Abstract

Intermolecular interactions of reactive intermediates derived from biomolecules with water are very important in the understanding of many biochemical channels. Pyridine-*N*-oxide is a heterocyclic compound with different types of hydrogen bonding donor/acceptor sites, which can be considered as a model system for studying such interactions with water. If a radical center is created in pyridine-*N*-oxide by homolytic cleavage of C-H bond, the intermolecular interactions is getting very interesting that can now be influenced by the position of the radical center and the type of interactions. In this regard, we investigated the interactions of water with the pyridine-*N*-oxide and their three isomeric radicals (**α**, **β** and **γ**-radicals). For understanding such interactions, computational studies have been carried out. In this regard, the above mentioned complexes have been optimized at different levels of theory (B3LYP/cc-pVTZ and M06-2X/cc-pVTZ and CBS-QB3). Followed by, thermochemistry studies, spin density, electrostatic potential surface, singly occupied molecular orbital (SOMO), NBO analysis and AIM analysis have also been carried out in understanding the electronic structural and stability aspects.

Thiazole is a biologically and pharmaceutically important heterocyclic moiety. The generation and catalysis of bio-inspired *N*-heterocyclic carbene based on thiamine molecule is well known in the literature. However, rather simpler radical molecule of thiazole is unknown. Based on a recent Miyazaki J. et al. photo fragmentation study of thiazole using FTIR matrix isolation spectroscopy has demonstrated that C-S in thiazole can be cleaved easily that can lead to multiple photoproducts. If an additional photo labile iodine atom is attached to the same carbon, the resulting 2-iodothiazole system will be interesting with respect to the photochemistry.

The competition between the cleavage of C-I and C-S bonds will decide the photoproducts and also the selectivity. However, this primary goal is in this regard is to use 2-iodothiazole as a precursor to generate 2-dehydrothiazole radical and further to study the photofragments of thiazole radical. Based on the preliminary experiments complimented by the computations, various dissociation channels primarily through three ring opening channels have been compared.