Photoionization of *s*-Tetracyanobenzene - Toluene Complex in Its Lowest Excited Singlet State

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The electron donor-acceptor interactions in *s*-tetracyanobenzene (TCNB) - aromatic hydrocarbon complexes in their lowest excited singlet state have been studied in detail by Mataga and Murata[1] by means of fluorescence measurements. They showed clearly that there is a considerable difference in energy as well as structure between the excited Franck-Condon state and equilibrium state. This difference was considered to originate from the large difference between the electronic structures in the ground and excited states of the complex including the surrounding solvent, and the electronic structure in the excited equilibrium state way supposed to be quite polar.

Another useful way for investigating the behaviors of excited EDA complexes might be the measurements of the absorption spectra of these species by means of the laser photolysis method.[2] In this paper, we report the results of measurements on the TCNB-toluene-acetonitrile system. We might expect for this system the ionic dissociation of the complex at the lowest excited singlet state, since the excited complex seems to have a quite polar electronic structure and the radical ions can be stabilized strongly in a polar solvent. Although there are many examples[3] of the ion radical formation in the excited singlet state when the electron donor and the acceptor are not associated with each other in the ground state, we have hardly any results for the photo-excitation of the EDA complex which is stable in the ground state. Moreover, in many cases, the electron transfer reaction, $D^*+A \rightarrow D_s^+ + A_s^-$ or $D+A^* \rightarrow D_s^+ + A_s^-$, in a strongly polar solvent does not seem to proceed *via* the intermediate EDA complex having a definite structure, but occurs due to a very weak interaction in a loose encounter complex.[4] The TCNB-toluene system, though it is a weak complex, seems to have a definite structure. Accordingly, the electron transfer in this system may be considered as a rearrangement relaxation process from the excited Frank-Condon state to the ion-pair state and dissociated ion-radical state. However, the problem whether the electron transfer and ionic dissociation occur at all in the lowest excited singlet state of an EDA complex, when it is excited by light absorption exclusively at the CT band, does not seem to have been elucidated yet. The present study will give a more or less clearcut information on this problem.

We have used a Q-switched ruby laser with an output power of *ca.* 1 J. The exciting light pulse was produced by an ADP frequency doubler with conversion efficiency of about 8%. The light pulse has a duration of 15—20 nsec. The transient absorption spectra were measured photographically or by means of photomultiplier and synchroscope. The laser breakdown sparks produced in O_2 and Xe was used as spectroflashes.

The absorption spectra of the transient species at room temperature obtained by exciting the TCNB-toluene complex to its lowest excited singlet state in acetonitrile solution are very similar to those of the TCNB anion.[5]

Our kinetic analysis showed that the light-induced production of the transient species was completed rapidly(during the time range smaller than a few 10 nsec). Thus, the observed spectra may be ascribed to the dissociated TCNB anion or to the solvated ion-pair $A_s^-\text{---}D_s^+$, although it was not possible to identify the transient spectra of toluene cation. It is also possible that the transient spectra are assigned to the excited singlet-singlet absorption of the complex in view of its polar structure in the excited equilibrium singlet state.[1]

In order to identify the transient species, we have measured the photoconductivity induced by laser photolysis.[6] The rise and decay curves of the photoconductivity were practically the same as those of the absorbance of transient spectra. This kinetic relation is an evidence for the ionic dissociation of the complex at the lowest excited singlet state.

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6) Details of the apparatus and measurements on various donor-acceptor systems will be described in a forthcoming paper by A. Taniguchi and N. Mataga.