ABSTRACT

The first chapter is pervaded with a general introduction of this work based on the mechanistic study of addition reactions. The background of the present thesis is briefly described. This chapter also represents the different objectives of this thesis.

The second chapter is devoted to the theoretical background for the estimation of electronic energy and charge density and potential energy surface of different species involved in a reaction. Theoretical background for the prediction of reactivity of a molecule has also been discussed here.

In the third chapter we have investigated mechanistic pathways for four different electrophilic addition processes with benzene (monoprotonation, diprotonation, monomethylation and dimethylation) in DFT framework. In all the cases, transition states have been isolated and characterized through intrinsic reaction coordinate calculations. Fukui functions, local softness values, local charge densities, different electrophile affinities, thermochemical parameters have been calculated and correlated. Fukui functions and local softness values have been found to be reliable descriptors for kinetically controlled products; whereas, prediction of thermodynamically controlled products can be made through local charge density values. Electrophile affinities are found to be additive and correlate well with thermochemical parameters.

In the fourth chapter we have investigated the mechanism of an unexpected reaction between two molecules of 1, 3-dicarbonyl compound and one molecule of the aldehyde in presence of molecular iodine by density functional theory based approach. The geometries and the frequencies of reactants, intermediates and transition states are calculated using Becke three parameter exchange and Lee-Yang-Parr correlation functional. The vibrational analysis, intrinsic reaction coordinate (IRC) calculation and ESP analysis verify the authenticity of the transition states. Depending on substitution pattern of 1, 3-dicarbonyl compound, there may be two pathways, one leads to furan derivative and the other to cyclopropane derivative. The nucleus independent chemical shift (NICS) values have been calculated for the intermediates, products and the corresponding transition states to ensure the aromaticity contribution to the reaction pathway. The results are in good agreement with the experimental findings.

In the fifth chapter we have computed and investigated the performance of Minnesota density functionals especially the M05, M06 and M08 suite of complementary density

functionals for the prediction of the heat of formations (HOFs) and the ionisation potentials (IPs) of various benchmark complexes, which are formed by addition reactions between first row transition metals and different ligands. The eight functionals of M0X family, viz. the M05, M05-2X, M06-L, M06, M06-2X, M06-HF, M08-SO and M08-HX are taken for the computation of the above mentioned physical properties of such metal complexes along with popular Los Alamos National Laboratory 2 double-ζ (LANL2DZ) basis set. Total 54 benchmark systems are taken for HOF calculation, whereas the 47 systems among these benchmark complexes are chosen for the calculation of IPs due to lack of experimental results on rest of the 7 systems. The computed values of HOFs and IPs are compared with the experimental results obtained from the literature. The deviation of these computed values from the actual experimental results is calculated for each eight different M0X functionals to judge their performances in evaluating these properties. Finally, a clear relationship between the exchange correlation energy of eight M0X functionals and their efficiency are made to predict the different physical properties.

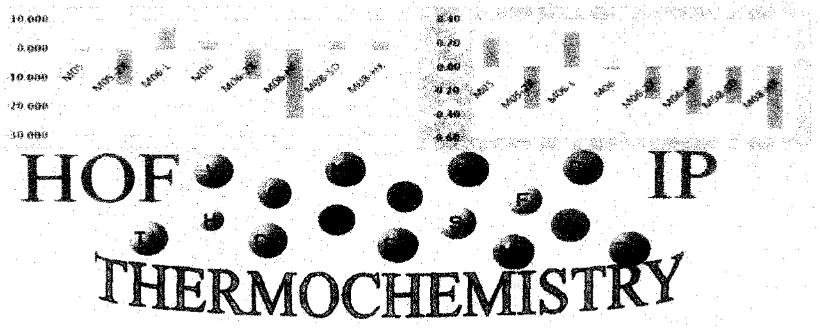

Figure 1. Thermochemistry with Minnesota Density Functionals.

In the sixth chapter, regio-controlled nitration of 4-quinolone, the highly privileged scaffold, has been investigated in density functional theory (DFT) based approach. Nitro group can selectively be introduced in diverse position simply by tuning the reactivity of the moiety. Discrimination is being achieved through the selective protection of free N-H group. The selection of protecting group is screened theoretically with the help of Fukui function and local softness calculations. Theoretical predictions are synchronized well with the experimental findings. Finally, this selective nitration allows the access of the structurally diverse 4-quinolones.

A comprehensive conclusion of this thesis is given at the last in chapter seven.