

Theoretical Study of Copper-Catalyzed Atom Transfer Radical Addition Reactions

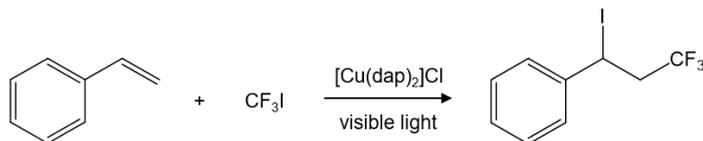
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Keywords: density functional theory, catalysis, photoredox reaction, copper complex

Photoredox catalysts using copper complexes are recently applied for various reactions, such as atom transfer radical addition (ATRA) reactions. The copper-based photocatalysts provide interesting reactivity, for example, $[\text{Cu}(\text{dap})_2]\text{Cl}$ (dap = 2,9-di(*p*-anisyl)-1,10-phenanthroline) catalyzes ATRA reactions between perfluoroalkyl iodides and styrenes under visible light irradiation, which are not promoted by commonly employed photocatalysts using ruthenium or iridium complexes.¹ It is proposed that these reactions proceed not only by conventional outer-sphere photoredox mechanisms but also by inner-sphere mechanisms.²

In the present study, the mechanism of the visible-light-mediated ATRA reaction of CF_3I with styrene utilizing $[\text{Cu}(\text{dap})_2]\text{Cl}$ is analyzed by means of density functional theory (DFT) using the M06 functional with the D3 version of Grimme's dispersion correction. Stuttgart/Dresden ECP (SDD) is used for Cu and I atoms, and Dunning/Huzinaga full double- ζ basis sets with polarization functions (D95(d,p)) for the others. The solvent effect of acetonitrile is considered with the polarizable continuum model.

The photoexcited Cu(I) complex reduces CF_3I and generates CF_3 radical ($^*[\text{Cu}(\text{dap})_2]^+ + \text{CF}_3\text{I} \rightarrow [\text{Cu}(\text{dap})_2]^{2+} + \text{CF}_3\cdot + \text{I}^-$). The generated Cu(II) complex was suggested to undergo ligand exchange ($[\text{Cu}(\text{dap})_2]^{2+} + \text{Cl}^- + \text{I}^- \rightarrow [\text{Cu}(\text{dap})(\text{Cl})(\text{I})] + \text{dap}$),¹ which is confirmed by the present calculation. When CF_3 radical binds to styrene, benzyl radical is formed ($\text{CF}_3\cdot + \text{C}_8\text{H}_8 \rightarrow \text{C}_9\text{H}_8\text{F}_3\cdot$). It is shown that the $\text{C}_9\text{H}_8\text{F}_3$ radical does not initiate radical chain process ($\text{C}_9\text{H}_8\text{F}_3\cdot + \text{CF}_3\text{I} \rightarrow \text{C}_9\text{H}_8\text{F}_3\text{I} + \text{CF}_3\cdot$), which is a common mechanism of the ATRA reactions. For the reaction of $\text{C}_9\text{H}_8\text{F}_3$ radical to generate the product, $\text{C}_9\text{H}_8\text{F}_3\text{I}$ ((3,3,3-trifluoro-1-iodopropyl)benzene), two mechanisms were proposed: rebound cycle in which the $\text{C}_9\text{H}_8\text{F}_3$ radical coordinates to Cu ($[\text{Cu}(\text{dap})(\text{Cl})(\text{I})] + \text{C}_9\text{H}_8\text{F}_3\cdot \rightarrow [\text{Cu}(\text{dap})(\text{I})(\text{C}_9\text{H}_8\text{F}_3)]^+ + \text{Cl}^- \rightarrow [\text{Cu}(\text{dap})(\text{Cl})] + \text{C}_9\text{H}_8\text{F}_3\text{I}$) and ligand transfer cycle in which the $\text{C}_9\text{H}_8\text{F}_3$ radical abstracts the iodide atom from $[\text{Cu}(\text{dap})(\text{Cl})(\text{I})]$ ($[\text{Cu}(\text{dap})(\text{Cl})(\text{I})] + \text{C}_9\text{H}_8\text{F}_3\cdot \rightarrow [\text{Cu}(\text{dap})(\text{Cl})] + \text{C}_9\text{H}_8\text{F}_3\text{I}$).¹ The calculations show that ligand transfer cycle is more plausible.



1) T. Rawnner, E. Lutsker, C.A. Kaiser, O. Reiser, *ACS Catal.* **2018**, *8*, 3950. 2) T. P. Nicholls, A.C. Bissember, *Tetrahedron Lett.* **2019**, *60*, 150883.