_{CR}$  vs.  $-\Delta G_{CR}$  relation including both normal and inverted regions was confirmed in 1986-1988 by means of direct ps laser spectroscopic observation of the CR process (3, 12). Various interpretations of these results were proposed and examined for these relations (13). Special attention was paid for the broad and rather flat  $k_{CS}$  vs.  $-\Delta G_{CS}$  relation which didn't exhibit inverted region. For this relation the most authentic mechanism seems to be distance distribution between fluorescer and quencher in CS reaction and increase of average distance with increase of the free energy gap,  $-\Delta G_{CS}$ , (13) in accordance with the model of the solvent and driving force dependent structures of EX's and IP's as discussed at the end of I. Namely, in Eq. 1, for the CS corresponding to a larger  $-\Delta G_{CS}$ , a larger  $\lambda_s$  is favorable to keep activation energy small and  $k_{CS}$  large, and a large  $\lambda_s$  means a large fluorescer - quencher distance where ET takes place, according to the Marcus equation. We made a quantitative analysis of the transient effect in the fluorescence quenching dynamics by fully considering the fluorescer - quencher distance distribution effects. The time dependent "rate constant"  $k_{CS}(t)$  related to the transient effect was calculated by averaging the distance dependent  $k_{CS}(r)$  with the distribution function  $p(r, t)$  obtained by numerically solving the diffusion - reaction equation, and was compared with the results of the analysis of the observed transient effect at various energy gap. From this comparison, for example, average positions of distribution corresponding to the reaction radius were obtained as, 6Å, 11.2Å and 12.4Å for the energy gap, 0.0eV, -1.4eV and -2.8eV, respectively in acetonitrile solutions (9, 13).

It should be noted here that the nearly bell-shaped  $k_{CR}$  vs.  $-\Delta G_{CR}$  relation of the geminate LIP's can be reproduced by assuming only a slight modification of initial distribution (9, 13), that is, the structures of the geminate LIP's are approximately maintained during CR, which is very important for considering the mechanisms of hydrogen abstraction reactions via geminate LIP's as discussed in IV (3, 14).

## III. NON-MARCUS TYPE ENERGY GAP LAW FOR CR OF CIP'S (COMPACT IP'S) FORMED BY EXCITATION OF CT COMPLEXES

We found non-Marcus type  $k_{CR}$  vs.  $-\Delta G_{CR}$  relation of CIP's (3, 15) which is also important for considering mechanisms of chemical reactions via geminate IP's (3, 14). The most noteworthy points on this energy

gap law are as follows. (a) The energy gap law for the CR of CIP is given by an exponential form of Eq. 2 where the slope  $\beta$  is considerably more gentle than that of  $k_{CR}$  (LIP) in the inverted region. (b) No normal-

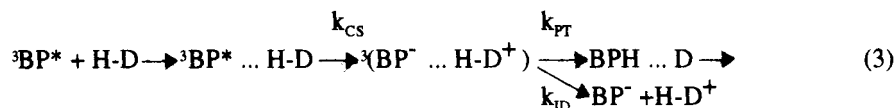
$$k_{CR}(\text{CIP}) = \alpha \exp[-\beta |\Delta G_{CR}|] \quad (2)$$

region-like behavior of CIP has been observed and there is an extremely large difference between the  $k_{CR}$  (CIP) and  $k_{CR}$  (LIP) of the same strong D, A systems,  $k_{CR}(\text{CIP}) \gg k_{CR}(\text{LIP})$ . (c) Little or no solvent polarity effect on the exponential energy gap law of CIP has been observed (15c) and, moreover, the CR of CIP's formed by exciting aromatic hydrocarbon - TCNB (tetracyanobenzene) CT complex adsorbed on porous glass without solvent showed exactly the same exponential energy gap law as in polar solutions (16a). (d) The activation energy for CR obtained by examining temperature effect in the adsorbed state was very small (<1kcal/mol) and especially smaller for CIP's with small  $-\Delta G_{CR}$  values (16b). (e) All experimental results on the CR of CIP's in various environments strongly suggest that the effect of the intramolecular high frequency quantum modes (and probably also the intracomplex vibrational modes) are dominant and the role of solvent reorganization is minor in the CR.

In view of the above described characteristics of the CIP and the form of Eq. 2, the CR process of the CIP is analogous to the intramolecular radiationless transition in the weak coupling limit, although the slope  $\beta$  is more gentle (15). The latter fact might be ascribed partly to the participation of many intramolecular and complex vibrational modes to CR and a considerable displacement of equilibrium configuration due to a large change of charge distribution associated with CR transition (15). In addition, the CT fluorescence Stokes shift of TCNB-aromatic hydrocarbon complexes in nonpolar solutions was shown to decrease with decrease of the energy gap of the CT transition (17), which indicates that the intracomplex reorganization energy associated with CR transition is smaller for the CIP with smaller  $-\Delta G_{CR}$  value and observation of the normal region in the CR of CIP is practically impossible.

#### IV. PHOTOINDUCED ET COUPLED WITH PROTON TRANSFER (PT) OR PROTON SHIFT (PS) IN BENZOPHENONE (BP) - AROMATIC AMINE AND SOME HYDROGEN BONDING EXCIPLEX SYSTEMS

One of the most typical organic photochemical reactions leading to the chemical product formation is the hydrogen abstraction reaction of triplet BP ( $^3\text{BP}^*$ ) from tertiary aromatic amines (D-H). We have made detailed ps-fs laser photolysis studies on this system and established the reaction mechanisms in acetonitrile solution. At encounter between  $^3\text{BP}^*$  and amine CS takes place leading to the formation of the geminate LIP which undergoes the intra-LIP PT leading to the ketyl radical formation in competition with ionic dissociation.



The most important results in this study are closely related with the D, A distance distribution in the photoinduced CS reaction and the dependence of the average distance on the energy gap for the CS reaction producing LIP as discussed in II. It has been confirmed that the  $k_{PT}$  decreases with decrease of the oxidation potential of amine as follows:  $k_{PT} = 8.2 \times 10^8 \text{ s}^{-1}$ ,  $5.4 \times 10^9 \text{ s}^{-1}$ ,  $7.3 \times 10^8 \text{ s}^{-1}$  and  $\ll 2 \times 10^8 \text{ s}^{-1}$  for N-methyldiphenylamine, DMA, N,N-diethylaniline (DEA) and N,N-diethyl-p-toluidine with oxidation potentials 0.86, 0.76, 0.72 and 0.69 V vs. SCE, respectively. This is a striking demonstration of the longer inter-ionic distance in geminate LIP produced by CS reaction with larger energy gap.

Another interesting example of coupled ET and PT processes was observed in the case of pyrene-N-ethylaniline (NEA) EX in nonpolar solvent, where the exciplex fluorescence was strongly quenched due to the intra-exciplex PT, producing 1-hydro-1-pyrenyl radical and enhanced intersystem crossing (ISC) (2a, c). The rapid PT strongly suggests the hydrogen (H) bonding between >N-H of NEA cation and pi-electron system of pyrene anion at C<sub>1</sub> position in the EX. Owing to this H-bonding interaction, this EX should have oblique (non-plane-parallel) configuration in nonpolar solvent where stabilization of such loose IP structure by solvation with polar solvent is absent. This assumption of loose structure is supported by the fact that the exciplex absorption band shape is very sharp and similar to those of D<sup>+</sup> and A<sup>-</sup> ion radicals contrary to the very broadened spectra of pyrene-DMA and -DEA exciplexes with strong D<sup>+</sup> - A<sup>-</sup> interaction in the sandwich structure. Moreover the oblique configuration is favorable for the enhancement of ISC, because the spin-orbit interaction matrix between <sup>1</sup>CT state and local triplet state is enhanced in this structure but not in the sandwich structure in accordance with observed results (2a, c). Thus the very local H-bonding interaction can play important role in facilitating CT interaction in nonpolar media.

The above described ET coupled with PT is due to a special type of H-bonding interaction between >N-H group and pi-electrons. We found many years ago strong fluorescence quenching caused by H-bonding interaction between heteroaromatic molecules in nonpolar solvents (2, 3) and proposed such ET mechanism as, (D<sup>\*</sup>-H ... A) → (D<sup>+</sup>-H ... A<sup>-</sup>) → (D-H ... A) for quenching (1956). We have verified the ET mechanism by means of ps transient absorption spectral measurements using some typical systems such as 1-aminopyrene-pyridine and dibenzocarbazole-pyridine (1982-83), and more recently elucidated detailed mechanism of ET coupled with proton shift in H-bond and dynamics of quenching process by means of fs laser spectroscopy (1993) (2c, 3, 18). Namely, H-bonding interaction and a slight shift of proton from donor toward acceptor in the H-bond greatly facilitate ET by increasing the driving force and leading to the ultrafast formation of the IP state, from which the rapid non-radiative crossing to the ground state takes place. This is also an example which shows that a local H-bonding interaction can play an important role in ET reaction in nonpolar media.

## V. EXTENSIONS OF EXCIPLEX STUDIES TO PHOTOSYNTHETIC REACTION CENTER MODELS

One of the most challenging problems to be solved is that of gaining an understanding of the ultrafast and very efficient CS processes which occur in the biological photosynthetic reaction center (RC). To gain such an understanding is necessary to construct model compounds which contain chromophores analogous to those found in the biological RC and which can undergo ultrafast and efficient CS as in the biological system. We demonstrated in 1983 for the first time the importance of the photoinduced multistep ET to achieve long-lived CS state formation by employing the linked porphyrin-quinone systems, P-(CH<sub>2</sub>)<sub>4</sub>-Q-(CH<sub>2</sub>)<sub>4</sub>-Q' (Q : trichloroquinone) (2a, 3, 19). Although this triad showed formation of the longer-lived CS state with lifetime of 400ps compared with 100ps of the dyad, P-(CH<sub>2</sub>)<sub>4</sub>-Q, in THF solution, production of a very long-lived CS state formation was not possible due to the flexible spacer. We extended investigations to various distance-fixed RC models (3, 20) and have observed recently high efficiency formation of long-lived CS state in diporphyrin-monoporphyrin- acceptor triads by the same ET modes as in RC (21).

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