

Radical formation and charge resonance interaction by photoinduced electron transfer reactions in ion-pair redox compounds

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Styrylpyridinium cations formed ion-pair charge-transfer (IPCT) complexes with tetraphenylborate in less polar solvents. Photoinduced electron transfer reactions between ion pairs occurred upon excitation of IPCT complexes of styrylpyridinium tetraphenylborate in 1, 2-dimethoxyethane solutions at room temperature to form fairly stable styrylpyridinyl radicals. In addition to the remarkable color changes due to a characteristic absorption of styrylpyridinyl radicals in the visible region, a charge resonance (CR) band was also observed in the near infrared region for the first time upon steady photolysis in solution. The CR band was attributed to the specific interaction of a photogenerated neutral radical with a styrylpyridinium cation in dimer radical cations. Higher stabilization of these systems can be expected from such long and planar structures of both a styrylpyridinium cation and a styrylpyridinyl radical with extensive charge delocalization which favor the electronic interaction.

Ultrafast photoinduced electron transfer reaction and dimer radical cation formation were studied by femtosecond laser flash photolysis. Transient absorptions of both radicals and dimer radical cations (CR band) showed very rapid rise in less than one picosecond, which was limited by the time resolution of our flash photolysis system. No interaction of nitrostyrylpyridinium cations was observed before photoexcitation. These results strongly suggested that the electronic interaction between styrylpyridinium ion and its reduced form occurred without a diffusion process immediately after photoinduced electron transfer. The higher rate of the back electron transfer in dimer radical cations than in monomer radicals was explained by the classical Marcus theory.