ACKNOWLEDGEMENTS

I would like to thank all my friends of Jamia Millia Islamia, New Delhi and Jamia Hamdard, New Delhi with whom I used to stay most of the times while going to home. I would also like to thank my friend Mr. Showkat Rashid from University of Kashmir for having fruitful discussions.

It would be an understatement to say that I would not be the person that I am today without my family. Henceforth, I would always be indebted to my parents Mr. Abdul Hamid Shah and Mrs. Syed Shahzada Andrabi for whom I have been able to see the light of this beautiful world. Their vision, ethical principles, moral support, endless patience and eternal inspiration to face any situation in life have guided me to the successful completion of this work. Thank you Abbu and Ammi for always believing in me and encouraging me through thick and thin! Lastly, I always cherish the sweet memories of my dearest sister, Ifrah. Perhaps her absence has made her omnipresent in every nook and corner of my life which I reminisce every now and then.

May **Almighty Allah** shower His choicest blessings and prosperity on all those who assisted me in any way during completion of my thesis work. Finally, looking back during this precious tenure of five years and five months of my life I often wonder over the ever inspiring lines of Robert Frost, "The woods are lovely, dark and deep. But I have promises to keep and miles to go before I sleep."

Place: Pilani
Date: 27/01/2021

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ABSTRACT

The present thesis concentrates on the development and applications of Density Functional Reactivity Theory (DFRT) based reactivity descriptors. The main aim of the thesis is to extend Comprehensive Decomposition Analysis of Stabilization Energy (CDASE) scheme (P. Bagaria, *et al. Phys. Chem. Chem. Phys.* **2009,** *11*, 8306), which is a modified form of Parr and Pearson equation (R. G. Parr, R. G. Pearson, *J. Am. Chem. Soc.* **1983,** *105*, 7512), as a valuable and an authentic tool for studying some chemical reactions. Apart from this, some modifications are made in the already existing equations of CDASE scheme which are further tested on some chemical reactions and correlated with experimental data.

In Chapter 1, an overview of literature, objectives and motivation behind the present thesis is discussed. The theoretical developments of the DFRT based local as well as global reactivity descriptors are thoroughly discussed in this chapter.

Chapter 2 introduces the new concept, 'charge transfer limit' and generates the full profiles of the components of stabilization energy as well as of stabilization energy itself. This is executed by choosing some adduct forming reactions, viz., Diels-Alder pairs and Charge transfer complexes formed between NH_3 and BH_3 and their derivatives. Apart from this, a qualitative relationship is developed in this chapter highlighting the role of non-bonding interactions (dipole–dipole, charge-induced dipole and London dispersion interactions) rather than only charge-transfer, in stabilizing the combined system at the initial stage of adduct formation. The analytical expression also helps to draw a conjecture on the influence of solvent polarity in stabilizing the adduct.

The conjecture drawn on the influence of solvent polarity in stabilizing the adduct in Chapter 2 is established in Chapter 3 by analytically introducing the thermodynamic parameter, 'net desolvation energy'. This new parameter introduces the effect of solvent polarity in the stabilization energy expression. Further, this formalism is tested on the two reactions viz., reaction of methyltrioxorhenium (MTO) with pyridine and [3+2] Huisgen cycloaddition reaction. The results generated are correlated with experimental formation constant (K) values for the former reaction.

In Chapter 4, an analytical relation is derived between equilibrium constant (K) and DFRT based stabilization energy with the help of chemical and statistical thermodynamics for reactions of the type $A + B \rightleftharpoons AB$. Further, CDASE scheme is applied on different sets of adduct formation processes viz., (i) methyltrioxorhenium(MTO)-Ligand adduct formation, where MTO

acts as an acceptor and a common species in all reactions and different mono- and bidentate N-donor ligands (acting as donors) and (ii) semicarbazone formation from semicarbazide (acting as a donor and a common species) and different ortho/para substituted benzaldehydes (acting as acceptors). Further DFRT based stabilization energies are correlated with experimental formation constant (K) values.

In Chapter 5, DFRT based Hammett equation from the kinetic component of CDASE scheme is proposed and then tested on six reactions viz., (i) reaction of para-substituted acetophenones with hydroxylamine, (ii) reaction of para-substituted cumenes with dimethyldioxirane, (iii) reaction of para-substituted benzylbromides with diphenylamine, (iv) reaction of 2,2,2-trifluroaceticacid with β-substituted ethanol, (v) reaction of norbornene with meta-substituted arylazide and (vi) reaction of norbornene with para-substituted arylazide. Further, a correlation is made between the experimentally generated Hammett plots and DFRT based Hammett plots.

Chapter 6 summarizes the overall thesis in the form of conclusions with an outline of probable future scope.

LIST OF ABBREVIATIONS AND SYMBOLS

BLYP	Becke exchange and Lee-Yang-Parr correlation energy functional
B3LYP	Becke three parameter exchange and Lee-Yang-Parr correlation energy functional
B3PW91	Becke three-parameter exchange and Perdew-Wang '91 correlation energy functional
$\left(\tilde{A}\tilde{B}\tilde{C}\right)_X$	Rotational constant in three dimensions for species X
CC	Coupled cluster
CDASE	Comprehensive Decomposition Analysis of Stabilization Energy
χ	Electronegativity
CI	Configuration interaction
COSMO	Conductor-like Screening Model
CRT	Chemical reactivity theory
ΔE_{SE}	Stabilization energy
$\Delta G^{\ominus}$	Standard Gibbs' free energy change
ΔN	Amount of charge transfer
$\Delta_r E_0$	Reaction energy
ΔSCF	Delta- Self consistent field
DFT	Density functional theory
DFRT	Density functional reactivity theory
DMM	Density matrix minimization
DNP	Double numeric with polarization
E	Energy
EA	Electron affinity
ECP	Effective core potential
EEM	Electron equalization method
ELF	Electron localization function
E_C	Correlation energy functional
E_{XC}	Exchange and correlation energy functional
ε	Dielectric constant

ε_i	Energy of the Kohn-Sham orbital.
η	Global hardness
$\eta(\vec{r})$	Local hardness at position r
FMO	Frontier molecular orbital
$F[\rho]$	Hohenberg-Kohn functional
$f(\vec{r})$	Fukui function
g	Degeneracy
GGA	Generalized gradient approximation
GVB	Generalized valence bond
$G_{corr.}$	Thermal correction to Gibbs free energy
h	Planck's constant
HOMO	Highest occupied molecular orbital
HPA	Hirshfeld population analysis
HSAB	Hard-soft-acid-base
$H_{corr.}$	Thermal correction to enthalpy
IP	Ionization potential
IPCM	Isodensity polarized continuum model
IEF-PCM	Integral equation formalism polarized continuum model
K	Equilibrium constant
k	Rate of reaction
k_B	Boltzmann constant
kcal mol^{-1}	Kilocalorie per mole
kJ mol^{-1}	Kilojoule per mole
L mol^{-1}	Litre per mole
LDA	Local density approximation
LFER	Linear free energy relationship
LSDA	Local spin density approximation
LUMO	Lowest unoccupied molecular orbital
LYP	Lee Yang Parr functional
MCSCF	Multiconfigurational self-consistent field
MEP	Molecular electrostatic potential

MESP	Molecular electrostatic potential
MGGA	Meta-generalized gradient approximation
MPA	Mulliken population analysis
MTO	Methyltrioxorhenium
μ	Chemical potential
N	Total number of electrons
NBO	Natural bond orbital
PBE	Perdew-Burke-Ernzerhof functional
PCM	Polarized continuum model
PMH	Principal of maximum hardness
PW	Perdew-Wang functional
PW91	Perdew-Wang (1991) correlation functional
P_K	Gross electronic population of atom k in the molecule
q_k	Effective atomic charge on atom k
$q_{X,m}^{\theta}$	Molar partition function of species X
R	Ideal gas constant
$\vec{r}$	Electronic position
$\rho(\vec{r})$	Electron density at position r
S	Global softness
$s(\vec{r})$	Local softness at position r
SCI-PCM	Self-consistent isodensity polarized continuum model
SCRF	Self-consistent reaction field
SMD	Solvation model based on density
σ_X	Symmetry number
ψ_i	Electronic wave function
T	Absolute temperature
$\theta_{V,K}$	Vibrational temperature of the mode K
$T(\rho)$	Electronic kinetic energy
$v(\vec{r})$	External potential
$V_{el}[\rho]$	Electron-electron interaction energy functional

$v_{XC}(\vec{r})$	Exchange-correlation potential
w	Global electrophilicity index
ZPE	Zero point energy

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and M06-2X/6-31G(d,p) levels of theory. Here, -X is the substituent on the meta -position of arylazide.

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