

# Triplet Energy Transfer and Triplet Exciplex Formation of Benzophenone

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In the course of our studies on excited proton transfer reactions with proton-induced quenching<sup>1)</sup>, we found hydrogen atom transfer (HT) from triplet 2-naphthylammonium ion ( $\text{NpNH}_3^+$ ) to the ground benzophenone (BP)<sup>2)</sup>. The HT reaction from triplet naphthol ( ${}^3\text{NpOH}^*$ ) to BP is shown to proceed via a triplet exciplex  ${}^3(\text{NpOH}\cdots\text{Bp})^*$ .<sup>3)</sup> At the initial event, triplet naphthalene derivatives ( ${}^3(\text{NpX}^*)$ ) are produced by triplet energy transfer of  ${}^3\text{BP}^*$ , and then the triplet exciplex  ${}^3(\text{NpX}\cdots\text{Bp})^*$  is produced.<sup>4)</sup>

Detailed studies on triplet energy transfer (TET) of BP competing with other processes and also dynamic behaviors of  ${}^3(\text{NpX}\cdots\text{Bp})^*$  have been carried out by means of nanosecond laser photolysis at 355nm.

## (1) Triplet-Triplet Energy Transfer (TET)

In the  ${}^3\text{BP}^*$  and NpOH system, TET, HT and induced quenching (IQ) take place competitively.<sup>5)</sup> In contrast to the prediction of Dexter Theory, the TET rate ( $k_{\text{TET}}$ ) increases with increasing the dielectric constant ( $\epsilon$ ) of the solvent used, while the HA rate is reduced.<sup>5,6)</sup> For IQ, the  $k_{\text{IQ}}$  value is independent on  $\epsilon$ . The solvent dependence of TET is interpreted in terms of not only the exchange mechanism (Dexter Theory) but also the dipole-dipole mechanism (Forster Theory), that is, the lowest  ${}^3(n,\pi^*)$  state of BP is perturbed by  ${}^1(\pi,\pi^*)$  due to that the energy gap between them becomes relatively small in polar media.

For the  ${}^3\text{BP}^*$  and NpNMe<sub>2</sub> system, the TET efficiency ( $\phi_{\text{TET}}$ ) is obtained as 0.58 ( $k_{\text{TET}} = 6.4 \times 10^9 \text{M}^{-1}\text{s}^{-1}$ ) and  $\phi_{\text{IQ}}$  is 0.42 in acetonitrile (ACN), whereas in ACN:H<sub>2</sub>O (4:1 v/v), ET occurs very effectively ( $\phi_{\text{ET}} = 1$ ).<sup>7)</sup> Similarly, ET from  $\text{NpO}^-$  to  ${}^3\text{BP}^*$  occurs with  $\phi_{\text{ET}} = 1$ .<sup>8)</sup>

From HT reactions of  ${}^3\text{BP}^*$ ,  $\text{HORNH}_3^+$ , HT is shown to be protic hydrogen atom transfer<sup>9)</sup>. For the IQ process is shown to be intersystem crossing of a triplet collision complex (i.e., a short-lived triplet exciplex) to the ground state by the experiments of the heavy atom effect.<sup>10)</sup>