

Theoretical Study on the Visible-Light-Induced Radical Coupling Reactions Mediated by Charge Transfer Complex

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Abstract : Charge transfer (CT) complex, also known as Electron donor-acceptor (EDA) complex, has received attentions increasingly in the field of synthetic chemistry community, due to the CT complex can absorb the visible light through the intermolecular charge transfer excited states, various of catalyst-free photochemical transformations under mild visible-light conditions. However, a number of fundamental questions are still ambiguous, such as the origin of visible light absorption, the photochemical and photophysical properties of the CT complex, as well as the detailed mechanism of the radical coupling pathways mediated by CT complex. Since these are critical factors for target-specific design and synthesis of more new-type CT complexes. To this end, theoretical investigations were performed in our group to answer these questions based on multiconfigurational perturbation theory. The photo-induced fluoroalkylation reactions are mediated by CT complexes, which are formed by the association of an acceptor of perfluoroalkyl halides $RF-X$ ($X = Br, I$) and a suitable donor molecule such as β -naphtholate anion, were chosen as a paradigm example in this work. First, spectrum simulations were carried out by both CASPT2//CASSCF/PCM and TD-DFT/PCM methods. The computational results showed that the broadening spectra in visible light range (360-550nm) of the CT complexes originate from the $1(\sigma\pi^*)$ excitation, accompanied by an intermolecular electron transfer, which was also found closely related to the aggregate states of the donor and acceptor. Moreover, from charge translocation analysis, the CT complex that showed larger charge transfer in the ground state would exhibit smaller charge transfer in excited state of $1(\sigma\pi^*)$, causing blue shift relatively. Then, the excited-state potential energy surface (PES) was calculated at CASPT2//CASSCF(12,10)/ PCM level of theory to explore the photophysical properties of the CT complexes. The photo-induced C-X ($X=I, Br$) bond cleavage was found to occur in the triplet state, which is accessible through a fast intersystem crossing (ISC) process that is controlled by the strong spin-orbit coupling resulting from the heavy iodine and bromine atoms. Importantly, this rapid fragmentation process can compete and suppress the backward electron transfer (BET) event, facilitating the subsequent effective photochemical transformations. Finally, the reaction pathways of the radical coupling were also inspected, which showed that the radical chain propagation pathway could easily accomplish with a small energy barrier no more than 3.0 kcal/mol, which is the key factor that promotes the efficiency of the photochemical reactions induced by CT complexes. In conclusion, theoretical investigations were performed to explore the photophysical and photochemical properties of the CT complexes, as well as the mechanism of radical coupling reactions mediated by CT complex. The computational results and findings in this work can provide some critical insights into mechanism-based design for more new-type EDA complexes

Keywords : charge transfer complex, electron transfer, multiconfigurational perturbation theory, radical coupling

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