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Estimation of S–H bond dissociation enthalpies and free energies of thiophenols: An *ab initio* Hartree-Fock study

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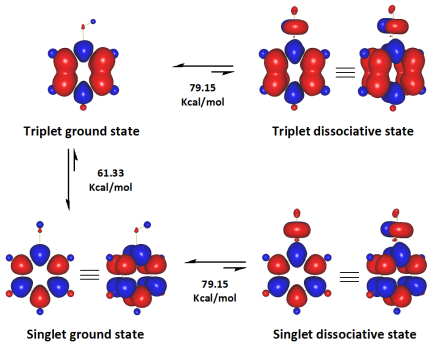
Ab initio Hartree–Fock method (UHF/6-31G(d)) was used to estimate the gas phase S–H bond dissociation enthalpies (BDEs) and free energies (BDFEs) of thiophenols with a considerable success. This was carried out by identifying the unimolecular dissociative states (DSs) of thiophenols, in a similar way recently described for hydroxylic antioxidants. The DSs of thiophenols forerunning S–H bond homolysis were vibrationally excited singlet or triplet states. In the DS, <C–S–H bond angle was fixed at 180°. The BDE of a given thiophenol was calculated as the relative change in enthalpy accompanying the formation of its DS with respect to a ground state of same multiplicity. BDFE was the corresponding change in Gibbs free energy. The calculated BDEs of thiophenol, its 12 monosubstituted derivatives (2-Me, 3-Me, 4-Me, 2-Cl, 3-Cl, 4-Cl, 4-Br, 3-CF_3, 4-NH_2, 4-MeO, 4-NO_2 and 2-CO_2Me) and 2-naphthalenethiol were remarkably similar to literature experimental values. The calculated BDE and BDFE of thiophenol were 79.1 and 80.1 kcal/mol, respectively. The average BDE and BDFE of the 13 thiophenols studied were 79.5±0.8 and 80.5±0.8 kcal/mol, respectively, the lowest and highest BDE/BDFE values being those of 2-methylthiophenol (77.7/78.5 kcal/mol) and 2-chlorothiophenol (81.3/81.9 kcal/mol). The BDE and BDFE of 2-naphthalenethiol were virtually identical with those of thiophenol's. The lower literature BDE values of 4-aminothiophenol (-9.3 kcal/mol) and 4-methoxythiophenol (-2.2 kcal/mol) in DMSO were satisfactorily explained by the stabilization of their respective dissociative states with hydrogen bonding of the *para* substituents with 2 and 1 DMSO molecules.



Biography

Ameha Seyoum Woldu got his B.Pharm and M.Sc. in Pharmacognosy from the School of Pharmacy, Addis Ababa University (Ethiopia). He has taught at different levels for over 9 years at the School of Pharmacy, Addis Ababa University before joining the School of Medicine, University of Western Sydney (Australia) in 2009 to pursue his Ph.D. He is currently engaged in the computational study of the antioxidant activities of flavonoids and other compounds.

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