PROGRESS REPORT

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PHOTOINDUCED DIPOLES AND CHARGE PAIRS IN CONDENSED MEDIA

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Three Year Progress Report

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Figure 1 (on the cover page). Schematic potential curve for RIPs in a moderately polar solvent

Abstract

Most of our work involves photogenerated donor (D^+) and acceptor (A^-) radical ion pairs and their escape and recombination. The geminate radical ions are produced by inter or intramolecular electron transfer quenching of photoexcited acceptors. We made great progress in understanding the effect of charge separation distance and other factors on free ion formation. For geminate radical ion pairs formed by intermolecular electron transfer quenching (see the figure on the cover page), we found that, at least in a medium polarity solvent like dichloromethane, free radical ions are mainly formed from solvent separated radical ion pairs (SSRIPs). Contact radical ion pairs (CRIPs) make a very small contribution to free radical ion formation. It is observed that CRIPs and SSRIPs are kinetically distinguishable species. There is a potential barrier between CRIPs and SSRIPs that prevents a fast equilibrium between the two during the recombination of radical ion pairs and free radical ion formation (Figure on the cover page). We confirmed for the first time that, for the recombination of both CRIPs and SSRIPs that are in the Marcus inverted region, rate constants of SSRIPs are larger than those of CRIPs. Our study indicates that initial charge separation distance and the potential barrier between CRIPs and SSRIPs play a more important role than recombination rate on free ion formation. Temperature dependence experiments reveal that through-tunneling back electron transfer is the dominant approach for the SSRIP recombination process. We believe that our discovery of the roles played by the initial charge separation distance and the potential barrier between radical ion pairs of different separation have very important implications for the development of new concepts for the design of organic photovoltaic (OPV) cells.

Photoinduced transient dipole experiments are used to probe the effective charge separation distance of flexible electron donor/acceptor systems, $D-(CH_2)_n-A$, where D is 4-N-N-dimethylaniline, A is 9-anthryl and $n=3, 4$. We find that the dipole moments increase strongly with solvent polarity. Under the simplifying assumption that the folded, contact configuration and the extended, solvent-separated configuration are the only two stable species after electron transfer quenching, the formation efficiencies of contact radical ion pairs (CRIPs) and solvent-separated ion pairs (SSRIPs) are estimated in different solvents. The results indicate that a significant fraction of the ion pairs exists as solvent-separated ion pairs when the dielectric constant of the solvent is larger than 10 and that electron transfer quenching can indeed happen at large separations in polar solvents.

Light-induced charge separation often occurs at the interfaces and surfaces in solar cells and other electro-optic devices. To produce a substantial photovoltaic effect, the electrically neutral excitons formed by photon absorption must diffuse to an interface and produce ion pairs by dissociation. Since low dielectric constants of 3-4 are typical for organic materials used to fabricate OPV cells, the geminate ion pairs formed after exciton dissociation are believed to have short separations and are strongly bound by Coulomb interaction. The binding energy can be estimated to be ~ 0.25 eV. However, the experimentally observed activation energies are typically less than 0.1 eV. The weak temperature dependence of carrier photogeneration indicates that, somehow, geminate ion pairs are formed at large separation or that some sort of energy assists separation of nearby geminate ion pairs into free ions. To understand the underlying mechanism behind the above observations, a model based on what we have learned from solution was

developed for charge separation at interfaces or surfaces. It was proposed that, in order for loose radical ion pairs with long separations to escape in media with dielectric constants of 3-4, a potential barrier that can effectively stop their collapse is critically needed. Based on our model, it is concluded that closely separated radical ion pairs do not form free radical ions by themselves. However, they do play a very important role in free ion formation. The closely separated radical ion pairs formed at the interface can effectively build a potential barrier that offers a boost for the escape of radical ion pairs formed at long distance. The counterproductive part of a high potential barrier is that a large portion of photoenergy is used to produce closely separated ion pairs. The existence of a high potential barrier is also expected to make the formation of distantly separated radical ion pairs less probable. In our opinion, an efficient OPV cell will be a device with a potential barrier that is enough to counterbalance the Coulomb interaction within the radical ion pairs. Meanwhile, the distantly separated (loose) ion pairs must be formed with high efficiency.

Highlights

By showing that the time constant for exciplex fluorescence is not equal to that for the rise in observed photocurrents, we have proved that CRIPs and SSRIPs are not in rapid equilibrium and that only SSRIPs dissociate with reasonable probability (papers#1 and 2). We observed that photocurrent risetimes, which are correlated with the decay of SSRIPs, are shorter than exciplex fluorescence decay time, which are correlated with decay time of CRIPs. Increasing the separation distance of radical ion pairs by using sterically hindered donor molecules results in the further decrease of time constants of

SSRIPs formed. Thus, increased recombination rate constants with increasing radical ion pair separation distance are confirmed. The fact that CRIPs and SSRIPs have different decay times indicates that they are kinetically distinguishable species and that there is a potential barrier between the two. The CRIPs (or exciplex) decay times measured by the single photon timing techniques are generally longer than that of SSRIPs measured by transient photocurrent techniques. In other words, the free radical ion signal reaches the maximum before the end of CRIP decay. This clearly indicates that long-lived CRIPs do not make significant contributions to free radical ion formation.

To probe the potential barrier between CRIPs and SSRIPs, free ion yields of geminate ion pairs formed after photoinduced electron transfer quenching are measured in several polar solvents at different temperatures (paper#6). We found that, generally, there is no significant increase in free ion yield as the temperature increases. By comparing escape probabilities of geminate ion pairs calculated at different initial formation and recombination separation distances with the measured free ion yields, it is clear that free ions are produced mainly from solvent separated ion pairs that are initially formed after electron transfer quenching. This offers further evidence for our proposed mechanism of free ion formation. Calculations also imply that recombination (through-tunneling) at separation distances larger than 7Å is the dominant decay process for solvent-separated ion pairs. Since an increase in temperature decreases the solvent viscosity, increasing ion mobility, we naively expected it to increase escape rates and free ion yields. Therefore the observed weak dependence of free ion yields on temperature is attributed to decreased Coulombic attraction with decreased dielectric constant at higher temperature.

Papers #3 and #4 describe the radiative exciplex formation and CT absorption of electrons acceptors with sterically hindered donors. We reported for the first time the formation of radiative exciplexes of a series of electron donor/acceptor pairs from 1,2,4,5-tetracyanobenzene (TCB) and sterically hindered substituted benzenes (paper#3). It is found that the exciplexes of donor/acceptor pairs of hindered and non-hindered donors with similar structures and electron transfer properties give almost the same fluorescence quantum yields. Based on the results we collected, it is concluded that there is no sterically controlled changeover from inner-sphere to outer-sphere mechanism, as proposed by others. In paper #4, electron-transfer absorption of substituted benzene donors with tetracyanoethene (TCNE) is studied in dichloromethane at several temperatures. The results from temperature dependence experiments with various electron donors demonstrated that the electron transfer absorption of the sterically bulky D/A pairs originates from unassociated random pairs.

In paper #5, the transient dc photocurrent method was used to investigate the dipole moment of the charge-separated state of a carotenoid (C) porphyrin (P) fullerene (C60) molecular triad in tetrahydrofuran and 2-methyltetrahydrofuran. The results show formation of a giant dipole with a moment in excess of 150 D, corresponding to separated charges located on the fullerene and carotene moieties of the triad.

In paper #7, photoinduced transient dipole experiments are used to measure the effective charge separation distance of flexible electron donor/acceptor systems, D-(CH₂)_n-A, where D is 4-N, N-dimethylaniline, A is 9-anthryl and n=3,4. We find that the dipole moments increase strongly with solvent polarity (Figure 2). For the compound with n=4 (DBA4), analysis of dipole signals indicates that the effective charge separation

distances in toluene, 1,4-dioxane, ethyl acetate, THF, dichloromethane, 1,2-dichloroethane, 2-methylpentanone-3, 3-pentanone and benzonitrile are 2.5, 2.2, 4.1, 4.5, 4.7, 5.5, 5.5, 4.8 and 6.8 Å, respectively. These values can be understood as the root mean square charge separation distance in the solutions of different solvents. If one

Figure 2. Photoresponses of DBA4 in 1,4-dioxane and in 1,2-dichloroethane after absorption of 10 μ J at 355nm with 800 V applied. 50 Ω scope input.

assumes that the folded, contact configuration has a separation distance of 3.5 Å, the extended, solvent-separated configuration has a separation distance of 8.0 Å and that they are the only two stable species after electron transfer quenching, the formation efficiencies of contact radical ion pairs (CRIPs) and solvent-separated radical ion pairs (SSRIPs) are estimated in different solvents. The results indicate that a significant fraction of the ion pairs exists as solvent-separated ion pairs when the dielectric constant of the solvent is larger than 10 and that electron transfer quenching can indeed happen at large separations in polar solvents. They also reveal that there is a barrier for ion pairs formed at large separations hindering collapse to a contact separation of around 3.5 Å.

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