PREDICTION OF REACTION MECHANISM AND ABSOLUTE RATE CONSTANT USING COMPUTER ALGORITHM: THE BROMATE ION IN ACIDIC MEDIA REACTION

By

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July 2009
DECLARATION

This thesis is my original work and has not been presented for a degree or examination at any other university.

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Lucy Wairimu Kiruri           Date

This thesis has been submitted for examination with our approval as university supervisors

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Chemistry department
University of Nairobi
DEDICATION

To my family
For their Patience & Prayers
ACKNOWLEDGEMENT

This work has been one of my most important concerns so far. Some people have participated in its formal performance; others volunteered to take part in its realization and supported me in my special situation here. I owe them sincere gratefulness.

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### ABBREVIATIONS, ACRONYMS AND SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\hat{H}$</td>
<td>Hamiltonian Operator</td>
</tr>
<tr>
<td>$\Psi$</td>
<td>Wave Function</td>
</tr>
<tr>
<td>3-21G</td>
<td>[Pople’s basis set] (Pronounced “three two one gee”)</td>
</tr>
<tr>
<td>6-31G</td>
<td>[Pople’s basis set] (Pronounced “six three one gee”)</td>
</tr>
<tr>
<td>6-31+G(d)</td>
<td>Defined as for 6-31G* with diffuse functions added</td>
</tr>
<tr>
<td>6-31G(d)</td>
<td>Defined as for 6-31G with polarization added</td>
</tr>
<tr>
<td><em>Ab initio</em></td>
<td>from first principles</td>
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<tr>
<td>AO</td>
<td>Atomic Orbital</td>
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<tr>
<td>B3LYP</td>
<td>Becke 3- Lee, Yang and Parr DFT method</td>
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</tr>
<tr>
<td>CALCFC</td>
<td>Calculate Force Constants</td>
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<tr>
<td>COSMO</td>
<td>Conductor-like Screening Model</td>
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<td>DFT</td>
<td>Density Functional Theory</td>
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<tr>
<td>FKN</td>
<td>Field, Körös, and Noyes</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized Gradient Approximations</td>
</tr>
<tr>
<td>GTO</td>
<td>Gaussian-Type orbital</td>
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<tr>
<td>HF</td>
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<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
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<tr>
<td>IC</td>
<td>Indigo Carmine</td>
</tr>
<tr>
<td>IRC</td>
<td>Intrinsic Reaction Coordinate</td>
</tr>
<tr>
<td>KS</td>
<td>Kohn – Sham</td>
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<tr>
<td>LCAO</td>
<td>Linear Combination of Atomic Orbitals</td>
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<tr>
<td>LDA</td>
<td>Local Density Approximations</td>
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<td>LSDA</td>
<td>Local Spin-Density Approximations</td>
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<tr>
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<td>Lowest Unoccupied Molecular Orbital</td>
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<tr>
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<td>Mega Bytes</td>
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<tr>
<td>MO</td>
<td>Molecular Orbital</td>
</tr>
<tr>
<td>NOSYMM</td>
<td>No Symmetry</td>
</tr>
<tr>
<td>Pc</td>
<td>Personal computer</td>
</tr>
<tr>
<td>PCM</td>
<td>Polarizable Continuum Model</td>
</tr>
<tr>
<td>RAM</td>
<td>Random access memory</td>
</tr>
<tr>
<td>RHF</td>
<td>Restricted Hartree-Fock</td>
</tr>
<tr>
<td>SCF</td>
<td>Self Consistent Field</td>
</tr>
<tr>
<td>SCRF</td>
<td>Self-Consistent Reaction Field model</td>
</tr>
<tr>
<td>STO</td>
<td>Slater Type Orbital</td>
</tr>
<tr>
<td>STQN</td>
<td>Synchronous Transit-Guided Quasi Newton</td>
</tr>
<tr>
<td>TS</td>
<td>Transition State</td>
</tr>
<tr>
<td>TSO</td>
<td>Transition State Optimization</td>
</tr>
<tr>
<td>TST</td>
<td>Transition State Theory</td>
</tr>
<tr>
<td>UGBS</td>
<td>Universal Gaussian Basis Set</td>
</tr>
<tr>
<td>VWN</td>
<td>Vosko, Wilk and Nusair</td>
</tr>
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<td>ZPE</td>
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ABSTRACT

Computational and theoretical advances have progressed sufficiently so that it is now possible to calculate reaction rates directly from *ab initio* theory without the intervening use of any analytical method. The rate constants of chemical reactions are calculated using information about the structures, energies, and Vibrational frequencies of reactants and transition states. Computer algorithms help in determining the structures of the molecules and in understanding how molecules react with one another. In the present work, one of the elementary steps in the chemistry of bromate ion in acidic medium was investigated. The highlighted step is:

\[
\text{HOBr}^+ + \text{Br}^- + \text{H}^+ \xrightleftharpoons[k_1]{k_{-1}} \text{H}_2\text{O} + \text{Br}_2^+
\]

The above reaction is not a simple binary reaction; three reactants are combining to generate two products. Derivation of a mechanism required combining the known experimental data with the various ways that these elementary reactions could happen to find the consistent path or paths. The one which was impossible was a single step which required three particles coming together concertedly. The Hartree-Fock (HF) and the Density Function Theory (DFT) at B3LYP were adopted to study the reaction mechanism of hypobromous acid and bromide ion in acidic medium in both gas phase and in solution phase. Moreover, this aimed at comparing the two levels of theory and various basis sets. Three different reaction pathways were derived and their potential energy surfaces (PES) computed. Reaction pathways were successfully verified using the Intrinsic Reaction Coordinate (IRC) approach. An outline of a general theoretical scheme for the various reaction mechanistic pathways is well illustrated. Reaction pathway 1 occurs in the atmosphere (gas phase), pathway 2 is a bromination reaction which occurs in dilute acid and pathway 3 is an oxidation reaction which occurs in strong acid. The optimized energies at minima and the first-saddle point (maxima) were used to estimate the rate constants using the transition state theory (TST). The rate constants \((k_1)\) computed using the B3LYP for reaction pathway 1, 2 and 3 are 6.1E-10 cm\(^3\) mol\(^{-1}\) s\(^{-1}\), 3.7E+12 M\(^{-2}\)s\(^{-1}\) and 6.3E+8 M\(^{-2}\)s\(^{-1}\), respectively. For the reaction pathway 1 and 3 the experimental data is at least 3.5E-15 cm\(^3\) mol\(^{-1}\) s\(^{-1}\) and 2.3E+9 - 1.6E+10 M\(^{-2}\)s\(^{-1}\) which compared relatively well with the calculated kinetic parameters. In addition, \(k_{-1}\) and \(K\) calculated were compared with a number of experimental values reported by earlier workers.
CHAPTER ONE

INTRODUCTION

1.1 Background

Computational chemistry is a field of chemistry that makes use of advanced mathematical tools and the fundamental laws of physics and chemistry to simulate chemical reactions and chemical structures numerically (Foresman and Frisch, 1996). This method can be used to model not only stable compounds, but also short-lived, unstable intermediates and even transition states which are required for kinetic information. In this way, they may provide information about molecules and reactions that may be impossible to obtain experimentally (Li and Zhang, 2008).

Computational science is a valuable tool for experimental chemists to bypass tedious, time consuming, costly and sometimes dangerous experiments. Furthermore, it allows one to analyze quantities (such as atomic charges) that are not experimentally observable and also rectify incorrect experimental assignments. For example, based on spectroscopic experimental results, Gerhard Herzberg, a Nobel Prize winner, concluded that the methylene radical (\(\text{CH}_2\)) with two unpaired electrons had a linear geometry (Herzberg, 1972; Rouvray, 1997). Sophisticated calculations by Bender and Schaefer, however, demonstrated that methylene radical was bent with a bond angle of 135.1\(^0\) (Schaefer, 1986). Further experiments of methylene confirmed the latter assignment. This molecule and the controversy surrounding it have played an important role in establishing the role of computational quantum mechanical methods in modern-day research and the relationship between theory and experiments (Leach, 2001).
In the area of chemical kinetics, there has been a lot of progress in developing direct *ab initio* dynamics methods based on the transition state theory framework for calculating rate coefficients from first principles (Truhlar, Garrett and Klippenstein, 1996). However, there are two major challenges in calculating accurate, *ab initio* rate constants for polyatomic systems. The first is determining the potential energy surface (PES) on which the reaction occurs. A large number of electronic structure theories are available for calculating the Born-Oppenheimer potential energy as a function of the nuclear coordinates (Niewieczerzał and Cieplak, 2008). The first and second derivatives of the potential energy with respect to the nuclear coordinates are also available from many electronic structure theories (Helgaker, Olsen and Jorgensen, 2000). Continuing improvements in electronic structure theory promise increasingly accurate energies and applications to larger systems in the future (Niewieczerzał and Cieplak, 2008).

The second challenge is to use the relevant features of the PES to calculate a rate constant. The widely successful solution to this second challenge has been the transition state theory (Bofill and Anglada, 2001). In the harmonic approximation, transition state theory (TST) requires only the energy and frequencies at three stationary points along the reaction pathway, i.e., in the reactant and product basins and at the saddle point between these basins (Anglada *et al*., 1999). The success of harmonic TST at predicting rate constants is truly remarkable because it relies on such a sparse description of the PES. There are, however, many systems that are not well described by harmonic TST. The failure of TST can result because of classical recrossing which decreases the rate or because of quantum tunneling which increases the rate. Recrossing and tunneling corrections are often neglected in calculating rate constants because these factors are
usually small compared to the error caused by an inaccurate estimate of the PES, which is magnified exponentially in the rate constant calculation (Truhlar, 2001).

Many theoretical (Field and Györgi, 1992; Ganapathisubramanian and Noyes, 1982; Rothenberg et al., 2002) and experimental works (Pink, 1970; Jonnalagadda, Muthakia and Simoyi, 1988; Muthakia and Jonnalagadda, 1989) have been accumulated to date towards the understanding of the chemistry of bromate ion in aqueous sulphuric acid and to the elucidation of the mechanism and kinetics of the oscillating chemical systems. The experimental results were explained by various methods. For example, by variation in the rates with which volatile intermediates, such as oxygen and bromine (Ševčík, Zuzana and Ľubica, 1989; Menzinger and Dutt, 1990), are transferred between the reaction mixtures and atmosphere; by the absorption of intermediates, i.e. bromine, on the hydrophobic walls of the reactor, Pt- electrode or stirrer (Dutt and Mueller, 1993); as well as, by monitoring the absorbance of indigo carmine (IC) at 610nm on the oxidation of Indigo Carmine (IC) by hypobromous acid (Jonnalagadda, Muthakia and Simoyi, 1988). Before proceeding to an experiment involving the chemistry of bromate ion in acidic solution the Field, Körös, and Noyes, (FKN), steps has to be considered. Its basic mechanism was elucidated in 1972 and is presented by the reactions in Scheme 1.1 (Field, Körös and Noyes, 1972):

Scheme 1.1: Mechanistic model of Belousov-Zhabotinskii (BZ) reactions

\[
\begin{align*}
2H^+ + Br^- + BrO_3^- & \rightleftharpoons HOB\, + \, HBrO_2 & (i) \\
H^+ + Br^- + HBrO_2 & \rightleftharpoons 2HOB\, & (ii) \\
2HBrO_2 & \rightleftharpoons H^+ + \, HOB\, + \, BrO_3^- & (iii) \\
H^+ + Br^- + HOB & \rightleftharpoons H_2O + \, Br_2 & (iv)
\end{align*}
\]
These fast chemical transformations (Scheme 1.1) involve complex equilibria between various species which surpass the experimental determination of the active species responsible for the oxidation and bromination (Muthakia and Jonnalagadda, 1989). When evaluating the oxidation and bromination mechanisms using acid bromate it is important to remember that the system is very sensitive to changes in substrates and conditions (Petrov, 1993). This is a result of the presence of three simultaneous processes (oxidation, bromination and violent decomposition of bromate to bromine and oxygen at high acid concentrations) in solution. Since the energies of these three processes are comparable, changing the substrate or slightly changing the reaction conditions may result in dramatic effects (Rothenberg et al., 2002). For example, in the absence of bromide ion in the initial stages of the reaction, HBrO₂ disproportionates rapidly through reaction 3 giving the intermediate, HOBr, which in turn competes with bromate ion (BrO₃⁻) for oxidation (Jonnalagadda, Muthakia and Simoyi, 1988). On the other hand, if the concentration of Br⁻ ion is high, it plays the dual role of autocatalysis through reactions (i) and (ii), rapidly increasing the concentration of HOBr (Orbán and Körös, 1979) and leading to equilibrium between different oxybromo species (Jonnalagadda, Muthakia and Simoyi, 1988). The rate constants for the reaction (iv) in scheme 1.1 have been measured by many investigators with the values of $k_1$ and $k_{-1}$ differing (Barkin, et al., 1977; Field and Försterling, 1986; Beckwith, Wang and Margerum, 1996; Nagy-Ungvarai, Rácz and Burger, 2006). Therefore, to reconcile these discrepancies that exist in the experimental data, computational tools may be desirable.
1.2 Statement of the problem

The important role that reaction (iv) plays in bromination and oxidation reactions has stimulated the study of the process in which it intervenes. In particular, in the past 85 years much research has been devoted to the kinetic studies of this reaction. Unfortunately, significant discrepancies exist in the rate constants (k values) reported for this reaction by different workers. This means that a consistent reaction mechanism is lacking. In order to harmonize these experimental values by theoretical principles, this study is set to explain a reaction mechanism, energies, Vibrational frequencies and estimate the rate constants of this fundamental reaction (iv) using ab initio (Hartree-Fock) method and the density functional theory.

1.3 Justification

One of the major goals of computational chemistry is to understand the kinetics of the underlying elementary (basic) chemical reaction. Due to the importance of reaction (iv) in bromination and oxidation chemistry of bromate ion in acidic medium, it is both important and timely to provide physical insight into how this reaction occurs and thus, estimate its rate parameters. Therefore, using the most recent methods and simulation software (Gaussian 03W) it is hoped that a more reliable value for the rate constant will be obtained.

1.4 Novelty

The novelty of this work includes calculation of the thermodynamic parameters (ΔG, ΔH, ΔS, E_a and partition functions) for the first time. Moreover, this research work uses the
transition state theory to calculate the rate constant of reaction (iv) (Scheme 1.1) for the first time.

1.5 Hypothesis

Computer algorithms may be used to calculate geometries, Vibrational frequencies and energies of the three stationary points (which are the reactants, transition states and products) along the potential energy surface (PES), shown in Figure 1.1 below. The computed results may be applied to the transition state theory to estimate rate parameters and to identify the reaction mechanistic pathway(s).

![Diagram showing the potential energy surface with three stationary points: A (Reactants), basin 1; B (Intermediate); C (Products), basin 2. The energy is plotted against reaction progress from Reactants (A) through a transition state (B) to products (C). B can also be described by the following terminologies: Activated complex; First-order saddle point; Maxima (second derivative < 0); ONE imaginary (negative) frequency, TS, area of maximum activation energy. A & C can also be described by the following terminologies: Minima (second derivative > 0); all second derivative are positive; all vibrational frequencies are real (positive).](image-url)

Figure 1.1: A two-dimensional potential energy surface showing the three stationary points along the PES.
1.6 Research objectives

1.6.1 General objective

This work employed Gaussian 03 series of programs to study the reaction mechanism of 

$$\text{HOBr} + \text{Br}^- + \text{H}^+ = \text{H}_2\text{O} + \text{Br}_2$$

and also used transition state theory to estimate the rate constants using information about their structures, energies and Vibrational frequencies of the reactants and the transition states.

1.6.2 Specific objectives

The specific objectives envisaged are to:

1) Use the HOMO-LUMO molecular orbital interaction theory to provide a theoretical framework to analyze the possibility of certain pathways.

2) Model the initial structures (HOBr, H⁺, Br⁻ and HBr) for the ground state using GaussView.

3) Optimize the geometry and frequency for the analysis of the ground state using Gaussian 03 program.

4) Model and search for the transition state of reaction (iv), and then optimize the geometry and frequency using Gaussian 03 program and GaussView.

5) Ensure the connectivity of the stationary points (basins) and the first saddle point (TS) by performing an Intrinsic Reaction Coordinate (IRC) calculation.

6) Use the resultant energies and partition function to estimate rate parameters using the Eyring’s equation.
CHAPTER TWO
LITERATURE REVIEW

2.1 Theoretical background

There are two broad areas of computational chemistry devoted to the structure of molecules and reactivity: molecular mechanics and quantum mechanics (Hu and Yang, 2008). They both perform the same basic types of calculations that include geometry optimizations, Vibrational frequencies and computing energies of a particular system.

2.2 Molecular mechanics

Molecular mechanics is a mathematical formalism which attempts to reproduce molecular geometries, energies and other features by adjusting bond lengths, bond angles and torsion angles to equilibrium values which are dependent on the hybridization of an atom and its bonding scheme. The underlying calculations consider the behavior of the nuclei of the atoms neglecting that of electrons (Levine, 2006). This method relies on laws of classical Newtonian physics and experimentally derived parameters to calculate geometry as a function of energy (Levine, 2006). There are many different methods of molecular mechanics. Each one of these methods is characterized by its particular force-field. A force-field comprises a set of equations defining how the potential energy of a molecule varies with the locations of its component atoms and a series of atom types, defining the characteristics of an element within a specific chemical context. The atom types describe different characteristics and behaviour of an element depending upon its environment. For example, a carbon atom in a carbonyl group (C = O) is treated differently than one bonded to three hydrogen; CH₃, (Toxvaerd, 1990). The atom type
depends on hybridization, charge and the types of the other atoms to which it is bonded. Molecular mechanics calculations do not explicitly treat the electrons in a molecular system. Instead, one performs computations based upon the interactions among the nuclei. Electronic effects are implicitly included in force-fields through parameterization. This approximation makes molecular mechanics computations quite simple and allows their use for very large systems containing many thousands of atoms. However, it also carries some limitations as well. The one main limitation is that each force-field achieves good results for a limited class of molecules, related to those for which it was parameterized (Leach, 2001). Generally no single force-field can be used for all molecular systems of interest. Neglect of electrons means that molecular mechanics cannot treat chemical problems where electronic effects predominate. For example, molecular mechanics cannot be used to describe processes which involve bond formation and bond breaking. Molecular properties which depend on subtle electronic details are also not reproducible by molecular mechanics.

2.3 Quantum mechanics

The Quantum mechanical methods include semi-empirical, \textit{ab initio} methods and density functional theory. In quantum mechanics, the Schrödinger equation (1) gives the wave functions and energies of a molecule (Ben-Nun and Martinez, 2002).

\[ \hat{H}\Psi = E\Psi \]  

where $\hat{H}$ is the molecular Hamiltonian operator which transfers electrons from one level to another, $\Psi$ (psi) is the wave function and $E$ is the energy of the system. Solving the Schrödinger equation for atoms with more than one electron has many complications. It is possible to calculate accurately the energy of a system using the
Schrödinger equation for small systems, such as the helium atom, which consists of just two electrons and one nucleus. For the helium problem, some considerations are made, whereby the two electrons can interact with the nucleus but not with each other. So this three-particle system can now be solved correctly using the separation of variables method, where the Hamiltonian can be divided into parts dependent only on subsets of the coordinates (Leach, 2001). This is an example of perturbation theory, which is best applied when the differences between the real and simple systems are small. However for more complicated systems, electron spin must be accounted for in the computation (Becke and Dickson, 1990). It is not possible to solve the Schrödinger equation exactly beyond the single nuclei and two electron systems, but the Schrödinger equation can be simplified by the Born-Oppenheimer approximation to obtain the energy of slightly complicated systems (Becke and Dickson, 1990). Since nuclei have a much larger mass compared to the electrons, it is reasonable to assume that they move slowly than electrons. This means that the electrons can adjust almost instantaneously to any changes in the positions of the nuclei. This implies that with the nuclei at a fixed position the electronic wave function will depend only on the positions of the nuclei and not the momentum. The original Hamiltonian for nuclei and electrons, a case of a complicated system, is written as:

\[
\hat{H} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}
\]  (2)
The $\nabla^2_i$ is the Laplacian operator (read as “del squared”) and is defined as:

$$\nabla^2_i \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2},$$

$Z$ is the nuclear charge, $r_{iA}$ is the distance between nuclei and electron at equilibrium position, $r_{ij}$ is the distance between electrons, $R_{AB}$ is the distance between nuclei and A and B refer to the atoms present. The first term in the equation is the kinetic energy of the electrons, the second term is the kinetic energy of the nuclei, the third term is the energy of the Coulombic attraction between nuclei and electrons, the fourth term is the potential energy of the repulsions between the electron, and the fifth term is the nuclear-nuclear repulsion, respectively. By applying the Born-Oppenheimer approximation, the kinetic energy of the nuclei is zero and the repulsion between nuclei can be considered constant. This leads to the electronic version of the Hamiltonian:

$$\hat{H}_{elec} = -\sum_{i=1}^{N} \frac{1}{2} \nabla^2_i - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}}$$

(3)

This leads to a modified Born-Oppenheimer Schrödinger equation:

$$\hat{H}_{elec} \Phi_{elec} = E_{elec} \Phi_{elec}$$

(4)

where $E_{elec}$ is purely electronic energy and $\Phi_{elec}$ is the electronic wavefunction. Practical considerations of Equation 4 are reviewed further in the chapter, under the thermodynamic quantities sections. The four main approaches to calculating molecular properties are \textit{ab initio} methods, semi-empirical methods and the density functional theory.
Semi-empirical methods employs a simpler Hamiltonian than the correct Hamiltonian and use parameters whose values are adjusted to fit experimental data or the results of *ab initio* (*ab initio* is Latin for “from the beginning” and indicates a calculation based on fundamental principles) calculations (Foresman and Frisch, 1996). In contrast *ab initio* methods use the correct Hamiltonian and also the values of the fundamental physical constants, for example, the Hartree-Fock calculations. The density-functional method attempts to calculate the molecular electron probability density $\rho$ and calculates the molecular electronic energy from $\rho$ (Levine, 2006).

Molecular mechanics and semi-empirical methods have several advantages over *ab initio* methods and density functional theory. The most important is that, these methods are fast. Although this may not be significant for small molecules, it is certainly important for large systems such as polymers and proteins (Saunders, 1987). Moreover, for specific and well-parameterized molecular systems, these methods can calculate values that are comparable to experimental results than low level *ab initio* and density function methods (Ben-Nun and Martinez, 2002). The accuracy of molecular mechanics or semi-empirical methods is highly dependant on the database used for parameterizing the system. The main disadvantage of these methods (molecular mechanics and semi-empirical methods) is the parameterization process where all the parameters must be available before running a calculation. Frequently, these methods give the best results for a limited class of molecules such as polymers and proteins (Saunders, 1987). This is the main problem in molecular mechanic and semi-empirical methods.
The \textit{ab initio} or density functional methods could overcome this problem. However, they are slower than molecular mechanics and semi-empirical methods. The speed and the accuracy of \textit{ab initio} calculations have been greatly improved by developing new algorithms and introducing better basis functions than the previous ones (Becke, 1993b). Density functional method is a modern technique that has a lot in common with \textit{ab initio} methods. The Density Functional Theory (DFT) has been used to predict how the energy depends on the electron density rather than the wavefunction as in the \textit{ab initio} method (Becke, 1993a). In particular, the Hartree-Fock potential of \textit{ab initio} calculations has been replaced with an exchange-correlation potential, which is a function of the electron density. The effects of electron correlation are included and hence DFT can in principle, be more accurate than \textit{ab initio} Hartree-Fock calculations (Parr, 1983). Its results (geometries, energies, Vibrational frequencies and transition states) will be compared with those of \textit{ab initio} Hartree-Fock methods.

Computational chemistry, as with other disciplines in chemistry, is used as a tool to understand chemical reactions and processes (Anglada et al., 1999). The challenges for computational chemistry are to characterize and predict the structure and stability of chemical systems, to estimate energy differences between different states, and to explain reaction pathways and mechanisms at the atomic/molecular level. For example, examination of potential energy surfaces of a reaction using computational methods requires one to perform several single point calculations, optimizations of ground and transition states, frequency and intrinsic reaction coordinates (IRC) calculations (Bofill and Anglada, 2001).
The following sections will highlight the commonly used methods in computational chemistry calculations which will be applied to the study of the reaction of hypobromous acid and bromide ion in acidic media in which my current research is based.

### 2.4 Hartree-Fock Method

The Hartree-Fock procedure or Self-Consistent Field (SCF) method introduces well-defined approximations to solve the Schrödinger equation. However, this leads to a one-electron eigenvalue problem that must be solved iteratively to selfconsistency (Pisani and Dovesi, 1980). This procedure introduces the molecular orbitals expansion and determines the corresponding coefficients based on the *variational principle* or *variational theorem*. This variational calculation means that the approximate energies calculated are all equal to or greater than the exact energy. Because of the central field approximation, the energies from Hartree-Fock calculations are always greater than the exact energy and tend to a limiting value called the Hartree-Fock limit (Pople *et al.*, 1965). This variational principle leads to the equation, (5), describing the molecular orbital expansion coefficients, derived by Roothaan and Hall (Roothaan, 1951; Hall, 1951):

$$
\sum_{\mu=1}^{N} (F_{\mu\mu} - \varepsilon_{i} S_{\mu\mu}) c_{vi} = 0
$$  \hspace{1cm} (5)

where, $\mu = 1, 2, \ldots N$, $c_{vi}$ is molecular orbital expansion coefficient and $\varepsilon_{i}$ is the one electron orbital energy of molecular orbital. Equation (5) can be re-written in matrix form:

$$
FC = SC \varepsilon
$$  \hspace{1cm} (6)
where \( F \) = the Fock matrix,
\( S \) = the overlap matrix,
\( \varepsilon \) = the diagonal matrix of orbital energies, and
\( C \) = is the matrix of eigenvectors which determine the SCF orbitals.

This is an eigenvalue equation except for the overlap matrix. One performs a transformation of basis to an orthogonal basis to make \( S \) vanish. Then, it is just a matter of solving an eigenvalue equation (equivalent to diagonalizing \( F \)). Since \( F \) depends on its own solution (through the orbitals), the process must be done iteratively. This is why the solution of the Hartree-Fock-Roothaan-Hall equations is often called the self-consistent-field procedure.

Hartree-Fock is a simple theory, which satisfies the commonly known features of fermionic wavefunctions (Levine, 2006). The theory generates wavefunctions that are antisymmetric with respect to the exchange of two electron positions and includes exchange between like-spin electrons. The cost of a Hartree-Fock calculation formally scales with the cube of the number of basis functions, but depending on implementation, the scaling can be between linear and quadratic with system size (Leach, 2001; Hinchliffe, 2003). It is insufficient for quantitative predictions of the properties of many compounds. By neglecting electron correlation, interaction energies are typically very poor (Pisani and Dovesi, 1980). This is due to the energy of the system being described by the sum of the one-electron spin orbitals. So the probability of finding an electron at a particular point in space is independent of the probability of finding any other electron at that point in space. This is responsible for much of the poor performance when applied to conjugated systems, that is, systems with more than one pair of alternating double bonds. However, Hartree-Fock calculations provides good structures and allows quantum-
mechanical calculations to be sufficiently fast to allow their application to more realistic problems (Becke, 1993a).

2.5 Density Function Theory

Density Function Theory (DFT) is a powerful method of calculation and has become an important research tool for chemists, physicists and materials scientists (Leach, 2001; Hinchliffe, 2003; Foresman and Frisch, 1996). The real breakthrough came with a paper by Hohenberg and Kohn in 1964 that showed that the ground state energy and other properties of a system were uniquely defined by the electron density (Hohenberg and Kohn, 1964). However, the second landmark paper in the development of DFT was by Kohn and Sham (KS) in 1965 who suggested a practical way to solve the Hohenberg-Kohn theorem for a set of interacting electrons (Kohn and Sham, 1965). The KS theorem suggested that $F[\rho(r)]$ should be approximated as the sum of three terms:

$$ F[\rho(r)] = E_{ke}[\rho(r)] + E_{H}[\rho(r)] + E_{xc}[\rho(r)] $$

(7)

where $F[\rho(r)]$ is the sum of kinetic energy of the electrons and the contribution from interelectronic interactions. $E_{ke}[\rho(r)]$ is the kinetic energy of a system of non-interacting electrons with the same density as the real systems:

$$ E_{ke}[\rho(r)] = \sum_{i=1}^{N} \int \psi_{i}(r) \left( -\frac{\nabla^2}{2} \right) \psi_{i}(r) dr $$

(8)

The second term $E_{H}[\rho(r)]$ is the electron-electron Coulombic energy or the electrostatic energy. In the Hartree approach the electrostatic energy arises from the classical
interaction between two charge densities, which, when summed over all possible pairwise interactions, gives:

$$E_n[\rho(r)] = \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2$$  \hspace{1cm} (9)$$

The energy, $E$, is expressed as a unique functional of $\rho(r)$. The third term, $E_{xc}[\rho(r)]$, contains contributions from exchange and correlation.

Combining the two equations (8 and 9) and adding the electron-nuclear interaction leads to the full expression for the energy of an N-electron system within the Kohn-Sham scheme:

$$E[\rho(r)] = \sum_{i=1}^{N} \int \psi_i^*(r) \left( \frac{\nabla^2}{2} \right) \psi_i(r) \, dr + \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2 + E_{xc}[\rho(r)] - \sum_{A=1}^{M} \int \frac{Z_A}{|r - R_A|} \rho(r) \, dr$$  \hspace{1cm} (10)$$

Kohn and Sham wrote the density $\rho(r)$ of the system as the sum of the square moduli of a set of one-electron orthonormal orbitals:

$$\rho(r) = \sum_{i=1}^{N} |\psi_i(r)|^2$$  \hspace{1cm} (11)$$

By introducing this expression for the electron density and applying the appropriate variational condition the following one-electron Kohn-Sham equations results:

$$\left\{ -\frac{\nabla^2}{2} - \left( \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \right) + \int \frac{\rho(r_2)}{r_{12}} \, dr_2 + V_{xc} [r_1] \right\} \psi_i(r_1) = \varepsilon_i \psi_i(r_1)$$  \hspace{1cm} (12)$$
The external potential is written in a way that is appropriate to the interaction with $M$ nuclei. $\varepsilon_i$ are the orbital energies and $V_{xc}$ is known as the exchange-correlation functional which is related to the exchange-correlation energy by:

$$V_{xc}[\rho] = \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)}$$

(13)

The total electronic energy is calculated from equation (10). To solve the KS equations a self-consistent approach is taken (Parr, 1983). An initial guess of the density is fed into Equation 12, from which a set of orbitals can be derived, leading to an improved value for the density, which is then used in the second iteration, and so on until convergence is achieved.

For calculations in which the energy surface is the quantity of primary interest DFT offers a practical and potentially highly accurate alternative to the wavefunction methods discussed above. In practice, the utility of the theory rests on the approximation used for $\delta E_{xc}[\rho(r)]$ value.

### 2.5.1 Exchange-Correlation Approximation

As seen in Equation 13, which is an expression of exchange correlation function, the key between obtaining valid results in DFT depends on the exact value of $\delta E_{xc}[\rho(r)]$. The most popular and simplest approximation of $V_{xc}$ is the local density approximation (LDA). This approximation is based upon a uniform electron gas model where the electron density is constant throughout the entire space (Parr, 1983). Despite its simplicity, the local density approximation performs well, particularly for metallic systems including organometallic species (Becke, 1993b). However, LDA has been
shown to be inadequate for some problems, for example, computing energy differences between rather different structures. An improved version of the LDA called local spin-density approximation (LSDA) has been derived. LSDA is an extension of DFT which is similar to the way the restricted and unrestricted Hartree-Fock extensions were developed in order to model appropriately systems with unpaired electrons. The LSDA uses different orbitals and different densities with the net spin density being the difference between the density of up-spin and down-spin electrons. This proved to work well for bond lengths and vibrations, but not for dipole moments or predictions of molecular binding energies, which tend to be overestimated. In order to overcome this overestimated character of the LSDA a new method has been introduced that uses gradient-corrected, ‘non-local’ functionals which depend upon the gradient of the density at each point in space and not just on its value (Leach, 2001). The lowest-order gradient correction of exchange is in the form:

\[ \beta = \frac{(\nabla \rho)^2}{\rho^{3/2}} \]  

(14)

where \( \beta \) is a dimensionless parameter.

Many alternatives for gradient-corrected exchange and correlation functionals have been reported, which go beyond the lowest-order gradient correction and are collectively referred to as generalized gradient approximations (GGA).

The gradient correction to the exchange functional proposed by Becke in 1988, was a greatly improved functional which is known as B-88. This takes into consideration the exchange energy for rare gases in addition to the known behavior for the uniform electron
gas (Becke, 1988). B-88 exchange functional depends on both density and density gradient. The B-88 functional was a great improvement in that the asymptotic exchange energy behavior could be reproduced exactly. Other popular correlation functionals include the Lee, Yang and Parr (LYP), Perdew-86, and Perdew and Wang (PW91). These GGAs yield good thermochemistry, with an average error of the order of ±6 kcal/mol in a standard thermochemical test (Becke, 1993b). GGAs are also useful in the energetics and structures of hydrogen-bonded systems, but start to fail when taking into account dispersion interactions.

Modern DFT functionals are as the result of the combination of exchange and correlation functionals. In Becke’s original paper his own gradient correction for exchange was used in conjunction with a gradient correction developed by Perdew and Wang. A more popular scheme is the B3LYP, the Becke three parameter functional, where the non-local correlation is provided by Lee, Yang and Parr (LYP) and the standard local correlation functional due to Vosko, Wilk and Nusair (Kohn, Becke and Parr, 1996). The model takes the form:

\[
E_{XC}^{B3LYP} = (1 - a_0)E_X^{LSDA} + a_0E_X^{HF} + a_x \Delta E_X^{B88} + a_c E_C^{LYP} + (1 - a_c)E_C^{VWN}
\]  

(15)

The first three terms are the exchange contributions and the last two terms describe the correlation energy. The empirical coefficients \(a_0\), \(a_x\) and \(a_c\) are obtained by least-squares fitting to experimental data (56 atomization energies, 42 ionization potentials, 8 proton affinities and the total atomic energies of the ten first-row elements). Their values are \(a_0 = 0.20\), \(a_x = 0.72\) and \(a_c = 0.81\) (Leach, 2001). The B3LYP functional is used in
this work for all density functional calculations for its increased accuracy in predicting molecular structures and properties and its improved speed over traditional methods, such as the Møller-Plesset method (Frisch, Trucks and Cheese, 1996).

A major drawback for DFT is the lack of inclusion of dispersive forces. Dispersive forces are due to instantaneous dipoles which arise during the fluctuations in the electron clouds. This instantaneous dipole can induce a dipole in a neighboring atom, which gives an attractive or repulsive inductive effect. These forces may be necessary to adequately model a particular system, which could lead to over- or underestimation of the energies predictions with DFT.

However, there are several similarities between DFT and the Hartree-Fock approach. In Hartree-Fock theory, the multi-electron wave function is expressed as a Slater determinant constructed from a set of N (number of electrons) single-electron wave functions. DFT considers single-electron functions as well. However, Hartree-Fock theory calculates the full N-electron wave function. On the other hand, DFT only attempts to calculate the total electronic energy and the electronic density distribution (Becke, 1993b). A limitation of the DFT, compared to traditional methods, is that in a traditional method an arbitrary level of accuracy can in principle be obtained for any system which is only limited by computational resources, while DFT depends on adequate knowledge of the exchange correlation energy functional (Frisch, Trucks and Cheese, 1996). The exchange correlation potential describes the effects of the Pauli principle and the Coulomb potential beyond a pure electrostatic interaction of the
electrons. More accurate forms are still being developed, but there is no known systematic way to achieve an arbitrarily high level of accuracy.

2.5.2 Application of DFT to study reaction pathways

Since the focus of this work is the elucidation of reaction pathways and rate constant calculation, it is natural to focus on HF and DFT methods’ ability to predict properly the energies and geometries of reactants involved in a chemical reaction. DFT has been successfully applied to the study of competing bromination and oxidation pathway in acid bromate. The principal electronic features and energetics of the two pathways have been investigated. Bromination has been suggested to occur via decomposition of HBrO$_3$ to HOBr and O$_2$, with subsequent protonation of the hypobromous acid generating Br$^+$ in situ. In addition, oxidation proceeds in the formation of HBrO$_2$ (Rothenberg et al., 2002).

DFT has also been successfully applied to pericyclic reactions, whereby comparison of results from different DFT calculations with extensive results from Hartree-Fock calculations and other molecular orbital based on the study of Diels-Alder reaction has confirmed the accuracy of these methods (Frisch, Trucks and Cheese, 1996). An extensively studied reaction is the Diels-Alder reaction between butadiene and acrolein (Houk, Gonzalez and Li, 1995). The calculated activation energy for Hartree-Fock predicts a value of 47.4 kcal/mol, while MP2/6-31G(d) calculations predict 17.6 kcal/mol. It is well-known that Hartree-Fock tends to overestimate the activation energy while MP2 underestimates it. In order to predict accurate energies near the experimental value of 24.8 kcal/mol, it was important to include electron correlation energy. B3LYP/6-31G(d) gave an activation energy of 25 kcal/mol, which was in excellent agreement with
experimental value (24.8 kcal/mol). The study of transition structures for the above stepwise, diradical pathway and the concerted pathway has been an area of concern for many years. It is now well-established that Diels-Alder cycloadditions proceed through a concerted mechanism (Houk, Gonzalez and Li, 1995). How the B3LYP method predicts these reactions is relevant to the discovery of these mechanisms. Results from DFT methods, specifically the B3LYP/6-31G(d), has confirmed the experimental estimates for the energy of a concerted pathway. This demonstrates confidence in DFT’s ability to calculate the kinetic rate parameters using transition state theory. Hence, my current work employs the use of DFT and HF to study the mechanistic pathway(s) of reaction 4.

2.6 Basis Sets

A basis set is a mathematical description of the orbitals of atoms within a system used to perform the theoretical calculations. Most methods require a basis set to be specified. The approximation involves expressing the molecular orbital as linear combination of a pre-defined set of one-electron functions known as basis function (Foresman and Frisch, 1996). These basis functions are usually centered on the atomic nuclei and so bear some resemblance to atomic orbitals (Almlof, Helgaker and Taylor, 1988). An individual molecular orbital is defined as:

\[ \phi_i = \sum_{u=1}^{N} c_{ui} \chi_u \]  

where the coefficients \( c_{ui} \) are known as the molecular orbital expansion coefficients. The basis functions \( \chi_1, \ldots, \chi_N \) are also chosen to be normalized.
Early the Slater-Type Orbitals (STO) were used as basis sets due to their similarity to atomic orbitals of the hydrogen atom (Andzelm, et al., 1984)). However, Slater functions are not the best choice for molecular orbital calculations because some of the integrals are very difficult to evaluate when the atomic orbitals are centered on different nuclei (Feller and Davidson, 1986). The solution is to replace the Slater orbitals with functions based on Gaussian orbitals (Huzinaga, 1965; Huzinaga and Domsky, 1971) as illustrated in the following section.

2.6.1 Gaussian-Type Orbitals (GTO)

Gaussian and other ab initio electronic structure programs use Gaussian-type atomic functions as basis functions (Frisch et al., 2004). A Gaussian has the function in the form of \( \exp(-\alpha r^2) \) and ab initio calculations use basis functions comprising integral powers of \( x, y \) and \( z \) (Ahlrichs and Taylor, 1981; Pople, et al., 1982):

\[
x^a y^b z^c \exp(-\alpha r^2)
\]  

where \( \alpha \) is a constant which determines the radial extent of a Gaussian function. In Gaussian, \( \exp(-\alpha r^2) \) is multiplied by powers of \( x, y \) and \( z \), and a constant for normalization, so that:

\[
\int \text{g}^2 = 1
\]  

A major advantage of using Gaussian functions is that the product of two Gaussians can be expressed as a single Gaussian. So in a two-electron integral, the product of \( \phi_{\mu}(1)\phi_{\nu}(1) \) where \( \phi_{\mu} \) and \( \phi_{\nu} \) are Gaussian functions on different centers which can be replaced by a single Gaussian function that is centered at an appropriate point (Foresman and Frisch,
Along with these advantages, comes some disadvantages, when compared to Slater type functions. In comparing the 1s Slater function and the best Gaussian approximation (Figure 2.1) shows that the Gaussian functions decay towards zero more quickly than the Slater functions (Almlof, Helgaker and Taylor, 1988). This means that the Gaussian functions underestimate the long-range overlap between atoms and the charge and spin density at the nucleus. The errors by a single Gaussian functional leads to large inaccuracies (Pople, et al., 1982). However, a workaround for this problem is to represent each atomic orbital as a linear combination of Gaussian functions, of the form:

\[
\phi_\mu = \sum_{i=1}^{L} d_{i\mu} \phi_i(\alpha_{i\mu})
\]

where \( d_{i\mu} \) is the coefficient of the primitive Gaussian function \( \phi_i \), which has exponent \( \alpha_{i\mu} \). \( L \) is the number of functions in the expansion.

Figure 2.1: Slater type orbital and the best Gaussian counterpart

The atomic radius is given by \( r \).
A Gaussian function that permits both the coefficient and the exponent to vary during a calculation is referred to as uncontracted or primitive Gaussian. However, this requires a significant computational effort. For this reason, basis sets typically consist of contracted Gaussian functions whereby the coefficient and the exponent do not vary. In other words the coefficients and exponents are pre-determined and remain constant throughout the calculation (Almlöf, Helgaker and Taylor, 1988).

A minimal basis set contains only the number of functions required to describe all the filled orbitals in each atom (1s, 2s, 2p…). Increasing the number of basis functions per atom makes the basis set larger, which imposes fewer constraints on the electron and more accurately approximates exact molecular orbitals (Li and Zhang, 2008). Split valence basis sets, such as 3-21G and 6-31G (involves size adjustment for valence electrons to speed calculations) have two sizes of basis functions for each valence orbital. For example, hydrogen is presented as, 1s 1s′ where the primed and unprimed orbitals differ in size:

\[
\begin{align*}
1s + 1s' &= \text{Figure 2.2 Split-valence basis set of hydrogen atom}
\end{align*}
\]

The term 3-21G basis set is used to describe the core orbitals. Three Gaussians are used by the valence electrons, where the contracted parts are described by two Gaussians for the inner valence and one Gaussian for the outer valence. Introduction of polarization
functions into the basis sets allows a higher angular quantum number, so they correspond
to p orbitals for hydrogen and d orbitals for first and second row elements:

\[ s + p = \]

Figure 2.3 Polarized basis set, p polarization added to s valence orbitals

A common polarized basis set is the 6-31G(d), which indicates the use of polarization
functions on the heavy (non-hydrogen) atoms. Another improvement to the basis set is
the use of highly diffuse functions, denoted by using a ‘+’, hence 6-31+G(d) which allow
orbitals to occupy a large region of space (Li and Zhang, 2008). For example:

\[ \text{Contracted limit} + \text{Diffuse limit} = \text{Adjusted size} \]

Figure 2.4 Diffuse basis set, mixed p orbitals

The above described levels of theory and the basis set will be employed in this current
study of hypobromous acid and bromine ion in acidic media. This study also seeks to use
available software namely Gaussian 03W and GaussView.

2.7 Software specification

2.7.1 Gaussian 03W

Gaussian 03W (Frisch et al., 2004) represents the latest development of the previous
series of Gaussian programs which began with GAUSSIAN 70, GAUSSIAN 92,
GAUSSIAN 94 and GAUSSIAN 98. Gaussian 03W was released in April 2003 (Levine,
The GAUSSIAN programs are general-purpose programs capable of performing *ab-initio* Hartree-Fock (HF) molecular orbital calculations based on the linear combination of atomic orbitals (LCAO) approach (Frisch *et al.*, 2004). As the name implies, the program deals mainly with Gaussian-type orbitals. However new methods have been added to Gaussian 03W so as to improve optimization procedures for transition-state calculations. Gaussian 03W can compute energies, molecular structures, vibrational frequencies and numerous other molecular properties for systems in the gas phase and in solution, including the ground state and excited states at a reasonable execution time. In addition, it includes new basis sets e.g. the universal Gaussian basis set (UGBS).

The input section to the GAUSSIAN programs consists of the molecular charge and the multiplicity, the symbols of the constituent atoms and a definition of the molecular structure, either in the form of Cartesian coordinates or the Z-matrix notation, which defines the molecular geometry in terms of bond lengths, bond angles and dihedral angles. The task to be performed, for example, a single-point calculation, geometry optimization or frequency calculation, must also be specified, together with the appropriate basis set and the level of theory.

### 2.7.2 GaussView

GaussView (Frisch *et al.*, 2004) is not integrated with the computational component of Gaussian 03 but rather is a front-end/back-end processor to aid in the use of Gaussian software. It is a graphical user interface designed to help in the preparation of input for submission to Gaussian and hence examine graphically the output that Gaussian03 gives.
GaussView 03 provides three main benefits to Gaussian users. First, through its advanced visualization facility, GaussView allows you to rapidly draw even very large molecules, then rotate, translate and zoom in on these molecules through simple mouse operations. Second, GaussView makes it easy to set up many types of Gaussian calculations. It makes preparing of complex input easy for both routine job types and advanced methods like transition structure optimizations (Frisch et al., 2004). GaussView can also examine the results of Gaussian calculations using a variety of graphical techniques. These include optimized molecular structures, molecular orbitals, animation of the normal modes corresponding to vibrational frequencies, animation of geometry optimizations and IRC reaction pathways.

2.8 Solvent-Solute interaction

Chemical reactions generally take place in condensed media (Leach, 2001). For the last half century, quantum chemistry has made significant progress in predicting properties of gas-phase processes. Recently, a considerable effort has been made toward solution chemistry. A typical solution consists of a small amount of one substance, the solute, dissolved in a larger amount of another substance, the solvent. When a solution forms, the solute’s individual chemical entities become evenly dispersed throughout the available volume and are surrounded by solvent molecules. Solvents can be treated as explicit or implicit as shown in Figure 2.5 and 2.6, respectively (Tomasi and Miertus, 1982).
2.8.1 Explicit treatments of solvent-solute interaction

Explicit solvent model includes individual solvent molecules and calculates the free energy of solvation by simulating solute-solvent interactions. This involves very lengthy calculations that require an empirical interaction potential between the solvent and solute and between the solvent molecules. Within this approach there are two general methodologies. The supermolecule model (Miertus, Scrocco and Tomasi, 1983) treats a small number of first-solvation- shell solvent molecules explicitly at the quantum mechanical level as the solute. This method offers a straight-forward and accurate way to account for the localized portion of the solvent-solute interaction. However, it cannot include the long-range electrostatic interactions with the bulk solvent. Another common method is to construct an approximate solvent-solute interaction potential either using molecular mechanics force fields (Jorgensen, 1989) or empirical bond valence method (Aqvist and Warshel, 1993). Then for calculating reaction profiles in solution, one performs classical free-energy simulations to evaluate the potential of mean force along a selected reaction coordinate.

The advantage of using explicit treatment approach is that they provide detailed solvation structure enabling one to elucidate specific roles of solvent in reaction mechanisms. The main difficulty of these models is the definition of the reaction coordinate. Due to the large number of solvent degrees of freedom there is no unique way to define a reaction coordinate. As a result, evaluating energy paths for complex reactions is not possible.
2.8.2 Implicit treatments of solvent-solute (solution) interactions

The general method used in this study is the implicit treatment of the solvent, the dielectric continuum approach, which offers the simplest and yet reasonably accurate results (Tomasi and Miertus, 1982). In the dielectric continuum approach, the solvated system is modeled as the solute inside a cavity surrounded by a dielectric continuum media represented by the dielectric constant.
2.8.2.1 Thermodynamic background

The solvation free energy ($\Delta G_{sol}$) is required to transfer a molecule from vacuum to solvent. The solvation free energy is considered to have three components:

\[
\Delta G_{sol} = \Delta G_{elec} + \Delta G_{vdw} + \Delta G_{cav}
\]

(20)

where $\Delta G_{elec}$ is the electrostatic component. This contribution is important for the polar and charged solutes due to the polarization of the solvent, which is modeled as a uniform medium of constant dielectric $\varepsilon$. $\Delta G_{vdw}$ is the free energy change due to van der Waals interaction between solute and solvent and $\Delta G_{cav}$ is the free energy required to form the solute cavity within the solvent.

Such model has some weaknesses (Truong, Truong and Stefanovich, 1997). In particular, it does not provide any information on the solvent structure. In addition, the size and shape of the cavity have no rigorous definitions. However, there are also several important advantages. First, one can select a desired level of quantum mechanical theory from a wide range of *ab initio* molecular orbital (MO) and density functional theory (DFT) levels which are sufficiently accurate for modeling bond-breaking and forming processes. Second, the reaction coordinate is uniquely defined because solvent effects from the continuum media are effectively included in the solute Hamiltonian and do not increase the dimensions of the system. Third, availability of analytical free-energy derivatives greatly enhances the ability to explore the free-energy surface and to characterize stationary points. With appropriate choice of van der Waals radii for cavity
construction, one can obtain reasonably accurate free energy of solvation for a wide range of solutes. Overall, for modeling reactions in solution the dielectric continuum approach provides the most effective method.

For more realistic molecular-shape cavities, three models have shown some promise due to the availability of analytical free-energy derivatives (Foresman and Frisch, 1996). One is known as the polarizable continuum model (PCM). Second is the reaction field factors formalism which is based on the Kirkwood multipole expansion model. Third is the Conductor-like Screening Model (COSMO) developed by Klamt and Schüürmann (1993). Unlike the other Self-Consistent Reaction Field model (SCRF), the PCM is a new continuum approach which is computationally quite efficient (Miértus, Scrocco and Tomasi, 1983). The expression for the total screening energy is simple enough to allow the first derivatives of the energy with respect to atomic coordinates to be easily evaluated (Rinaldi et al., 1983). The PCM procedure generates a conducting polygonal surface around the system (ion or molecule), at the van der Waals distance. PCM uses a numerical representation of the polarization of the solvent and integration is numerical rather than analytical. This is because PCM has a cavity that is non-analytical in shape (no rigorous definition) and $\Delta G_{\text{elec}}$ is therefore calculated numerically.

The SCRF and PCM models have been used to investigate the effect of the solvents upon energetics and equilibria. For example, Wong, Wilberg and Frisch used the SCRF method to investigate the effect of different solvents upon the tautomeric equilibria of 2-pyridone (Wong, Wilberg and Frisch, 1992). Geometry optimizations were performed for the various tautomeric species at high levels of theory, and Vibrational frequencies
calculated. Results were reported for the gas phase, for a non-polar solvent (cyclohexane, \( \varepsilon = 2.0 \)) and for an aprotic polar solvent (acetonitrile, \( \varepsilon = 35.9 \)). The calculated free energy changes in the gas phase, cyclohexane and acetonitrile were \(-0.64\) kcal/mol, \(0.36\) kcal/mol and \(2.32\) kcal/mol, respectively which compared favourably with the experimental values of \(-0.81\) kcal/mol, \(0.33\) kcal/mol and \(2.96\) kcal/mol. This study will employ the implicit treatment of solute, in specific the PCM.

2.9 HOMO-LUMO orbital interactions

Geometry optimization of molecular species involved in a chemical reaction is the first step in studying a chemical pathway. In order to predict the interaction of two colliding molecules and decide whether such an interaction would really lead to a reaction, one can use the molecular orbital theory based on the HOMO-LUMO interactions. Fukui discovered the importance of orbital symmetry and suggested that the majority of chemical reactions should take place at the position occupied by molecules and in the direction of maximum overlap between the highest occupied molecular orbital (HOMO) of one species and the lowest unoccupied molecular orbital (LUMO) of the other component (Fukui, 1971). The kind of interaction between HOMO and LUMO is illustrated in figure 2.7. These orbitals are collectively known as the frontier orbitals because they lie at the outermost boundaries of the molecules. A chemical reaction between Reactants 1 and reactant 2 stabilizes through electron sharing to form a product.
Chemical reactions consist of the breaking of some bonds and the formation of new bonds. In order to form new bonds and break old ones a rearrangement of electron density has to take place through charge transfer interactions. The increase in electron density in the intermolecular region originates from the overlap of the occupied molecular orbitals (MOs) (particularly the HOMO) of the reactant and the unoccupied MOs (particularly the LUMO) of the reagent and vice versa. Fukui and colleagues have shown that the nodal properties of the HOMO and LUMO are important in predicting the evolution of reactants in a chemical reaction. Electron flow between two orbitals cannot occur unless they have a net overlap. For example, the most favourable reaction pathway for the approach of reaction of CH$_3^+$ to acetylene to give cyclo-C$_3$H$_3^+$ + H$_2$ goes through a \( \pi \)-transition state to the products in agreement with experimental evidence; this
transition structure presents a null HOMO-LUMO overlap which prevents electron density rearrangement from taking place by HOMO-LUMO interaction. This is an unfavourable orbital overlap at the transition state. A theoretical analysis carried out with the GAUSSIAN 90 series of program using the HF/6-31+G(d) shows that the HOMO-LUMO interaction directly leads to an unstable situation, and that bonding has to be established by HOMO-HOMO and LUMO-LUMO interactions (López, Sordo and Sordo, 1993). This valuable information was used as the preliminary work for the current work in suggesting the various favourable mechanistic pathways.

2.10 Intrinsic Reaction Coordinate (IRC) Methods

The important points involving the path of a chemical reaction include minima, corresponding to reactant and product and saddle points corresponding to transition structures (Figure 1.1). Once the transition state (TS) has been found, it should be verified that it indeed connects to the desired minima (Fukui, 1981). At the TS the vibrational normal mode gives an imaginary frequency and an inspection of the corresponding atomic motions can strongly indicate the correct TS. In this case the imaginary mode has a negative Vibrational frequency and represents a bond forming and bond breaking process. In addition isodesmic reaction results when the number of bonds broken is equivalent to the number of bond formed. A clear proof, however, requires a determination of the Minimum Energy Path (MEP) from the TS to the connecting minima. If the MEP is located in mass-weighted Cartesian coordinates, it is called the intrinsic reaction coordinate (IRC). Fukui (1981) introduced the concept of the IRC
defined as a classical trajectory of a system's motion over the potential energy surface (PES). The IRC path is defined by the differential equation (22):

$$\frac{dx}{ds} = -\frac{g}{|g|} = \nu$$  \hspace{1cm} (21)

Here $x$ is the (mass-weighted) coordinates, $s$ is the path length and $\nu$ is the negative normalized gradient, (Hinchliffe, 2003). Determining the IRC requires solving the equation above starting from TS, but slightly displaced from the TS along the normal coordinate in a direction to the minima (Fukui, 1981).

Another method of following the IRC, which does not rely on the integration of the differential equation, has been developed by Gonzales and Schlegel (Gonzales et al., 1991). The idea is to generate points on the IRC via a series of constrained optimizations.

The TS corresponds to the energy being a maximum in one direction and a minimum in all other directions (Truhlar, Garrett and Klippenstein, 1996; Li and Zhang, 2008). The frequency and thus its vibrational mode along the eigenvector with a negative eigenvalue will formally be imaginary. The eigenvector is the direction leading downhill from the transition state towards either the reactants (reverse reaction path) or the products (forward reaction path). At the TS the eigenvector with the imaginary frequency is the reaction coordinate. The whole reaction path may be calculated by sliding downhill to each side from the TS. This can be performed by taking a small step along the TS eigenvector calculating the gradient and taking a small step in the negative gradient direction (Gonzales et al., 1991). The negative of the gradient always points downhill and
by taking a sufficiently large number of such steps a stationary point (minima) from the TS is eventually reached (Leach, 2001). This is equivalent to the steepest descent minimization.

2.11 Computational results for thermodynamic quantities

Modeling and analysis are needed to test the validity of the suggested reaction mechanisms. The suggested mechanistic steps of the reactions for the current work will be studied computationally by the Hartree-Fock method and Density Function Theory (DFT). This study includes ground state optimization, transition states and their intrinsic reaction coordinates (IRC) for all the suggested steps. Thermochemical quantities may be extracted from a potential energy surface (PES) in terms of internal energy, $E$, enthalpy, $H$, and Gibbs free energy, $G$ (Truhlar, 2001). The procedure described here is based upon the implementation in the Gaussian software package (Frisch et al., 2004). By default, thermochemistry analysis is carried out at 298.15 K and 1 atmosphere pressure, which is easily modified. The equations used to compute thermochemical data from a PES can be found in most standard thermodynamic textbooks.

The electronic Hamiltonian used in ab initio calculations gives the total electronic energy, $E_{elec}$. A real molecule, however, has vibrational energy even at 0 K, which is the quantum mechanical, zero-point energy (ZPE), $\frac{1}{2}h\nu$. At absolute zero, the internal energy, $E_0$, is defined as the computed electronic energy plus the zero-point energy (Walter, 2000).

$$E_0 = E_{elec} + ZPE$$

(22)
Thermal corrections of the computed internal energy are necessary in order to obtain energies at temperatures that are directly comparable to experimental values. The thermal corrections to the internal energy are determined by contributions from the translational \((q_t)\), electronic \((q_e)\), rotational \((q_r)\) and vibrational \((q_v)\) partition functions (Equation 23).

\[
E_{\text{temp,thermal}} = E_t + E_r + E_v + E_e
\]  

(23)

The internal thermal energy correction term is the sum of all four contributions. It is important to realize that thermal energy corrections already include the zero-point energy through the vibrational partition function contribution and therefore it is not added. The term \(E_t\) is the contribution from translation partition function defined as:

\[
E_t = \frac{3}{2} RT
\]  

(24)

\(E_r\) is the contribution from rotational partition function defined as:

\[
E_r = RT
\]  

(25)

\(E_v\) is the contribution from vibrational partition function defined as:

\[
E_v = R \sum_k \Theta_{v,k} \left( \frac{1}{2} + \frac{1}{e^{\Theta_{v,k}/RT} - 1} \right)
\]  

(26)

and \(E_e\) is the contribution from electronic motion which is zero because there are no temperature dependant terms in the partition function.

The internal energy at a specific temperature is then determined by the sum of the internal thermal energy correction term and the computed electronic energy (Walter, 2000). For example, at 298 K the internal energy is given by equation 27:
Two thermodynamic quantities defined in Figure 2.6 are of common interest. The first thermodynamic quantity involves a change of the activation energy, $\Delta E_{298}^{\text{act}}$, which is the internal energy difference between the transition structure and the ground state reactants (Equation 28):

$$\Delta E_{298}^{\text{act}} = E_{298}^{\text{TS}} - E_{298}^{\text{react}}$$

(28)

The second quantity is the energy of reaction, $\Delta E_{\text{rxn}}^{298}$, which is the energy of the products minus the energy of the reactants.

$$\Delta E_{\text{rxn}}^{298} = E_{298}^{\text{prdt}} - E_{298}^{\text{react}}$$

(29)

Figure 2.8 Computed thermodynamic quantities (Truhlar, 2001).
Gaussian vibrational analysis output provides absolute thermochemical quantities, which follow from the discussion above. Energies are measured in Hartrees defined as Coulomb repulsion between two electrons separated by 1 Bohr \( (1 \text{ Hartree} = \frac{e^2}{a_0}) \).

Table 2.1: Example of Gaussian Vibrational analysis output

| Sum of electronic and zero-point Energies | \( E_{\text{elec}} + ZPE = E_0 \) |
| Sum of electronic and thermal Energies   | \( E_{\text{elec}} + E_{\text{thermal}}^{298} = E_{298} \) |
| Sum of electronic and thermal Enthalpies  | \( E_{\text{elec}} + H_{\text{thermal}}^{298} = H_{298} \) |
| Sum of electronic and thermal Gibbs Free Energies | \( E_{\text{elec}} + G_{\text{thermal}}^{298} = G_{298} \) |

The Gibbs free energy can be used to estimate entropy \( (S) \) of the molecule as shown in equation 30:

\[
G_{298} = H_{298} - TS
\]  
(30)

The thermal enthalpy is given by equation 31:

\[
H_{298} = E_{298} + RT
\]  
(31)

2.12 Assessment of Computed Results

Derivatives of the relevant equations are required for energy minimizations. The direction (sign) of the first derivative of the energy indicates where the minimum lies, while the second derivative gives the curvature of the function (Anglada and Bofill 1997). The first derivative is used to lower the energy of the system by moving each atom in response to the forces acting on it (steepest descent method). The second derivative (Newton-Raphson method) predicts whether the function is either a minimum (positive curvature, normal vibration) or maximum (negative curvature, imaginary frequency). The number of negative eigenvalues resulting after Vibrational analysis on the Hessian matrix
distinguishes the different types of stationary points. For a ground state, all of the
eigenvalues correspond to real vibrations of the molecule and can be observed
experimentally. The transition structure is special since it has a single negative
eigenvalue describing the vibration at the transition structure (Truhlar, Garrett and
Klippenstein, 1996). The vibration has an imaginary negative frequency (symbolizing
bond breaking and bond forming) since as the molecules move along the reaction path,
the energy decreases as the reactants or products are approached (Ke-Li, Li-Ping and
Zhang, 2008). The curvature (tangent) of such vibrational behavior is negative. The
relationship between the frequency of vibration and force constant is well known. The
vibrational frequency, \( \nu \), is proportional to the square root of the force constant, \( k \),
divided by the reduced mass, \( \mu \):

\[
\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \tag{33}
\]

where the reduced mass is \( \frac{m_1 m_2}{m_1 + m_2} \) and \( m \) represents the masses of the atoms involved.

The methods discussed above will be used in the present work to calculate the energetics,
geometry optimization, rate constants and validate the suggested reaction mechanisms of
chemical reaction (iv) in scheme 1.1.

2.13 Competing bromination and oxidation pathways in acid bromate solutions

The combination of bromate and acid features some unique chemical properties. For
example, under neutral conditions, alkali metal bromate salts are stable and can be safely
kept on the shelf. However, in the presence of a Brønsted acid, the bromate salts become
strong brominating agents that can be used for difficult transformations such as the bromination of benzaldehyde to 3-bromobenzaldehyde (Scheme 2.1). Remarkably, the addition of an acid also enhances the oxidative properties of the bromate ion so much that mixing bromate and acid with an oxidizable substrate can cause runaway reactions. This high reactivity generates interest in acid bromate as a cheap and powerful oxidizing and brominating reagent (Rothenberg et al., 2002).

Scheme 2.1: Oxidation and bromination of PhCHO using acid bromate

However, the co-existence of two distinct reaction pathways, and the fact that these fast chemical transformations involve complex equilibria between various species, has precluded the experimental determination of the active species responsible for the oxidation or bromination reactions. In such cases, computational tools may be advantageous. In the current work, we combine experimental (Jonnalagadda, Muthakia and Simoyi, 1988) and theoretical methods to demonstrate that selectivity towards oxidation or bromination when using acid bromate may depend on specific pathways of the reaction (iv):
\[ \text{HOBr} + \text{Br}^- + \text{H}^+ \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} \text{H}_2\text{O} + \text{Br}_2 \]  

(iv)

### 2.13.1 Kinetics of reaction (iv)

The above reaction (iv) is based on the mechanism of the cerium-bromate-bromide system in a continuous-flow stirred tank reactor (CSTR) as illustrated by Field, Körös and Noyes in 1972. It is a reversible elementary reaction for the bromate-bromide reaction in acidic solution. The rate constant is given as:

\[ v_1 = \frac{d[\text{HOBr}]}{dt} = -k_1[\text{HOBr}][\text{Br}^-] + k_{-1}[\text{Br}_2] \]  

(34)

Although many investigators have worked out the forward, reverse and the equilibrium rate constants of this fundamental reaction for the past eight decades (Liebhafsky, 1933; Barkin et al., 1977; Field and Försterling, 1986; Beckwith, Wang and Margerum, 1996; Nagy- Ungvárai et al., 2006), there are a number of considerable disagreements about the experimental values as shown in Table 2.1.

The reverse reaction involves the hydrolysis of bromine gas. There are a number of reasons why these fundamental constants are difficult to measure. For example, aqueous bromine is quite volatile. Hypobromous acid disproportionate slowly as in reaction (v):

\[ 3\text{HOBr} \rightarrow \text{BrO}_3^- + 2\text{Br}^- + 3\text{H}^+ \]  

(v)
Moreover, direct dilution of liquid bromine in water is reported to give appreciable amounts of bromate ion.

Table 2.1: Reported rate constants values for the reaction (iv)

<table>
<thead>
<tr>
<th>$k_1$ M$^{-2}$s$^{-1}$</th>
<th>$k_2$ s$^{-1}$</th>
<th>$K$ M$^{-2}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0E+9</td>
<td>110</td>
<td></td>
<td>Barkin et al., 1977</td>
</tr>
<tr>
<td>2.3E+9</td>
<td>2.0</td>
<td>6.7E-8</td>
<td>Field and Försterling, 1986</td>
</tr>
<tr>
<td>1.6E+10</td>
<td>97±8</td>
<td>6.2±0.3E-9</td>
<td>Beckwith, Wang and Margerum, 1996</td>
</tr>
<tr>
<td>8.0E+8</td>
<td>80</td>
<td></td>
<td>Nagy-Ungvarai, Rácz and Burger, 2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.1E-8</td>
<td>Försterling, Murányi and Schreiber, 1989</td>
</tr>
<tr>
<td>1.6E+10</td>
<td>110</td>
<td></td>
<td>Eigen and Kustin, 1962</td>
</tr>
<tr>
<td>8.0E+9</td>
<td>68</td>
<td></td>
<td>Citri and Epstein, 1986</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Too fast</td>
<td>Lifshitz and Perlmutter, 1959</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.7E-8</td>
<td>Liebafsky, 1933</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.2E-9</td>
<td>Liebafsky, 1933</td>
</tr>
<tr>
<td>1.45E+8</td>
<td>1.5E-9</td>
<td></td>
<td>Field et al., 1988</td>
</tr>
</tbody>
</table>

Different experimental methods and conditions for calculating the above kinetic values were employed. For example, Field et al. (1988) estimated the value of $K$ by studying the reaction of Br$_2$(aq) with BrO$_3^-$ at room temperature in 1M H$_2$SO$_4$. Försterling, Murányi and Schreiber, determined the value of $K$ by combined titrimetric and spectrophotometric measurements in 1M H$_2$SO$_4$ at 22°C and Eigen and Kustin used temperature-jump relaxation methods to estimate both $k_1$ and $k_2$. More than forty rate constants have been reported with each investigator trying to modify the previous experimental conditions (Beckwith, Wang and Margerum, 1996). Our review of these controversial reported values compelled us to use computational modeling approach
coupled with TST, which had not been considered previously to study the current problem.

2.14 Transition state theory (TST)

The TST was developed in the 1930s and has since formed a framework for much of the discussion of rate processes. It is a model used to determine the rate constants based on the potential energy surface (PES) with a statistical representation of the dynamics involved (Alberty and Silbey, 2001). In addition to the Born–Oppenheimer approximation it uses three more assumptions: there is a boundary that divides a reactant region and product region; the reactant equilibrium is assumed to maintain a Boltzmann energy distribution and the transition state or activated complex is assumed to have Boltzmann energy distribution corresponding to the temperature of the reacting system (Barreto, Vilela and Gargano, 2003).

2.14.1 Transition state optimization (TSO)

Chemists are interested not only in the thermodynamics of a process (relative stabilities of the various species) but also in the kinetics (rate of conversion from one structure to another). This requires one to investigate the nature of the PES shown in Figure 1.1 (Chapter One). In order to determine the energy barrier to reaction rate, the energy of this transition-state species is needed. The geometry and energy of a transition structure include important pieces of information for describing reaction mechanisms (Truhlar, 2001) as shown below in Figure 2.9:
As a system moves from one minimum to another, the energy increases to a maximum at the transition state and then falls. At a saddle point the first derivative of the potential function with respect to the coordinates are all zero. The number of negative eigenvalues in the Hessian matrix is used to distinguish different types of saddle points; an $n$th-order transition or saddle point has $n$ negative eigenvalues. This current study will elucidate the first-order saddle point in which the energy passes through a maximum for movement along the pathway that connects two minima and is a minimum for displacements in all other directions perpendicular to the path (Schlegel, 1987). This is shown schematically for a two-dimensional energy surface in Figure 2.7. To locate the minima of either reactants or products ($A$ and $B$) of functions is simple. On the other hand, to find first-order saddle point, which is the transition state ($X$), is much more difficult (Dewar, Healy and Stewart, 1984). It is difficult to predict what a transition structure will look like without the aid of computer simulation. Experimentally, it has only become possible to

Figure 2.9: Schematic diagram illustrating the energy as a function of reaction coordinate
examine reaction mechanisms directly using femtosecond pulsed laser spectroscopy (Gentili et al., 2005). Furthermore, these techniques yield indirect information such as vibrational information rather than a likely geometry for the transition structure. Many different strategies have been proposed for locating the TS, the majority of which can be divided into two general categories, those based on interpolation between two minima, and those using only local information (Leach, 2001; Hinchliffe, 2003). The former method is the QST2 and QST3 methods in Gaussian which has the facility for automatically generating a starting structure for a transition-state optimization based upon the reactants and products that the transition-state connects, known as the Synchronous Transit-Guided Quasi Newton (STQN) method. This method uses a quadratic synchronous transit approach to get closer to the quadratic region of the transition-state, and uses a quasi-Newton or eigenvector-following algorithm to complete the optimization. QST2 requires two molecule specifications, i.e., the reactants and products. QST3 requires three molecule specifications, that is, the reactants, the products and an initial structure for the transition-state, respectively. The QST2 and QST3 methods are utilized in cyclic studies.

In the present work the later method was employed. That is, if one starts from geometry that is close to the transition state, one can use Newton-Raphson minimization to find the transition state (Havlas & Zahradník, 2004). This requires that you calculate the force constant matrix accurately and then diagonalize it. You should then obtain 3N-7 positive eigenvalues and one negative corresponding to a first-order saddle point.
2.14.2 Hammond postulate of a transition state

A reaction involving reactants of high energy will require relatively little change in geometry to reach the transition state compared to a reaction involving reactants of low energy (Abraham and Nasehzadeh, 1981). In highly exothermic reactions, the transition state should resemble the reactants (early transition state). On the other hand, in highly endothermic reactions, the transition state should resemble the products (late transition state).

2.15 Rate constant estimation

In order to obtain the thermal rate constant, \( k \), we employed the transition state theory (TST) using the Eyring’s equation given below (Rooney, 1998):

\[
A + B \rightarrow X^\pm \rightarrow P
\]

\[
k_{\text{TST}} = \frac{k_B T}{h} \frac{Q_{X^\pm}}{Q_A Q_B} \exp \left( - \frac{\Delta G^\pm}{RT} \right)
\]  

(35)

where \( Q_{X^\pm} \), \( Q_A \), \( Q_B \) are partition functions of the first saddle points and the reactants A and B, respectively. \( k_B \) is the Boltzmann constant, \( h \) is the Planck constant, \( T \) is the absolute temperature and \( R \) the universal gas constant, \( \Delta G^\pm \) is the energy barrier between the TS and the reactants. The partition functions, \( Q_{X^\pm} \), \( Q_A \) and \( Q_B \) are given by:

\[
Q_j = Q_{\text{trans}} \times Q_{\text{rot}} \times Q_{\text{vib}} \times Q_{\text{elect}},
\]

\( j = X^\pm, A, B \): where \( j \) could be \( X^\pm, A \) or \( B \).

\( Q_{\text{trans}}, Q_{\text{rot}}, Q_{\text{vib}} \) and \( Q_{\text{elect}} \) are the components of the translational, rotational, Vibrational and electronic partition functions. The translational partition function is:
\[ Q_{\text{trans}} = \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2} \]  

(36)

where \( m \) refers to reduced mass and other parameters are as defined previously. The rotational partition function depends on the molecular structure and for a linear molecule the rotational partition function, \( Q_{\text{rot-2D}} \), is:

\[ Q_{\text{rot-2D}} = \left( \frac{8\pi^2 I_k k_B T}{\sigma_e \hbar^2} \right) \]  

(37)

whereas for a nonlinear molecule the rotation partition function, \( Q_{\text{rot-3D}} \), is:

\[ Q_{\text{rot-3D}} = \left[ \frac{\pi^{1/2}}{\sigma_e} \left( \frac{8\pi^2 I_m k_B T}{\hbar^2} \right) \right]^{3/2} \]  

(38)

where \( I \) and \( I_m = I_A I_B \) denote the moment of inertia and the product of inertia, respectively, \( \sigma_e \) is the symmetry number of the molecule. The vibrational partition function in the harmonic approximation is given by:

\[ Q_{\text{vib}} = \prod_i \left[ 1 - \exp \left( \frac{-h \sigma_i}{k_B T} \right) \right]^{-d_i} \]  

(39)

where \( \sigma \) is the frequency, \( i = 1,...,F \) and \( F \) is the degree of freedom. The vibrations \( (F = 3N - 5) \) are for linear molecule and \( F = 3N - 6 \) for nonlinear molecule. For the system in transition state, the Vibrational frequencies are \( F = 3N - 7 \) for nonlinear molecule and one imaginary Vibrational frequency. The term \( d_i \) is the mode degeneracy.

The electronic partition function is given by:

\[ Q_{\text{elect}} = \sum_i g_i \exp \left( \frac{-\epsilon_i}{k_B T} \right) \]  

(40)
where \( g_i \) is the degeneracy of the \( i \)th level, and \( \varepsilon_i \) is the electronic energy of \( i \)th level and is measured from the overall zero of energy.

The rate constant in the forward direction, \( k_f \), determined by TST, may be conveniently written in the Arrhenius form as:

\[
k_f = A \exp \left( -\frac{E_a}{RT} \right)
\]  

(41)

where \( E_a \) is the activation energy and is given by the following equation:

\[
E_a = \Delta H^\ddagger + RT
\]  

(42)

\( A \) is the pre-exponential factor given by equation 43:

\[
A = \left( e^{\frac{k_B T}{h}} \right) \exp \left( \frac{\Delta S^\ddagger}{R} \right)
\]  

(43)

The rate constants in the reverse direction, \( k_{-1} \), can be determined using the forward rate constant and the equilibrium constant, \( K \) as:

\[
k_{-1} = K \times k_f
\]  

(44)

Equilibrium constant \( K \) is given by equation 45:

\[
K = k_p \left( \frac{P}{RT} \right)^{2\nu_s}
\]  

(45)

\( \Delta G \) is given by equation 46:
\[ \Delta G = -RT \ln k_p \]  

(46)

where \( \Sigma v_j \) is the stoichiometric factor that is said to be positive for products and negative for reactants and \( p \) is the pressure.

For the Hartree-Fock and DFT methods, the Berny algorithm is the default algorithm for minimizations to a local minimum and optimizations to transition-states and higher-order saddle points (Frisch and Frisch, 1998). The purpose of geometry optimization is to locate the lowest energy of the molecular structure that is in close proximity to the specified starting structure. In order to determine the nature of the stationary point found, a frequency calculation is performed. The frequency output file has information that is critical in characterizing the stationary point, namely, the number of imaginary frequencies and the normal mode corresponding to the imaginary frequencies. Imaginary frequencies are listed in the output file as negative numbers. By definition, a structure which has \( n \) imaginary frequencies is an \( n^{th} \) order saddle point. Thus transition structures are usually characterized by one imaginary frequency since they are first-order saddle points. The movement of atoms associated with the imaginary frequency should follow the atoms on the reaction coordinate between the reactant and product. Further verification of the TS involves carrying out the IRC test. The Eyring’s equation is then used to calculate the various rate constants of reaction (iv) of scheme 1.1 with aim of shedding light on its kinetics.
CHAPTER THREE
METHODOLOGY

3.1 Hardware specification

The current calculations were carried out using a personal computer (Pc). The hardware specifications of the computer used was Pentium 4 Intel Celeron, a processor of 2.0 Giga Hertz (GHz) and 512 Mega bytes (MB) cash memory of Random access memory (RAM). Gaussian03 software was used for the intended calculations. GaussView which is a graphical user interface was used to visualize the Gaussian input and output results.

3.2 Selection of the computational method

Generally, two methods were used to examine the reaction pathways of reaction (iv) (scheme 1.1). These were restricted Hartree-Fock and DFT methods. A solvation correction was calculated using the cavity techniques discussed earlier. The polarizable continuum model (PCM) was used at the same level of theory as the geometry optimizations. Moreover, vibrational modes presentation of optimized transition states showed the optimum suggested reaction paths in both methods.

3.3 Selection of the basis set

The basis functions employed by the ab initio Hartree-Fock and density functional methods are contracted Gaussian-type functions and are given by equation 47:

\[ \chi_y = \sum_{w=1}^{b} d_{wy} g_w \]  

(47)
where the constants $d_{wy}$ are called contraction coefficients, the $g_w$ are primitive Gaussian functions and the values of $b$ typically range from 1 to 7. The primitive Cartesian Gaussian function has the form:

$$g = N x^m y^n z^o e^{-\alpha r^2}$$  \hspace{1cm} (48)

The quantities $m$, $n$, and $o$ are integers; $x$, $y$, and $z$ are Cartesian coordinates and $\alpha$ is the orbital exponent. When $m + n + o = 0$, then $g$ is said to be a $s$-type Gaussian function; when $m + n + o = 1$, then $g$ is a $p$-type Gaussian; and when $m + n + o = 2$, then $g$ is a $d$-type Gaussian. The values of the contraction coefficients $d_{wy}$ and the orbital exponent $\alpha$ are obtained by fitting a contracted Gaussian function to a STO (Figure 3.1) or by finding the contracted Gaussian functions that minimize the self-consistent-field energies of atoms. These optimized $d_{wy}$ and $\alpha$ values are stored in the Gaussian03 software and treated as constants when a contracted Gaussian function is used in a calculation (Levine, 2006). In this particular work Gaussian functions were used in all calculations.

Figure 3.1: Schematic diagram illustrating 3 Gaussian primitives simulating Slater-Type orbitals (STO)
A basis set is a mathematical description of the orbitals in a system used to perform theoretical calculations. Basis sets flexibility provides a better description of intermolecular interactions tailored to the need imposed upon by the chemical reaction being studied. We used the split-valence (6-31G) and polarization basis set 6-31G(d) in this work as the primary basis set. Larger basis sets such as, 6-31+G(d), were finally employed, since they allow orbitals to occupy a larger region of space. This was useful for anions and molecules containing lone pairs which have a significant amount of electron density away from the nuclear center (Ben-Nun and Martinez, 2002).

3.4 Estimation of rate constants using computational chemistry

3.4.1 Building Molecules

The initial guess structure of the ground state molecules and transition states was modeled using the GaussView. The molecules were built using the connectivity description known as the Z-matrix. In the Z-matrix notation, the atoms in the molecule are defined by bond length to one of the preceding atoms, by a bond angle made to two preceding atoms and by a dihedral angle made to three preceding atoms. When working with Z-matrices it is easier to start from an atom relatively close to the geometrical center of the molecule and work outwards. For example, when building hypobromous acid, water was picked and then bromide atom added by clicking it in one of the hydrogen atom in water molecule. The bond lengths and bond angles were adjusted to reflect the local geometry of the molecule. For example, when building the transition state, the bonds speculated to break were made longer and those supposed to form were shortened appropriately. The structures were then saved as Gaussian03 input files.
The Z-matrix internal coordinates can be used to describe the relationship between the atoms in a single molecule and are commonly used in quantum mechanics program. On the other hand, Cartesian coordinates are more appropriate when describing a collection of discrete molecules and is employed in molecular mechanics calculations (Leach, 2001).

### 3.4.2 Ground state structure optimization

The input section to the Gaussian03 program consists of the molecular charge and the multiplicity, the symbols of the constituent atoms and a definition of the molecular structure, either in the form of Cartesian coordinates or the Z-matrix notation, which defines the molecular geometry in terms of bond lengths, bond angles and dihedral angles. The task to be performed, that is, a single-point calculation, geometry optimization or frequency calculation together with the appropriate basis set and the level of theory to be used is specified at the route section.

The organization of the input and the keywords are program specific. During the geometry optimization of a reaction in gas-phase the following commands were used: B3LYP/6-31+G(d) OPT FREQ. The keyword B3LYP/6-31+G(d) indicates the level of theory to be DFT and the diffuse basis set. The OPT and FREQ specified a geometry optimization and Vibrational analysis to be computed, respectively (Table 3.1).

Table 3.1: Input file for ground state optimization of hypobromous acid

```plaintext
%chk=hobr.chk
%mem=100mb
%nproc=1
# b3lyp/6-31+g(d) opt=(Z-matrix) freq
Ground state opt
```
In addition to the above keywords for geometry optimization in gas-phase, the solution-phase calculation also specifies the solvent type as follows: SCRF=(SOLVENT=WATER, PCM). The keyword (SCRF) means that the calculation is in solution phase. Water, which has a dielectric constant of ~78.39, was used as the solvent for all the calculations in solution phase. The dielectric continuum approach, PCM, was employed for the current calculations.

3.4.3 The transition state search: Input file

The input file of the transition state modeled using GaussView was submitted for calculations with the following commands: HF/6-31+G(d) OPT=(CALCFC, TS, NOEIGENTEST) FREQ. In this case, \textit{ab initio} Hartree-Fock method was used at 6-31+G(d) basis set. The keyword TS requested optimization to a transition state rather than a local minimum, CALCFC specified that the force constants be computed at the first point using the current method available for DFT or HF.

The keyword NOEIGENTEST requested the computation of the exact Hessian matrix at the initial guess geometry and was also an instruction to Gaussian03 not to kill the job if the number of negative eigenvalues in the Hessian was not always equal to unity. In
addition the FREQ keyword was used to compute the partition functions, enthalpies, entropies and free energies.

3.5 Verification of transition states

The transition state was verified by the analysis of Hessian eigenvalues, which were printed out in the output file and by the visualization of normal Vibrational modes with GaussView. This eigenvector with the negative Vibrational frequency value that corresponded to the reaction coordinate required to be verified that it indeed connects the reactants and the products. The output file of the transition state was used as an IRC input file. The route specification of the input file for the intrinsic reaction coordinates calculation was as follows: B3LYP/6-31+G(d) IRC=(CALCFC) NOSYMM.

The keyword NOSYMM requested that a reaction path be followed by ignoring the molecule symmetry. The IRC calculations were important since they were also used to determine the various reaction pathways.

3.6 Calculation details

The results reported herein are based on ab initio molecular orbital calculations and density function theory, carried out with modified versions of the Gaussian03 system programs (Frisch et al., 2004). Such calculations enable one to determine the equilibrium and transition structures in the potential energy surface and their relative energies (Niewieczerzał and Cieplak, 2008). Optimized structures were obtained with at least six basis sets. Vibrational frequencies were evaluated, first to characterize rigorously the stationary points in the potential surface as minima (representing equilibrium structures)
or saddle points (representing transition structures), and secondly, to evaluate zero-point contributions to relative energies. Intrinsic reaction coordinate (IRC) was also calculated to demonstrate the connectivity between stationary points and first-saddle points and the mechanistic pathways suggested. The output files containing results for the geometries, energies and frequency analysis of the minimum and the transition states were generated and used to calculate various kinetic parameters of the chemical reaction (iv) in scheme 1.1.
CHAPTER FOUR
RESULTS AND DISCUSSIONS

4.1 Analysis of Results

This chapter focuses on the detailed results obtained for the current work. The reaction mechanisms of the three possible pathways, which were proposed for the current study, were based on the basic chemical principles and intuition of molecular orbital theory as discussed in Chapter two. In the study reaction (iv) was computed in gas phase and in solution phase. The suggested pathway 1 occurred in gas phase, whereas suggested pathway 2 and 3 occurred in solution phase. Mechanism 2 and 3 are described as bromination and oxidation, respectively in accordance with the experiments carried out by a number of researchers. Out of the ten basis sets employed in this study the Becke-3 Lee Yarr Parr at 6-31G (B3LYP/6-31G) provided the reaction pathway 2. The following sections illustrate what was computed in details.

Recall reaction (iv) in scheme 1.1 as highlighted below:

\[
\text{HOBr} + \text{Br}^- + \text{H}^+ \xrightleftharpoons[k_1]{k_{-1}} \text{H}_2\text{O} + \text{Br}_2 \tag{iv}
\]

4.2 Suggested Pathway 1

A two steps elementary reaction was suggested to constitute reaction (iv) as shown below:
According to molecular orbital theory, H⁺ ion has an empty valence orbital and can accept electrons. On the other hand, bromide ion is capable of donating electrons and their interaction leads to HOMO-LUMO stabilization as illustrated in the Figure below:

![Molecular orbital diagram of HBr formation](image)

Figure 4.1 Molecular orbital diagram of HBr formation

HBr is a simple diatomic molecule with eight valence electrons occupying four molecular orbitals. The two highest energy MO's are degenerate (\(\pi\)-type) and have no electron density associated with the hydrogen atom, i.e. they are Non-Bonding Orbitals and in Lewis Theory are represented as two "Lone Pairs". There is a much greater electron density around the bromine atom. This is because bromine is more electronegative than
hydrogen, and in each bonding molecular orbital it will take a greater share of the
electron density \((H^\delta^+ Br^\delta^-)\).

HOBr is both a Brønsted base (capable of accepting a proton) and a Lewis base, with one
of its unshared pairs acting as HOMO. HBr is a Brønsted acid, capable of donating a
proton and using the \(\sigma\) antibonding orbital as LUMO. The interaction of HOBr and HBr
stabilizes the unshared pair of electron on the oxygen atom, while simultaneously
breaking the H-Br bond because the interaction is with an antibonding orbital as
illustrated by scheme 4.1.

\[
\begin{align*}
\text{H} & \quad + \quad \text{H-Br} \quad \leftrightarrow \quad \text{H}_2\text{O} \quad + \quad \text{Br}_2 \\
\text{O} & \quad \text{Br}
\end{align*}
\]

Scheme 4.1: Suggested Mechanistic Pathway 1

By considering only the products the reaction appears to be quite fast because of very
stable products being formed. However, this is not the case because each of the reactants
is already in a very stable state. Using the above information, geometry optimization of
the minima (HOBr and HBr) was computed using the two levels of theory (HF and DFT).
The TS was searched and verified through frequency calculation and IRC test. The
calculations were carried out in gas-phase. Scheme 4.1a illustrates the GaussView output
visualization data of the suggested mechanism 1 as described above.
Scheme 4.1a: The Suggested Pathway 1 (gas phase) at B3LYP/6-31+G(d)

4.0: Br⁻ + H⁺  \rightarrow  4.1: HBr

4.2: HOBr + HBr  \rightarrow  4.3: TS

4.4: H₂O + Br₂
From Scheme 4.1a, the minima of the reaction are indicated as 4.0, 4.1, 4.2 and 4.4. Structure 4.3 of scheme A represents a transition state (TS). In the DFT calculations the TS resembled the reactants (early TS) whereas in the HF calculations the TS resembled the products (late TS) as shown in structure 4.5:

Structure 4.5: Transition state at the HF level of theory

The reaction therefore is a one-step concerted mechanism since it involves one transition state.

The optimized bond lengths and bond angle of hydrogen bromide and hypobromous acid calculated are presented in Table 4.1.

<table>
<thead>
<tr>
<th>Level of Theory</th>
<th>$R_{\text{H-Br}}$(HBr)</th>
<th>$R_{\text{H-O}}$(HOBr)</th>
<th>$R_{\text{O-Br}}$(HOBr)</th>
<th>$\angle$ HOBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/6-31G(d)</td>
<td>1.4193</td>
<td>0.951</td>
<td>1.809</td>
<td>105.0</td>
</tr>
<tr>
<td>HF/6-31+G(d)</td>
<td>1.4181</td>
<td>0.951</td>
<td>1.803</td>
<td>106.1</td>
</tr>
<tr>
<td>B3LYP/6-31g(d)</td>
<td>1.4378</td>
<td>0.975</td>
<td>1.869</td>
<td>101.9</td>
</tr>
<tr>
<td>B3LYP/6-31+G(d)</td>
<td>1.4369</td>
<td>0.975</td>
<td>1.864</td>
<td>103.5</td>
</tr>
<tr>
<td>Expt</td>
<td>1.4144</td>
<td>0.961</td>
<td>1.834</td>
<td>102.3</td>
</tr>
<tr>
<td>% Variation in HF</td>
<td>0.3464</td>
<td>0</td>
<td>0</td>
<td>3.715</td>
</tr>
<tr>
<td>% Variation in DFT</td>
<td>1.6544</td>
<td>1.457</td>
<td>1.908</td>
<td>1.173</td>
</tr>
</tbody>
</table>

The percentage (%) variation was calculated as follows:
\[
\% \text{ variation} = \frac{\text{Highest value} - \text{Experimental value}}{\text{Experimental value}} \times 100
\] (50)

The calculated geometries were compared with the experimental data. The density functional theory at the two levels (basis set) overestimated the interatomic distance. The variation between the calculated values for the H-Br, H-O, and O-Br were 0.023Å, 0.034Å and 0.022Å respectively. For the Hartree-Fock methods, the interatomic distance for the HBr compared relatively well with the experimental data. The interatomic distances for H-O and O-Br had small variations of -0.01Å and -0.028Å respectively when compared to experimental results. On the other hand, the HF methods overestimated the bond angle of HOBr whereas the DFT methods gave significantly good estimation compared to experimental data. Further, it was observed that there was no major difference between the basis sets. Moreover, as per Table 4.1, the calculated percentage variation showed that the HF gave precise bond lengths whereas DFT gave reproducible bond angles as it accounts for electron density.

The total energy of each reactant computed at Hartree-Fock level and density function level are given in table 4.2:

<table>
<thead>
<tr>
<th>Level of Theory</th>
<th>HBr</th>
<th>HOBr</th>
<th>H⁺</th>
<th>Br⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/6-31G(d)</td>
<td>-2570.4656</td>
<td>-2645.2605</td>
<td>0.0</td>
<td>-2569.9375</td>
</tr>
<tr>
<td>HF/6-31+G(d)</td>
<td>-2570.4780</td>
<td>-2645.2796</td>
<td>0.0</td>
<td>-2569.9713</td>
</tr>
<tr>
<td>B3LYP/6-31g(d)</td>
<td>-2572.3013</td>
<td>-2647.4648</td>
<td>-</td>
<td>-2571.7613</td>
</tr>
<tr>
<td>B3LYP/6-31+G(d)</td>
<td>-2572.3150</td>
<td>-2647.4881</td>
<td>-</td>
<td>-2571.8032</td>
</tr>
</tbody>
</table>
Table 4.2 shows the calculated energies for the reactants. The calculated energies using the HF methods were higher than those calculated using DFT method (Table 4.2). This is because the DFT includes electron correlation to a varying degree of accuracy contrary to Hartree-Fock method that uses wavefunction to estimate energy. The energies of H⁺ using the DFT methods were not computed because DFT requires electron density values but unfortunately hydrogen ion has an empty valence. In fact, attempts to optimize hydrogen ion using DFT method failed (link died) abruptly.

During the calculation of bond lengths, bond angles and energies of the reactants, the frequency analysis was also computed. In Table 4.3, the Vibrational frequencies for the HOBr and HBr are given.

<table>
<thead>
<tr>
<th>Level of Theory</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>1*</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/6-31G(d)</td>
<td>719</td>
<td>1330</td>
<td>4088</td>
<td>2800</td>
</tr>
<tr>
<td>HF/6-31+G(d)</td>
<td>725</td>
<td>1313</td>
<td>4078</td>
<td>2805</td>
</tr>
<tr>
<td>B3LYP/6-31g(d)</td>
<td>620</td>
<td>1217</td>
<td>3718</td>
<td>2594</td>
</tr>
<tr>
<td>B3LYP/6-31+G(d)</td>
<td>622</td>
<td>1192</td>
<td>3710</td>
<td>2597</td>
</tr>
<tr>
<td>Expt</td>
<td>620</td>
<td>1163</td>
<td>3615</td>
<td>2649</td>
</tr>
</tbody>
</table>

The HOBr had three Vibrational frequencies (F = 3N-6) and the HBr had only one Vibrational frequency since it is a linear molecule (F = 3N-5). The calculated Vibrational frequencies (Table 4.3) for hypobromous acid (1, 2 and 3) and hydrogen bromide (1*) in all levels were compared with the experimental data. The Hartree-Fock methods do not account for electron density and therefore they gave high values for all the four modes of vibration with average errors of 130cm⁻¹(1), 125cm⁻¹(2), 460cm⁻¹(3) and 152cm⁻¹(1*). However, the DFT calculations yielded Vibrational frequencies which were
quantitatively (with small variations of 1cm\(^{-1}\)(1), 41cm\(^{-1}\)(2), 99cm\(^{-1}\)(3), and -53cm\(^{-1}\)(4)) close to the experimental values.

From Gaussian output files, other important parameters included the Gibbs free energy, enthalpy, entropy and activation energy in Table 4.4. The rate constant was calculated using the Eyring’s equation discussed in chapter two. Table 4.4 gives the thermodynamic values and the absolute rate constant.

Table 4.4: Calculated thermodynamics parameters for the reaction \( \text{HOBr} + \text{HBr} = \text{H}_2\text{O} + \text{Br}_2 \)

<table>
<thead>
<tr>
<th>Method/Basis set</th>
<th>(\Delta G^\ddagger/\text{kcal mol}^{-1})</th>
<th>(\Delta H^\ddagger/\text{kcal mol}^{-1})</th>
<th>(\Delta S^\ddagger/\text{cal mol}^{-1})</th>
<th>(E_a/\text{kcal mol}^{-1})</th>
<th>(k_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/6-31G(d)</td>
<td>56.31</td>
<td>46.84</td>
<td>-31.76</td>
<td>47.44</td>
<td>1.1E-29</td>
</tr>
<tr>
<td>HF/6-31+G(d)</td>
<td>55.87</td>
<td>46.47</td>
<td>-31.54</td>
<td>47.06</td>
<td>2.4E-29</td>
</tr>
<tr>
<td>B3LYP/6-31g(d)</td>
<td>28.23</td>
<td>18.69</td>
<td>-32.00</td>
<td>19.28</td>
<td>4.5E-09</td>
</tr>
<tr>
<td>B3LYP/6-31+G(d)</td>
<td>29.41</td>
<td>19.85</td>
<td>-32.05</td>
<td>20.44</td>
<td>6.1E-10</td>
</tr>
<tr>
<td>Literature value</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.5E-15</td>
</tr>
</tbody>
</table>

From Table 4.4, the energies (\(\Delta G^\ddagger, \Delta H^\ddagger, E_a\)) of HF methods are higher than those of DFT methods. As a result, this leads to differences in the calculated rate constants with HF method resulting in a slow rate constants and DFT in higher rate constants. The calculated rate constants at the DFT level are slightly closer to the literature value thus confirming the existence of reaction pathway 1.

Finally, the intrinsic reaction coordinate (IRC) calculation was performed to clearly illustrate the connectivity of the reactants (HOBr and HBr) and products (H\(_2\)O and Br\(_2\)) through a transition state. Table 4.5 gives the optimized bond lengths and bond angles of the products using two different basis set for the two levels of theory.
As per Table 4.5, the HF methods gave high values of the bond angle by 2 degrees and underestimated the interatomic distance of O-H by 0.02 Å. The DFT methods showed a small error for the two interatomic distances, O-H and Br-Br. There was also a discrepancy in bond angles in the two DFT methods. The B3LYP/6-31+G(d) had an error of 2° whereas the B3LYP/6-31G(d) had an error of 1°. From these results, the experimental value for the bond angle of H_2O has been found to be an average value of DFT and HF methods. In case of Br-Br bond length, the calculated and experimental values agree.

### 4.2.1 The minimum energy path

The reaction path from reactants to products through a saddle point was then followed using Gonzalez- Schlegel method (Gonzalez and Schlegel, 1990). The DFT levels of theory used in gas phase exhibited intrinsic reaction coordinate (IRC) as shown below in Figure 4.2a:

<table>
<thead>
<tr>
<th>Level of Theory</th>
<th>R_{H-O}(H_2O)</th>
<th>&lt;H_2O</th>
<th>R_{Br-Br}(Br_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/6-31G(d)</td>
<td>0.947</td>
<td>106.6158</td>
<td>2.279</td>
</tr>
<tr>
<td>HF/6-31+G(d)</td>
<td>0.946</td>
<td>106.6015</td>
<td>2.281</td>
</tr>
<tr>
<td>B3LYP/6-31g(d)</td>
<td>0.956</td>
<td>103.1619</td>
<td>2.278</td>
</tr>
<tr>
<td>B3LYP/6-31+G(d)</td>
<td>0.966</td>
<td>102.0242</td>
<td>2.285</td>
</tr>
<tr>
<td>Expt</td>
<td>0.961</td>
<td>104.4776</td>
<td>2.281</td>
</tr>
</tbody>
</table>

Table 4.5: Equilibrium structures of products (distance in Å, angles in degrees)
According to Figure 4.2a, the reactant energy moved from the reactants (left side) to the products (right side) through TS. The resulting activation energy was low leading to a high reaction rate. The IRC calculated using DFT level of theory (Figure 4.2a) suggests that the reaction is endothermic as the products have high energy than the reactants.

Similarly, IRC calculation using the HF method depicted a reaction coordinate shown in Figure 4.2b (reactants on the left side). For this method the activation energy was high compared to DFT method and this lead to a slow reaction rate constant. Its graphical representation (Figure 4.2b) of IRC calculation suggests an exothermic type of reaction whereby the products have low energy than the reactants.
Figure 4.2b: IRC for the TS at HF Level of theory

The two levels of theory depicted one transition state each confirming the experimental results and earlier suggestion that it is a concerted reaction.

### 4.2.2 The solution phase reaction

Reaction pathway (1) was also carried out in solution phase. The geometries and energies of the reactants were computed at all levels of theory (HF and DFT). The first-saddle point was calculated using B3LYP with the 6-31G+(d) basis set. The TS had one imaginary frequency (Structure 4.6), corresponding to bond breaking and bond forming. An attempt to compute the connectivity of the reactants and products through the TS using IRC calculation failed. This was due to an error in the Z-matrix i.e., a fusion of O-H atoms (Structure 4.7). The Gaussian03 calculation was supposed to give thirteen convergence points each corresponding to a particular geometry tending to either reactants or products. But in this case, conversion of Z-matrix to Cartesian coordinates failed at card number 4. The heart of the problem is the definition of the dihedral angles. By definition, dihedral angle D(1/2/3/4) is the angle between two planes, the first being
described by atoms 1/2/3 and the second one described by atoms 2/3/4. As soon as atoms 1/2/3 or 2/3/4 fall on one line, the definition of one of the planes has vanished and the dihedral angle is undefined. This was a clear indication that the suggested pathway 1 could not occur in solution phase.

Structure 4.6: Transition state (in solution phase) at B3LYP/6-31+G(d)

Structure 4.7: Point 4 of the failed IRC calculation in solution phase

4.2.3 Comparison of the experimental and theoretical results

Carter and Ernesto carried out experiments to investigate the gas-phase reactions of simple bromine compounds under atmospheric conditions. This was aimed at reducing uncertainties in model calculations of the atmospheric ozone impacts of propyl bromide and other bromine containing compounds (Carter and Ernesto, 2000). Ozone was found to react with HBr with an apparent rate constant of $4 \times 10^{-19} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, with the data
suggesting that HOBr is formed in the initial reaction, but that it reacts with HBr to form Br₂, with a rate constant of at least $3.5 \times 10^{-15} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Carter and Ernesto, 2000). This experimental finding reaffirms the existence of reaction pathway 1 (Scheme 4.1a) in gaseous phase. Our earlier attempt to confirm the validity of the pathway 1 by computing IRC calculations in solution phase failed suggesting the nonoccurrence of this pathway in solution medium. Considering the fact that there are no experimental data on solution phase reported so far, results obtained in this work indicate that the reaction can only take place in the gaseous phase but not in solution phase.

4.3 Suggested Pathway 2

Referring to reaction (iv) in scheme 1.1, the expected reaction mechanism is taken to follow an $S_N2$ type reaction which in this case is considered to be pathway 2. The first step involves the interaction of hydrogen ion (LUMO) and the HOMO of hypobromous acid stabilizing to form water and the “bromonium” ion (reaction $x_4$). The $\text{Br}^+$ (LUMO) then reacts with the $\text{Br}^-$ (HOMO) to form the final product (reaction $x_5$)

$$
\text{H}^+ + \text{H}_3\text{O}^+ \rightleftharpoons \begin{array}{c}
\text{H}_2\text{O} \\
\text{Br}^+
\end{array} \rightleftharpoons \text{H}_2\text{O} + "\text{Br}^+" \quad x_4
$$

$$
\text{H}_2\text{O} + \text{Br}^+ + \text{Br}^- \rightarrow \text{H}_2\text{O} + \text{Br}_2^+ + \text{H}_2\text{O} \quad x_5
$$

Scheme 4.2: Suggested Mechanistic Pathway 2

Out of the six basis sets that were tested in our proposed objectives, only the 6-31G basis set at B3LYP level of theory supported reaction pathway 2. The reaction profile was
investigated by first calculating the geometries and energies of the minima on the energy surface. The structures and energies of the corresponding TS were then calculated. The procedure for locating the TS used is described in Chapter 3. Scheme B shows the Gaussian visualization output of the reaction pathway 2 as described above.

**Scheme 4.2b: The Suggested mechanistic Pathway 2 at B3LYP/6-31G**

![Scheme 4.2b: The Suggested mechanistic Pathway 2 at B3LYP/6-31G](image)
4.4 Result Analysis for Suggested Mechanistic Pathway 2

4.4.1 The scheme profile

Structures 4.9, 4.11, 4.12 and 4.14 shown above are stationary points classified as local minima on the energy profile of the reaction whereas structure 4.10 and 4.13 are transition state structures.

The TS calculation was verified by performing a frequency (FREQ) calculation resulting in ONE negative eigenvalue. The FREQ calculation was viewed using the GaussView program, enabling the vibration mode, associated with the negative eigenvalue, so that the bond formation and bond breaking is clearly visualized. In addition, an IRC calculation for the two transition states was computed to show that the TS indeed connected the right reactants and products. The first transition state involved an O-H bond formation with simultaneous O-Br bond breaking as shown in structure 4.10. The second transition state when viewed using GaussView program clearly indicated the Br-Br bond formation. This is presented in structure 4.13 above. The reaction profile as calculated using IRC for the two transition states are shown below.
Figure 4.3a: IRC for TS 1 at B3LYP/6-31G Level of theory

Figure 4.3b: IRC for TS 2 at B3LYP/6-31G Level of theory

Structure 4.13 presents an early transition state which resembles the reactants. This is also evident from our graphical representation (Figure 4.3b) which shows that reactants have higher energy than the products. Therefore the reactants required a relatively little
change in geometry to reach the first saddle point. In addition, this reaction is exothermic. The presence of the two graphical presentations (transition states) confirms that the reaction is not a simple binary reaction but rather consists of two steps.

The bond lengths and bond angles for the optimized structures of the products are presented in Table 4.6.

<table>
<thead>
<tr>
<th>Level of Theory</th>
<th>$R_{\text{H-O}(\text{H}_2\text{O})}$</th>
<th>$&lt;\text{H}_2\text{O}$</th>
<th>$R_{\text{Br-Br}(\text{Br}_2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/6-31G</td>
<td>0.983</td>
<td>107.1653</td>
<td>2.464</td>
</tr>
<tr>
<td>Expt</td>
<td>0.961</td>
<td>104.4776</td>
<td>2.281</td>
</tr>
</tbody>
</table>

From Table 4.6, it is evident that the low basis set at B3LYP level of theory overestimates the bond lengths and the bond angles when compared to the experimental data. Therefore, from our earlier discussion it can be concluded that adding diffuse functions would yield a more accurate structure.

### 4.4.2 Comparison of the experimental and theoretical results

It has been mentioned that bromination occurs due to the reaction of the “bromonium” ion which is formed in the equilibrium as shown below (Rothenberg et al., 2002):

$$\text{HOBr} + \text{H}^+ \rightleftharpoons [\text{H}_2\text{OBr}]^+ \rightleftharpoons \{\text{H}_2\text{O}+"\text{Br}^{+}\"\} \quad (\text{vi})$$

This study was carried out in dilute acid solution. This followed an earlier study that dealt with kinetics of electrophilic aromatic bromination under dilute acidic conditions that showed that it was unlikely that “Br$^{+}$” exists by itself in solution. A better explanation was the presence of $\{\text{ArH} + \text{H}_2\text{OBr}^{+}\}$ complex in the rate determining step (Gilow and Ridd, 1973).
The above experimental findings support the theoretical data and confirm the existence of this suggested pathway 2. The formation of H$_2$O leaves a positive bromine ion that is responsible for bromination reactions.

The thermodynamic parameters computed using Gaussian03 for this reaction mechanism are given in Table 4.7 for step 1 and 4.8 for step 2 (Scheme B).

**Table 4.7: Calculated thermodynamic parameters—solution phase for step 1.**

<table>
<thead>
<tr>
<th>Method/Basis set</th>
<th>$\Delta G^\ddagger$ /kcal mol$^{-1}$</th>
<th>$\Delta H^\ddagger$ /kcal mol$^{-1}$</th>
<th>$\Delta S^\ddagger$ /cal mol$^{-1}$</th>
<th>$E_a$ /kcal mol$^{-1}$</th>
<th>$k_1$ (M$^{-2}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/6-31G</td>
<td>0.32</td>
<td>0.12</td>
<td>-0.66</td>
<td>0.72</td>
<td>3.67968E+12</td>
</tr>
</tbody>
</table>

**Table 4.8: Calculated thermodynamic parameters—solution phase for step 2.**

<table>
<thead>
<tr>
<th>Method/Basis set</th>
<th>$\Delta G^\ddagger$ /kcal mol$^{-1}$</th>
<th>$\Delta H^\ddagger$ /kcal mol$^{-1}$</th>
<th>$\Delta S^\ddagger$ /cal mol$^{-1}$</th>
<th>$E_a$ /kcal mol$^{-1}$</th>
<th>$k_1$ (M$^{-2}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/6-31G</td>
<td>-3.46</td>
<td>-10.55</td>
<td>-23.78</td>
<td>-9.96</td>
<td>3.96267E+14</td>
</tr>
</tbody>
</table>

Comparing the data in the two tables above, the first step is the rate determining step since it has a low rate value compared to step 2. The energies in Table 4.8 are relatively low leading to a high rate value. However, the rate constant of this pathway is still lacking in the literature, i.e. a reaction involving dilute acid. Step 1 involves a nonspontaneous process characterized by a positive $\Delta G^\ddagger$. In addition, $\Delta H^\ddagger > 0$ and $\Delta S^\ddagger < 0$, both suggesting a nonspontaneous process.

Step 2 is a spontaneous process characterized by a negative delta $G^\ddagger$ and both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are negative. Since $\Delta S^\ddagger$ term is smaller than $\Delta H^\ddagger$ then this confirms a spontaneous reaction at room temperature.
4.5 Suggested Pathway 3

This suggested pathway 3 was studied using two levels of theory and two basis sets. Scheme 4.2 shows the suggested pathway 3 and the four main steps. Step-I involves the HOMO of Hypobromous acid and the LUMO of Hydrogen ion. In step-III, the positively charged reactant (H₂OBr) has empty valence orbital (LUMO) which interacts with the HOMO of Bromide ion.

For additional clarity, the above two steps can simply be represented by:
This reaction pathway was calculated using B3LYP/6-31G(d), B3LYP/6-31+G(d), HF/6-31G(d) and HF/6-31+G(d) levels of theory. The reaction profile was investigated by first calculating the geometries and energies of the minima on the potential energy surface. The structures and energies of the corresponding transition states were then calculated. The procedure for locating the TS used is described in Chapter 3. All the four levels of theory followed a common pathway 3.

Based on the investigation made during the computational experiment, the following mechanism was obtained (Scheme 4.3c):
Scheme 4.3c: The Suggested mechanistic Pathway 3 at B3LYP/6-31+G(d)

The input structure 4.15 had the hypobromous acid and the hydrogen ion estimated at bond length 1.1 Å coming in to attach to the Oxygen-atom thereby forming a bond. In the output structure, structure 4.16 (TS 1), the hydrogen ion attached to the O-atom and a bond formed between the two atoms. The Br-O bond length increased in size from
structure 4.15 to 4.16. The TS structure was verified to be correct since the FREQ calculation produced only ONE negative eigenvalue. In addition IRC was performed to confirm the existence of valid TS. The graphical presentations (IRC test) for the TS1 were identical for all the levels of theory (Figure 4.8a):

![Figure 4.4a: IRC for TS 1 at all the Levels of theory](image)

The final structure 4.17 of this IRC test clearly shows the partial bonds between O-H atoms. The O- Br atom bond length is 1.94Å. In contrast, the standard value is 1.8Å, suggesting that the bond is about to break. The bromide ion is then added to structure 4.17 and a TS search performed. The GaussView visualization of TS 2 (structure 4.19) confirmed a bond formation movement between the two Br-atoms.

The graphical representation (Figure 4.4b) computed for structure 4.19 shows connectivity between the reactants and the products. Figure 4.4b, the reactants has higher energy than the products thus symbolizing an exothermic reaction as illustrated below:
Figure 4.4b: IRC for TS 2 at B3LYP/6-31g Level of theory

4.5.1 Comparison of the experimental and theoretical results

A detailed kinetic study of the oxidation of Indigo Carmine (IC) with acidic bromate was reported by Jonnalagadda and co-workers in 1988. A possibility of reaction 4 being involved in the oxidation process is well outlined in this paper. HBrO$_2$ disproportionates rapidly through reaction 3 as outlined in chapter 1 (Scheme 1.1) giving HOBr which competes with bromate ion for IC.

\[
\text{HOBr} + \text{IC} \rightarrow \text{I} + \text{Br}^- \\
\text{(vii)}
\]

HOBr further oxidizes the intermediate I, in a fast reaction step to form isatin-5-monosulphonic acid (P), Br$^-$ and H$^+$ ions.

\[
\text{HOBr} + \text{I} \rightarrow \text{P} + \text{Br}^- + 2\text{H}^+ \\
\text{(viii)}
\]
Comparison of these experimental findings and the newly computed mechanism reaffirms the existence of reaction pathway 3. The reaction of oxidation involves an oxygen-atom transfer:

\begin{align*}
\text{HOBr} + \text{H}^+ & \longrightarrow [\text{H}_2\text{OBr}]^+ \longrightarrow \{2\text{H} + \text{Br} + \text{O}\}^+ \quad (\text{ix})
\end{align*}

Further theoretical work on oxidation of bromate ion (Rothenberg \textit{et al}., 2002) showed that oxidation occurred as a result of oxygen-atom transfer from HBrO3 molecule. In addition, the two dissociation pathways are dictated by the type of substrate and the acidity of the medium. For example, bromination dominates in dilute acid medium whereas oxidation will dominate in strongly acidic solutions.

Computational methods have been shown to produce realistic results regarding the competing reactions of bromination and oxidation of bromate ion in acidic solution. Specifically, in our findings all the levels of theory used have confirmed the above experimental findings of oxidation according to reaction (vi) in section 4.4.2.

The calculated total energies for the Structure 4.15 are presented in Table 4.9.

<table>
<thead>
<tr>
<th>Level of Theory</th>
<th>H\textsubscript{2}OBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/6-31g(d)</td>
<td>-2647.8666199</td>
</tr>
<tr>
<td>B3LYP/6-31+G(d)</td>
<td>-2647.8836129</td>
</tr>
<tr>
<td>HF/6-31g(d)</td>
<td>-2645.6629622</td>
</tr>
<tr>
<td>HF/6-31+G(d)</td>
<td>-2645.6789189</td>
</tr>
</tbody>
</table>

From the results presented in Table 4.9, it is evident that the DFT method produces significantly lower energy value compared to HF methods as a result of electron
correlations. Also it is worthy noting that the energies obtained with different basis sets are relatively insensitive to the level of theory at which computations are done.

Computational methods used for the calculation of the local minima energies were utilized in locating the geometries of the transition-state structures. The IRC test was further used to locate the end product. A summary of bond distances and bond angles is given in Table 4.10.

Table 4.10: Equilibrium structures of products (distance in Å, angles in degrees)

<table>
<thead>
<tr>
<th>Level of Theory</th>
<th>R_{H-O(H_2O)} (Å)</th>
<th>&lt;H_2O</th>
<th>R_{Br-Br(Br_2)} (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/6-31G(d)</td>
<td>0.976</td>
<td>102.781</td>
<td>2.323</td>
</tr>
<tr>
<td>B3LYP/6-31+G(d)</td>
<td>0.980</td>
<td>104.632</td>
<td>2.325</td>
</tr>
<tr>
<td>HF/6-31G(d)</td>
<td>0.955</td>
<td>105.4522</td>
<td>2.288</td>
</tr>
<tr>
<td>HF/6-31+G(d)</td>
<td>0.960</td>
<td>105.8052</td>
<td>2.283</td>
</tr>
<tr>
<td>Expt</td>
<td>0.961</td>
<td>104.4776</td>
<td>2.281</td>
</tr>
</tbody>
</table>

Table 4.10 shows the geometries of the product from an intrinsic reaction coordinate calculation. The results suggest that bond lengths can be calculated using the HF methods and a more demanding method that incorporates the effects of electron correlation can be used to evaluate the bond angles. The large basis sets of the DFT and HF theory shows an excellent agreement to the experimental data of the bond angle and the bond lengths, respectively.

**4.5.2 Calculation of the thermodynamic parameters**

The computed activation energies, enthalpies and Gibbs energies of the two steps are presented in Table 4.11 and Table 4.12.
Table 4.11: Calculated thermodynamic parameters-solution phase for step 1.

<table>
<thead>
<tr>
<th>Method/Basis set</th>
<th>$\Delta G^{\ddagger}$/kcal mol$^{-1}$</th>
<th>$\Delta H^{\ddagger}$/kcal mol$^{-1}$</th>
<th>$\Delta S^{\ddagger}$/cal mol$^{-1}$</th>
<th>$E_a$/kcal mol$^{-1}$</th>
<th>$k_1$ ($M^2$ s$^{-1}$)</th>
<th>$k_\text{-1}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/6-31+G(d)</td>
<td>2.38</td>
<td>2.30</td>
<td>-0.28</td>
<td>2.89</td>
<td>1.1E+11</td>
<td></td>
</tr>
<tr>
<td>B3LYP/6-31+G(d)</td>
<td>4.56</td>
<td>4.46</td>
<td>-0.33</td>
<td>5.05</td>
<td>2.8E+9</td>
<td>532</td>
</tr>
</tbody>
</table>

Table 4.12 Calculated thermodynamic parameters-solution phase for step 2.

<table>
<thead>
<tr>
<th>Method/Basis set</th>
<th>$\Delta G^{\ddagger}$/kcal mol$^{-1}$</th>
<th>$\Delta H^{\ddagger}$/kcal mol$^{-1}$</th>
<th>$\Delta S^{\ddagger}$/cal mol$^{-1}$</th>
<th>$E_a$/kcal mol$^{-1}$</th>
<th>$k_1$ ($M^2$ s$^{-1}$)</th>
<th>$k_\text{-1}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/6-31+G(d)</td>
<td>32.75</td>
<td>25.79</td>
<td>-23.34</td>
<td>26.38</td>
<td>3.9E-12</td>
<td></td>
</tr>
<tr>
<td>B3LYP/6-31+G(d)</td>
<td>4.47</td>
<td>-2.31</td>
<td>-22.71</td>
<td>1.71</td>
<td>6.3E+8</td>
<td>134</td>
</tr>
</tbody>
</table>

Calculated $K$ at B3LYP/6-31+G(d) = 1.6±0.3E-7M$^2$

In table 4.11 the calculated Gibbs free energies of step 1 does not conform to the known facts. The energies at HF/6-31+G(d) are low than those of DFT level of theory. B3LYP/6-31+G(d) incorporates electron effect, and its energy is expected to be lower than that of HF methods. Therefore, the unusual behaviour of these energies could not be explained at this level and is being recommended as a basis for further investigation.

As expected the energies of the second step (Table 4.12) computed at HF/6-31+G(d) are higher than those computed at B3LYP/6-31+G(d). The results of the two methods show that the second step is the rate determining step of the overall reaction.

4.6. Overall rate constant determination

Results from DFT methods, specifically the study of the well-established reaction of the bromate ion that resulted to two dissociation pathways is in excellent agreement with the experiments. This lends confidence in DFT’s ability to predict energetics with insignificant errors and this is the reason why it was used to estimate the rate parameters.

From the results in Table 4.11 and Table 4.12, the rate determining step is not the initial step (2.8±0.3E+9) but rather the second step (6.3±0.3E+8). The initial step acts like a
bottleneck later in the reaction sequence. As a result, the product of a fast initial step builds up and starts reverting to reactant while waiting for the slow step to remove it. Consequently, the fast initial step reaches equilibrium:

\[
\text{HOBr} + \text{H}^+ \xrightleftharpoons[k_{-1}]{k_1} [\text{H}_2\text{OBr}]^+ \tag{x}
\]

\[
[\text{H}_2\text{OBr}]^+ + \text{Br}^- \xrightarrow{k_2} \text{Br}_2 + \text{H}_2\text{O} \tag{xi}
\]

The overall rate law for this reaction is expressed as:

\[
k = \frac{k_2 k_1}{k_{-1}} [\text{HOBr}] [\text{Br}^-] [\text{Br}_2] \tag{xii}
\]

From the above mechanism, the overall rate calculated was \(3.30\text{E}+15\text{M}^{-2}\text{S}^{-1}\) which is higher than the rate determining step. Rate law is not useful in this study because it is very difficult to measure the concentrations of the intermediate. In addition, no matter how fast the first reaction is, the overall reaction cannot proceed any faster than the second step in the reaction.

For various reasons discussed in chapter 2, there has been no systematic study of bromine hydrolysis \((k_{-1})\) due to the difficulty involved in measuring its rate parameters. Other investigators who attempted to measure this rate constant in the presence of a phosphate buffer found that the reaction was too fast to be measured by their continuous-flow method (Lifshitz and Perlmutter, 1959). Several data have been reported for this reaction ranging from 2 to 110 \(\text{s}^{-1}\). Our computed \(k_{-1}\) value is \(134\text{s}^{-1}\) which shows a reasonable agreement with the experimental value of 110\(\text{s}^{-1}\). On the other hand, a comparison was
made between our calculated $K$ and the reported values between 6.7E-8 to 1.6E-10 M$^2$. The value we calculated using B3LYP/6-31+G(d) basis set was in excellent agreement with the experimental values.
CHAPTER FIVE
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The Hartree-Fock and the density function methods at B3LYP were adopted to study the kinetics of reaction (iv) in Scheme 1.1. In addition, three basis sets available in Gaussian03 were used for this study. The test included: derivation of a consistent mechanism(s), calculation of geometrical parameters, calculations of thermodynamic parameters and estimation of the absolute rate constant of the reaction (iv) using the two levels of theory. Our computational results were compared with the available literature and experimental data. In this work a detailed computational calculation was carried out both in gas phase and in solution phase.

From our findings, it can be concluded that this reaction is not a simple binary reaction but it involves a two step mechanism. It is now evident that three different reaction pathways exist, one in gas phase and two in solution phase. The first reaction mechanism discussed in our results has one transition state. This confirms the existence of a concerted-type of mechanism. The pathway 1 is one of the steps in the investigation of the gas phase reactions of bromine compounds under atmospheric conditions.

Pathway 2 was computed at B3LYP/6-31G level of theory. The reaction is clearly seen as an \( S_N^2 \)-type of reaction since water molecule was formed at the rate determining step leaving a bromonium ion. This mechanism can account for experimentally observed
bromination reaction which takes place in dilute acidic media. In addition, from the computational analysis, the reaction takes place in two steps.

Pathway 3 was computed at B3LYP/6-31+G(d) and HF/6-31+G(d) level of theory. The rate determining step suggests the possibility of an oxygen atom transfer since it is not attached to any other atom. In experiment, this pathway is suggested to take place during oxidation reaction when a strong acid is used in the media.

Two distinct observations from the computations emerge. First, the energies are sensitive to the level of theory chosen. Hartree-Fock energies are high reinforcing the need to include electron correlation energy evaluation. On the other hand, the DFT method that includes electron effect be used to evaluate energies and bond angles. Secondly, the key geometries that include the bond length can be calculated by the less demanding HF methods. The rate constant values compare relatively well with the experimental values for reaction pathway 1 and pathway 3.

5.2 Recommendations

The experimental activation energy of reaction (iv) in Scheme 1.1 is still unknown. The experimental value will help us to understand which level of theory is most appropriate for this reaction. In addition, the energies of the suggested pathway 3 (Table 4.11) are contradictory to the known facts. Further theoretical work would be necessary in order to clarify the reliability of such findings.

How the bromide ion and hydrogen ion are generated and whether there are side reactions, for example, isotopic scrambling (reaction involving deuterium) should be
investigated experimentally. Finally, additional experimental and computational work is required to confirm the possibility of the suggested pathway 1 in solution phase.
REFERENCES


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APPENDIX

6.1 Thermodynamic Properties
The thermodynamic properties, internal energy, entropy, and heat capacity, can be written in terms of the partition functions as:

\[ E = k_B T \left( \frac{\partial \ln Q}{\partial \ln T} \right)_v \]  
(46)

\[ S = k_B \ln Q + k_B \left( \frac{\partial \ln Q}{\partial \ln T} \right)_v \]  
(47)

\[ c_v = k_B \left( \frac{\partial \ln Q}{\partial \ln T} \right)_v + k_B \left( \frac{\partial^2 \ln Q}{\partial (\ln T)^2} \right)_v. \]  
(48)