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East Tennessee State University

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Theoretical Study on the Mechanism of

Removing Nitrogen Oxides Using Isocyanic Acid

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A Thesis

Presented to

the Faculty of the Department of Chemistry

East Tennessee State University

In Partial Fulfillment

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Master of Science in Chemistry

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by

Taraneh Nowroozi-Isfahani

August 2001

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ABSTRACT

Theoretical Study on the Mechanism of

Removing Nitrogen Oxides Using Isocyanic Acid

Taraneh Nowroozi-Isfahani

The mechanism of RAPRENO$_x$ reactions - RAPid REduction of Nitrogen Oxides using Isocyanic acid – proposed by Robert A. Perry[1] in an attempt to help control the emission of nitrogen oxides pollutant into the atmosphere, has been re-investigated theoretically. The study of reaction mechanisms was carried out using Chemist software[2]. All mathematically possible elementary steps have been evaluated and the chemically reasonable ones have been considered to propose new sets of reaction mechanisms. Density Functional Theory (B3LYP/6-31 G**) calculations using Gaussian 98 [3] were made in order to study the relative energies of all species and to predict the energy barrier of each elementary step. As a consequence of our study, there are two more sets of reaction mechanisms (in addition to Perry's mechanism) that could be possible for the propagation step of RAPRENO$_x$ process.

ACKNOWLEDGEMENTS

DEDICATION

To those who enlightened my life;

My dearest parents,

My beloved family,

My intimate friends

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CHAPTER 1

INTRODUCTION

<u>Oxides of Nitrogen</u>

Nitrogen oxides (NO_x) are among the top pollutant species in the atmosphere. The generic term of nitrogen oxides covers various oxides of nitrogen; however, it is mainly used to refer to the principal species of nitric oxide (NO) and nitrogen dioxide (NO_2) in the current literature.

Nitrogen oxides (NO_x) are well recognized by their harmful effect on human health and the environment. The hazards may be caused both from direct emission of NO_x to the environment and from their role in the formation of secondary compounds.

In the presence of sunshine, NO_x can react with hydrocarbons to make ground-level ozone. The effect called photochemical smog can cause serious respiratory problems for humans while it damages vegetation. In addition, NO_x together with sulfur dioxide react with other substances in the air such as water to form acid rain. The impact of acid rain is damaging forests and water ecosystems as well as contributing to the deterioration of cars and buildings.

<u>Sources of NO_x Emission</u>

The global emission of NO_x into the atmosphere has been increasing over the past 50 years. Just in the U.S.A., NO_x emission increased by 300% , from 7 million to 21 million tons, during the years 1940 through 1970 [4]. This significant increase is mainly attributed to human activities, particularly motor vehicles, utilities, industrial/commercial/residential, and all other sources as described in Figure 1-1[5]. Meanwhile according to the EPA record on 1995, about 7% of the total NO_x emission in 1990 was attributed to natural sources, of those lightning and soil are the two important ones.

5%

19%

49%

27%

Motor Vehicles

Utilities

Industrial/Commercial/
Residential

All Other Sources
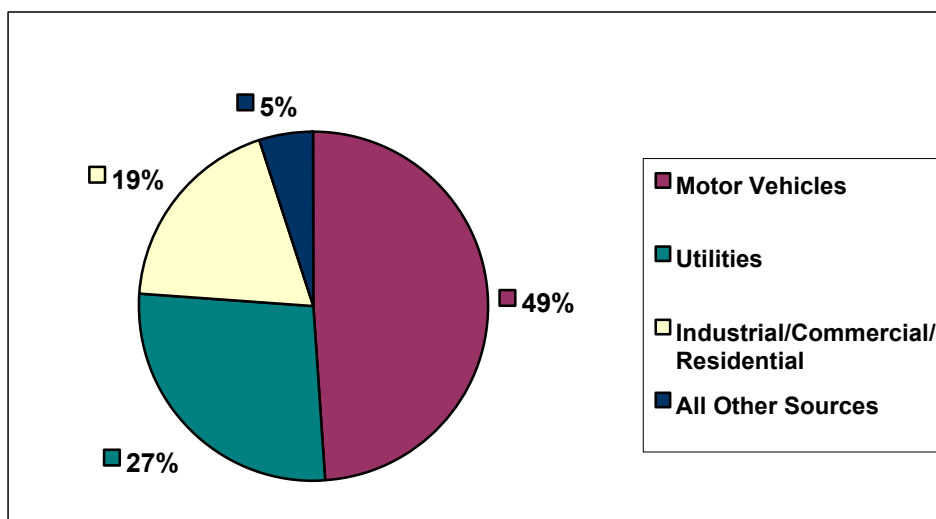
Figure 1-1: Sources of NOx Emission to the Atmosphere

Formation Mechanisms of Nitric Oxide

Nitric oxide is the primary nitrogen oxide emitted from most combustion sources. Therefore, the first approach to control NO_x emission is to reduce the initial production of nitric oxide. Scientists believe that there are three major sources of NO formation during combustion process[6].

1) Thermal NO Mechanisms

This term is related to the system when the original fuel contains no nitrogen atom. Nitric oxide formation from atmospheric nitrogen occurs at high temperature (about 2100 K). The equilibrium equation is given as below:

$N_2 + O_2 \leftrightarrows 2\,NO$
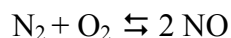
The kinetic route is explained by formation of oxygen atoms from the H_2-O_2 radical pool or possibly from the dissociation of O_2. The next step is the attack of an oxygen atom to a nitrogen molecule to start a chain reaction postulated by Zeldovich as indicated below:

$O + N_2 \leftrightarrows NO + N$

$N + O_2 \leftrightarrows NO + O$
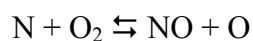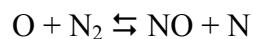
2) Prompt NO Mechanisms

Proposed by Fenimore, prompt NO forms in the flame zone when a hydrocarbon species and atmospheric nitrogen are present. The reaction equations are as below:

$$CH + N_2 \leftrightarrows HCN + N$$

$$C_2 + N_2 \leftrightarrows 2CN$$
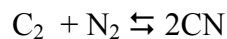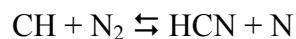
The nitrogen atom then forms nitric oxide through a thermal NO mechanism. In the meantime CN would yield NO by the attack of oxygen atom.

3) Fuel-bound Nitrogen NO Mechanisms

The NO formed during the combustion of fuels containing one or more nitrogen atoms is known as an important source of nitric oxide. The mechanism is described by noting that prior to entering the combustion zone, the nitrogen compounds in fuel decompose to low molecular weight nitrogen containing compounds or radicals such as NH_3, NH_2, NH, CN, etc. This will further facilitate oxidation of fuel-bound nitrogen compound to form nitric oxide rapidly.

Furthermore, a comparison of bond dissociation energies for N-N bond (225 Kcal/mol) with N-C bond (60-150 Kcal/mole) confirms that the NO formation from oxidation of N-C is predominant while using nitrogen-containing fuel[7].

Methods to Control NO_x Emission

It is believed that NO are the most difficult to control pollutants. This is due to the complexity of the chemistry of the members of NO_x family and their ease of interchangeable reactions. The other important issue in controlling NO_x is that these pollutant species can be transported over long distances and impact areas far from the original sources.

Due to the great emphasis on environmental concerns, EPA has made a serious effort to control NO_x emission since 1970. The efforts did ban the extra increase of NO_x although it did

not greatly reduce the annual emission of NO_x. Yet, only in the U.S.A., over 23 million tons[5] of nitrogen oxides were emitted into the air in 1997.

During the past 30 years, a wide variety of methods have been proposed and applied to decrease NO_x emission and its polluting consequences to the atmosphere. These methods are classified into two major techniques consisting of combustion process modification and post-combustion flue gas treatment (FGT)[8]. Even though many methods characterized as combustion process modification are useful, scientists have been working on FGT methods for more effective and economical techniques to reduce NO_x emission.

FGT processes include different groups of reduction techniques. One important group is Selective Non-Catalytic Reduction technique (SNCR) such as injecting Ammonia or Urea into high temperature post combustion gas. These processes are called Thermal DeNOx and NOxOUT respectively[8].

In the most recent and successful SNCR technique, the possibility of using Cyanuric Acid $(HOCN)_3$ for the reduction of NO_x has been proposed. The mechanism of this reaction is our concern in this research.

RAPRENO$_x$ Technique

In 1986, RAPRENO$_x$ for RAPid REduction of NO_x was proposed by Robert A. Perry as a simple, effective, relatively inexpensive, and non-polluting method for removing nitric oxide from gas stream[1]. The method is based on the addition of gaseous Isocyanic acid (HNCO) to the exhaust gas stream containing NO. Isocyanic acid is formed from decomposition of Cyanuric acid in temperatures higher than 330°C.

$(HOCN)_3 \rightarrow 3\ HNCO$
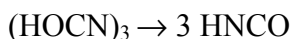
Ever since the invention of the RAPRENO$_x$ method, many experiments have been carried out by different groups of experts in order to study the exact function of Isocyanic acid in reducing NO_x under different experimental conditions. One of the early experiments done by Perry and Sieber[9] indicated that when HNCO mixed with an exhaust gas stream at temperatures higher than 400°C, HNCO and NO are consumed while carbon dioxide, carbon monoxide, water,

and nitrogen gas are produced. The process was studied using a long-pass optical cell with Forrier Transform Infra Red (FTIR) detection. The obtained data proved a molar ratio of 1:1 for the reaction of HNCO and NO. Meanwhile a possible reaction mechanism was proposed as below:

(1) $HNCO \rightarrow NH + CO$

(2) $NH + NO \rightarrow H + N_2O$

(3) $H + HNCO \rightarrow NH_2 + CO$

(4) $NH_2 + NO \rightarrow N_2H + OH$

(5) $NH_2 + NO \rightarrow N_2 + H_2O$

(6) $N_2H \rightarrow N_2 + H$

(7) $OH + CO \rightarrow H + CO_2$

According to the suggested scheme, the speed and high efficiency of the system for nitric oxide removal has been related to the chain characteristic of the reaction. The chain is initiated by hydrogen free radicals, which are generated in the presence of a surface catalyst. While reaction number (6) is considered as the reaction to regenerate hydrogen free radicals, further experiments done by Perry[10] indicated the effect of carbon monoxide presence to improve chain branching through reaction number (7). In the meantime, the mechanism was mis-interpreted by Corio[11], where he considered this mechanism a non-chain reaction and suggested that the mechanism must consist of eight elementary steps.

CHAPTER 2

THEORETICAL CALCULATION

<u>Reaction Mechanism Analysis</u>

Investigating the mechanism of chemical reactions is one of the major concerns of a physical chemist. However, understanding the actual procedure of chemical reactions will be beneficial for scientists in all areas of chemistry.

Reaction mechanism analysis is the study of the individual steps responsible for conversion of reactants into products in a chemical reaction. These individual steps called elementary steps introduce intermediate species, which are produced and consumed during the reaction. Elementary steps are generally unimolecular or bimolecular; however, termolecular steps may occur between atoms and small molecules in the gas phase [12].

Although there are numerous elementary steps that can be proposed as possible steps for the mechanism of a specific reaction, the number of actual elementary steps are limited depending on the total numbers (K) of reactant, product, and intermediate of that reaction. This is in accord with the principles of mass and charge conservations and can be explained as below[11]:

$$K = \rho + \pi + \iota = \eta + \nu$$

where ρ is the number of reactants, π is the number of products, ι is the number of intermediates, η is the number of independent elementary steps, and ν is the number of mass and charge conservations.

Nevertheless, for a complete mechanism, the linear combination of all elementary steps must generate the observed stoichiometry of the reaction, which automatically eliminates all the intermediates involved.

The reaction coordinate diagram for each elementary step represents the free energy surface connecting reactants to products[12]. The imaginary species at the free energy maximum is called transition state, and the standard free energy difference between reactant and transition

state is defined as the free energy of activation $\Delta G^{\ddagger}$. Free energy of activation is considered to be an important factor in determining reaction mechanism, keeping in mind that the paths with the lowest activation energy are generally favored.

The Advantage of Using Chemist Software

A proper investigation for a reaction mechanism requires that the expert predict all the possible elementary steps and reaction channels of the reaction for further evaluation. It is also necessary to recognize those sets of steps that all together could give the stoichiometry of the reaction. Though the prediction of all possible steps may sometime be difficult, computer programs can add to the convenience and accuracy of the investigation.

Chemist is a software that allows the investigator to input an unbalanced chemical equation and proposed intermediates[2]. It translates the chemical equation to a language of vector spaces and applies certain chemistry rules so as to provide new formulas and algorithms to perform matrix calculations. These rules include the basic laws of conservation of mass and conservation of charge and the law of definite proportions. The calculated results are further translated to the chemical equations to present a balanced equation, all mathematically possible reaction channels, elementary steps, and reaction mechanisms.

Ab initio Calculating Methods

The quantum mechanical approach to determine electronic energy and other physical properties of a molecule is to solve the Schrodinger equation:

$$H\Psi = E\Psi$$

where the wave function Ψ is the eigenfunction and energy E is the eigenvalue of the Hamiltonian operator H. The Hamiltonian operator is the quantum mechanical corresponding term for the classical mechanical Hamiltonian function, which is composed of kinetic and potential energies of the system.

One of the basic methods to solve the Schrodinger equation is the *Ab initio* method. *Ab initio*, which means "from the scratch"[13], is a calculation based on the fundamental principles of

quantum mechanics and physical constants such as speed of light, electron mass and charge, and Plank's constant. It does not apply any experimental data to the Schrodinger equation.

<u>Model Chemistry</u>

It is practical to solve the Schrodinger equation for a small atom like hydrogen. However, when it comes to large systems with a complex Hamiltonian term, the equation is only solvable by applying different mathematical approximations called model chemistry.

The first approximation to solve the Schrodinger equation is to eliminate kinetic energy of the nuclei from the Hamiltonian term. This approximation named after Born-Opppenheimer is based on the assumption that nuclei are much heavier than electrons and, therefore, can be considered as constant objects comparing to electrons. There are three other contributions to the energy for many electron atom as listed below[14]:

- kinetic energy of each electron
- mutual potential energy of nucleus and each electron
- mutual potential energy of each pair of electrons.

The potential energy of electron-electron interaction provides multi-variable terms to the Schrodinger equation, which hinders the separation of variables and, consequently, the solution to the differential equation. While electron-electron interaction cannot be ignored, model chemistries need to be applied.

Hartree-Fock Consistent Self Field (HF-SCF) theory introduces the average potential of electron-electron interaction to the Schrodinger equation. This approximation appears to be reasonable for different applications such as computing equilibrium molecular geometries and frequencies of stable molecules. But it dramatically fails for chemical processes like bond dissociation where electron effects predominate[15].

A more reliable approach to calculate molecular properties is using the most recent model chemistry of Density Functional Theory (DFT), introducing electron correlation to the electronic Schrodinger equation. DFT computes molecular electron probability density ρ instead of molecular wave function computed in *Ab initio* methods. This was following the Hohenberg-

Kohn theorem, which confirms that the electron density of a ground state determines uniquely the energy of that electronic state.

Further work by Kohn and Sham, in an attempt to find a practical method of calculating the electron density, led to the current DFT method, which introduces electronic energy as below[15]:

$$E = E^T + E^v + E^j + E^{xc}$$

where E^T is the kinetic energy of electrons, E^v includes terms describing the potential energy of the nuclear electron attraction and of the repulsion between pairs of nuclei, E^j is the electron-electron repulsion term, and E^{xc} is the exchange-correlation term and includes the remaining part of the electron-electron interactions.

The best known of the DFT is Beck's three parameter exchange functional and the Lee-Young-Parr correlation functional, which is available in Guassian 98 [3] via B3LYP keyword.

Basis Set

In order to solve the Schrodinger equation for many electron molecules, it is also required to make molecular orbitals based on the Linear Combination of Atomic Orbitals, that is LCAO approximation. In this method, different sets of pre-defined functions known as basis sets may be applied to represent each Atomic Orbital (AO). Slater-Type Orbitals (STO) and Gaussian-Type Orbitals (GTO) are the two commonly used basis orbitals. Although STO provides more accurate results, GTO is more favored due to the ease of the calculation process.

For instance, the minimal basis set, shorthanded by STO-3G, includes the least number of basis functions required for each atom, that is, one STO for each inner-shell and valence-shell AO of each atom[16]. The extended basis sets introduce more accuracy to the LCAO approximimation by increasing the number of basis functions per atom (split valence basis sets) and applying higher-level orbitals (polarized basis sets) to the approximation[15].

The 6-31G** basis set was primarily used in this research. It represents a fixed linear combination of six primitive Gaussians for non-valence atomic orbital, a fixed linear combination of three primitives for the inner part of valence AO, and an additional primitive for the outer part of AO. It also added a polarization factor for hydrogen and heavy atoms[17].

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Equilibrium Geometry

The equilibrium geometry is defined by the nuclear arrangement at which the molecular electronic energy, including internuclear repulsion, is minimized. This can be mathematically expressed as when the gradient (first derivative) of the energy with respect to the coordinates is zero, and the force constant (second derivative) is positive.

The potential energy diagram is a method for explaining the electronic energy of a molecule as a function of its coordinates. For the simplest molecule consisting of two atoms, the potential energy is only a function of one variable, which is the internuclear distance. In such case, there is only a single minimum geometry appearing in the potential energy curve.

When it comes to non-linear polyatomic molecules, there are 3N-6 normal modes of vibration where each has corresponding normal coordinates. Consequently the potential energy diagram is complicated with very many minima called local minima. The one with the lowest energy is named the global minimum, which corresponds to the best-minimized energy geometry (see Figure 2-1).

The aim for geometry optimization is, therefore, to find the global minimum if possible. Today, the calculation for geometry optimization is practical using computer software such as Gaussian. It is required to input the initial structure as Cartesian coordinates or internal coordinates (z-matrix) and to specify the model chemistry and the particular basis set for the calculation. The program computes the energy and its gradient until it finds a stationary point. After each calculation cycle with an unsuccessful result, the program will change the geometry based on the size of the gradient and repeat the calculation until it reaches convergence. Meanwhile the sign of the gradient indicates the direction of potential energy change and, when negative, it shows the direction toward a local potential energy minimum.

Transition State

Transition state refers to the molecular structure at the maximum of the potential energy connecting two minima of reactants and products. It is described mathematically as a first order saddle point, being maximum in one direction and minimum in the others. (See Figure 2-2)

Like other stationary points, the gradient for a saddle point is zero. However, the second derivative of the energy with respect to the coordinates has a negative value. The second derivatives are in fact the force constants, which are numbered to 3N-6 for non-linear polyatomic molecules with N atoms. The force constants can be found as eigenvalues of the Hessian matrix from which vibrational spectra may be calculated. Therefore, it can be concluded that transition state structure has one single imaginary (negative) vibrational frequency.

Due to the saddle point characteristic of transition state, it is not possible to locate a transition state with a simple minimization procedure and a further calculation of vibrational frequencies on the optimized geometry is required. The calculation must be carried out at the same level of theory to be valid. One single imaginary frequency indicates a transition state structure. However, it is necessary to animate the imaginary frequency to make sure that the motion does indeed connect reactants and products.

For saving computation time, it is often suggested to locate the specific transition state desired at the lower level of theory and then proceed to the desired level.
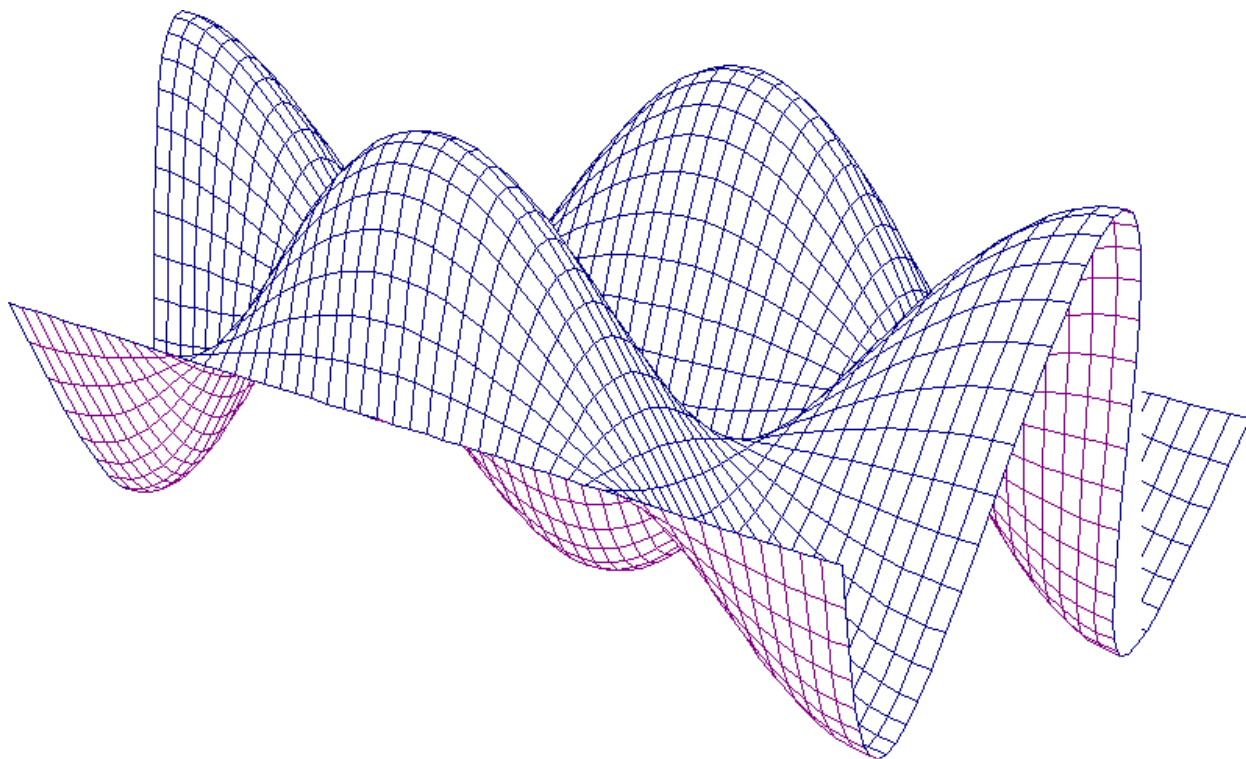
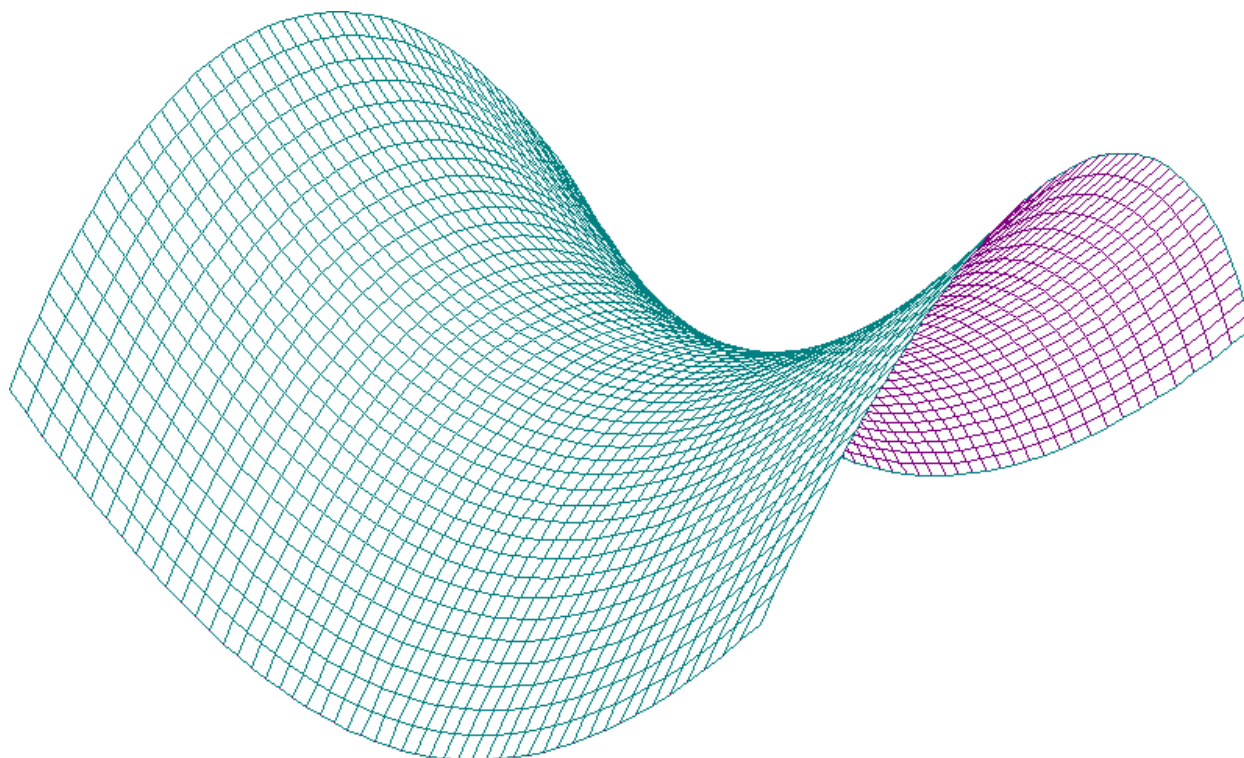Figure 2-1: Minima and Maxima in Potential Energy Surface

Figure 2-2: Saddle Point in Potential Energy Surface

CHAPTER 3

RESULTS AND DISCUSSION

Reaction Mechanism

A complete set of mechanisms must generate the observed stoichiometry of the reaction by algebraic elimination of the intermediates. For RAPRENOx reaction, there are many species involved in the reaction that can introduce various intermediate species. This leads to numerous possible elementary steps and reaction mechanisms. Because the study of all the possibilities were beyond the scope of this thesis, we confined our attention to the propagation step proposed by Perry. Assuming the same initiation steps for hydrogen production and the same intermediate species of H, OH, NH_2, and N_2H involved in the propagation steps, we studied additional possible elementary steps and reaction mechanisms.

Nevertheless, the investigation of all possible elementary steps, reaction channels, and reaction mechanisms could be a time demanding procedure. Chemist software provides a convenient environment to predict all the possibilities mathematically. Obviously, some of them may not be chemically plausible. Therefore, we performed reaction mechanism analysis by selecting those elementary steps that might be chemically possible. For a broader investigation, we repeated the analysis for several trials, each time considering some different selection of elementary steps. Reviewing the obtained results, there are various chain initiators introduced to the analyses. Yet, based on our first assumption, only those with a hydrogen chain initiator are suitable for our interests.
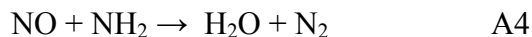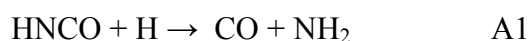
A sample procedure for reaction mechanism analysis using Chemist has been provided in appendix A.

Possible Propagation Schemes

Following several trials of reaction mechanism analysis, it is noticeable that there are

five schemes (besides Perry's mechanism) that may describe the propagation step for RAPRENOx reaction. One of the schemes (scheme A) includes four elementary steps while others include five steps for the propagation chain. Conforming to the principles of mass and charge conservation (Corio's rule), it is obviously necessary to append one extra initiation step for scheme A. The possible propagation schemes are presented as below:

Scheme A:

$$HNCO + H \rightarrow CO + NH_2 \qquad A1$$
$$NO + NH_2 \rightarrow N_2 + H + OH \qquad A2$$
$$HNCO + OH \rightarrow CO_2 + NH_2 \qquad A3$$
$$NO + NH_2 \rightarrow H_2O + N_2 \qquad A4$$

This scheme introduces a four-step propagation. As it shows, hydrogen radical is consumed and generated in steps A1 and A2 respectively. There are two different pathways that have been suggested for the reaction of NO and NH_2 as it shows in steps A2 and A4. Step A2 is of major importance in that one propagating intermediate is converted into two. This branching reaction increases the rate of reaction. At the same time step A4 competes with A2 to give two products, thus reducing the branching reaction.

It can be concluded that as long as step A2 dominates step A4, the reaction is self-sustaining through formation of H and OH radicals where each of them can react with Isocyanic acid as described in this scheme. Experimental data[18] for the reaction pathway of NO and NH_2 show inconsistency, even though the majority favor the existence of a radical channel.

Scheme B:

$$HNCO + H \rightarrow CO + NH_2 \qquad B1$$
$$NO + NH_2 \rightarrow N_2H + OH \qquad B2$$
$$N_2H \rightarrow N_2 + H \qquad B3$$

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$$HNCO + OH \rightarrow CO_2 + NH_2 \qquad B4$$

$$NO + NH_2 \rightarrow H_2O + N_2 \qquad B5$$
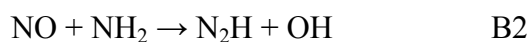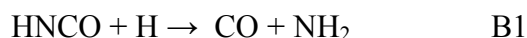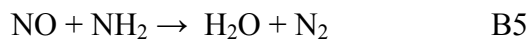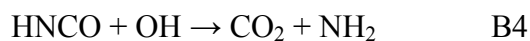
The above scheme is very similar to scheme A. It only suggests that step A2 can be considered as two independent steps of B2 and B3; hence introduces a five-step propagation scheme.

Scheme C:

$$HNCO + H \rightarrow CO + NH_2 \qquad C1$$

$$NO + NH_2 \rightarrow N_2H + OH \qquad C2$$

$$HNCO + OH \rightarrow CO_2 + NH_2 \qquad C3$$

$$NO + NH_2 \rightarrow N_2 + H + OH \qquad C4$$

$$OH + N_2H \rightarrow H_2O + N_2 \qquad C5$$
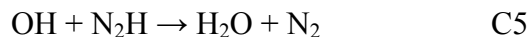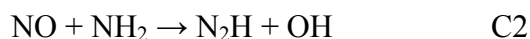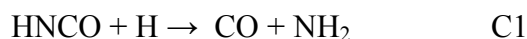
Scheme C, another five-step propagation mechanism, introduces the possibility of reaction between N_2H and OH (C5). Here the competition is between step C2 and C4. Considering the experimental data on a very short lifetime of N_2H [19], the difference between these two steps should be minor.

Scheme D:

$$HNCO + H \rightarrow CO + NH_2 \qquad D1$$

$$NO + NH_2 \rightarrow N_2H + OH \qquad D2$$

$$HNCO + N_2H \rightarrow N_2 + CO + NH_2 \qquad D3$$

$$NO + NH_2 \rightarrow H_2O + N_2 \qquad D4$$

$$OH + CO \rightarrow CO_2 + H \qquad D5$$
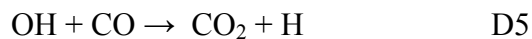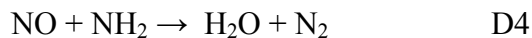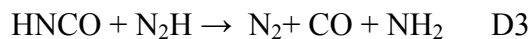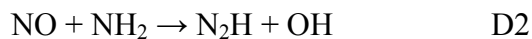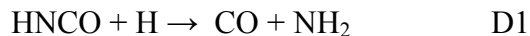
The above scheme shows the possibility of reaction between HNCO and N_2H (D3) to give three different species of N_2, CO, and NH_2 as products. It also introduces a new elementary

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step (D5) for hydrogen reproduction. As mentioned in chapter one, the effect of this step for chain-branching improvement has been experimentally displayed by Perry.

Scheme E:

$$HNCO + H \rightarrow CO + NH_2 \qquad \text{E1}$$
$$2\,NO + 2\,NH_2 \rightarrow 2\,N_2H + 2\,OH \qquad \text{E2}$$
$$2\,N_2H \rightarrow 2\,N_2 + 2\,H \qquad \text{E3}$$
$$HNCO + OH \rightarrow CO_2 + NH_2 \qquad \text{E4}$$
$$H + OH \rightarrow H_2O \qquad \text{E5}$$
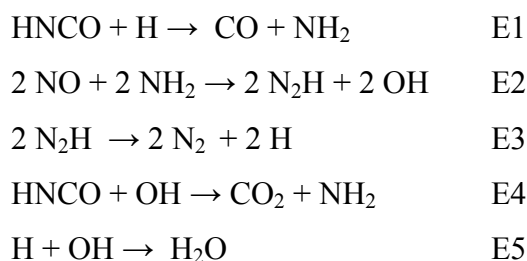
In this mechanism, only one pathway (E2) has been considered for the reaction of NO and NH_2 that leads to the production of two intermediates. Reproduction of hydrogen is through step E3. This is while the OH resulted from E2 leads to more chain branching through reaction with Isocyanic acid. The formation of water (E5) has been added to satisfy the stoichiometry of the overall reaction by linear combination of elementary steps.

Scheme F: (Perry's mechanism)

$$2\,HNCO + 2\,H \rightarrow 2\,CO + 2\,NH_2 \qquad \text{F1}$$
$$NO + NH_2 \rightarrow N_2H + OH \qquad \text{F2}$$
$$NO + NH_2 \rightarrow H_2O + N_2 \qquad \text{F3}$$
$$N_2H \rightarrow N_2 + H \qquad \text{F4}$$
$$OH + CO \rightarrow CO_2 + H \qquad \text{F5}$$
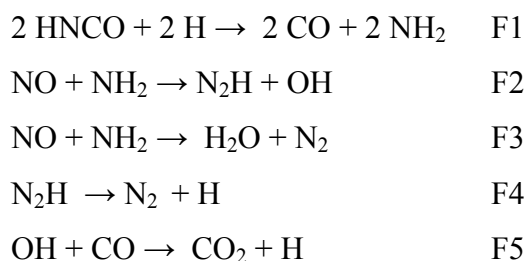
We also noticed that the propagation chain proposed by Perry needs a modification to satisfy the stoichiometry of the reaction. This has been done by multiplication of step F1 by 2. The complete set of possible schemes has been displayed as above.

<u>Proposed Elementary Steps</u>

So far we have considered six schemes (including Perry's mechanism) as possible reaction mechanisms for RAPRENOx reaction. The total number of 10 elementary steps involved in all described schemes are presented as below:

1. $HNCO + H \rightarrow CO + NH_2$ (TS1 & TS2 in Schemes 3-1 & 3-2)
2. $HNCO + OH \rightarrow CO_2 + NH_2$ (TS3 in Scheme 3-3)
3. $HNCO + N_2H \rightarrow N_2 + CO + NH_2$ -
4. $NO + NH_2 \rightarrow N_2 + H + OH$ -
5. $NO + NH_2 \rightarrow H_2O + N_2$ (TS4 in Scheme3-4)
6. $NO + NH_2 \rightarrow N_2H + OH$ (TS5 & TS6 in Scheme 3-5)
7. $N_2H \rightarrow N_2 + H$ (TS7 in Scheme 3-6)
8. $OH + N2H \rightarrow H_2O + N_2$ (TS8 in Scheme 3-7)
9. $OH + CO \rightarrow CO_2 + H$ (TS9 in Scheme 3-8)
10. $H + OH \rightarrow H_2O$ (TS10 in Scheme 3-9)

The profound understanding of the actual reaction mechanism requires the study of potential energy surface for each individual step. Therefore, the next step is to calculate the electronic energy of all species involved in the above-mentioned steps and to make a comparison of energy barriers for each elementary step.

<u>Computational Details for *Ab initio* Calculation</u>

All the calculations were carried out using Gaussian 98 program software in an IBM 6000 workstation. In order to perform *Ab initio* calculation, it is required to specify the geometry of molecule in an input file. As earlier described, this would be possible by guessing the Cartesian structure or internal coordinates (Z-matrix) of the molecule.

In this research, we used PC-Spartan[20] to obtain the Cartesian structure on a Gateway 2000 PC. Spartan provides an easy way of constructing the desired molecules using the standard

bond lengths and bond angles. It is also possible to adjust dihedral angles to build a specific conformation.

Having made each structure and performed simple geometry optimization, AM1, we obtained the Cartesian structures for all species involved in the listed elementary steps. The resulting molecular geometries for reactants, intermediates, and products were then applied to an input file for further optimization at Density Functional Theory B3LYP/6-31G** using Gaussian 98. We also carried out vibrational frequency calculations for the optimized geometries at the same level of theory in order to identify the local minima. All vibrational frequencies for a true minimum must be real. The optimized geometries of all minima are presented in Figure 3-1 (reactants & products) and Figure 3-2 (intermediates).

In the meantime, we also needed to determine the electronic energies of transition states for all the elementary steps. Doing so, we guessed a transition state structure - which should have structured approximately between reactants and products' geometries- and obtained the related Cartesian structure using Spatran. We further carried out geometry optimization for transition state structure while using addredundant option to Opt keyword (normal optimization). Addredundant option allows one to predict values for the bond lengths and bond angles of interest and to make sure that these predicted values are included in the optimization output[15]. This option will help find the closest structure to the desired transition state. However a further geometry optimization, with option keywords "ts" and "nofreeze" (to remove all redundant values) is required to be made on the produced geometry to find out the true transition state.

All transition state calculations were carried out using the same method with B3LYP/6-31G** basis set. The first order saddle point characteristic of transition state requires one single imaginary vibrational frequency. For each elementary step, the nature of the imaginary frequency has been checked using GaussView (a visualization package for Gaussian) to make sure that the transition state structure would certainly connect the reactants and the products. The optimized geometries of Transition States are presented in Figure 3-3.

Sample input and output files for geometry optimization, including vibrational frequency calculations and for transition state calculations, have been displayed in Appendix B.

HNCO

172.15
1.17
1.22
124.71
1.01

CO

1.11

NH₂

1.03
101.83

OH

0.96

CO₂

180
1.14

N₂H

1.18
117.08
1.06

H₂O

0.97
103.75

N₂

1.08

NO

1.13
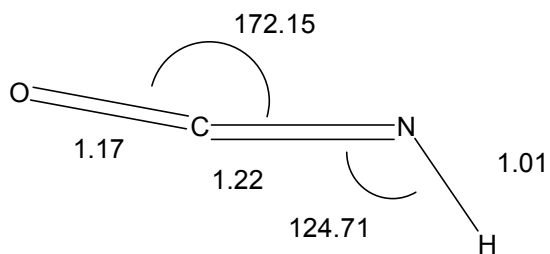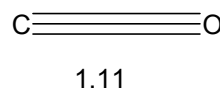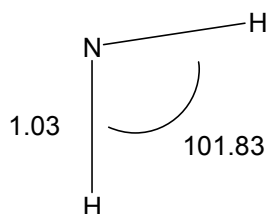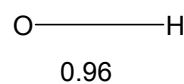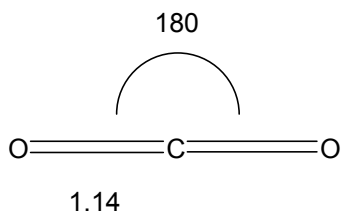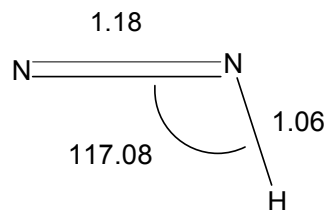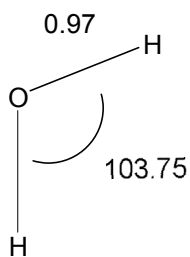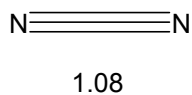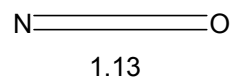
Figure 3-1. The Geometry of Equilibrium Structures

Bond lengths in Å and bond angles in degree
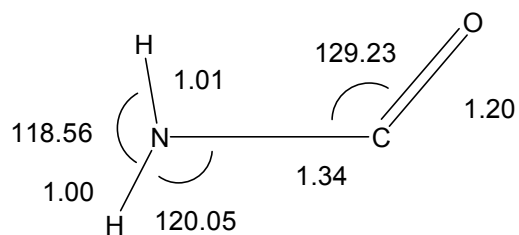
H₂NCO – INT1
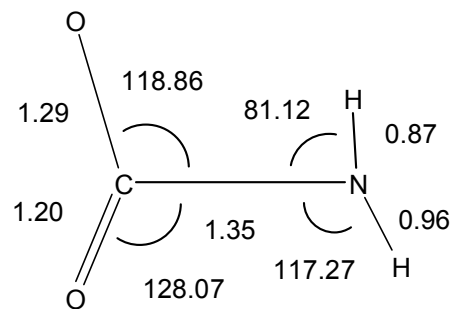
H₂NCO₂ – INT2
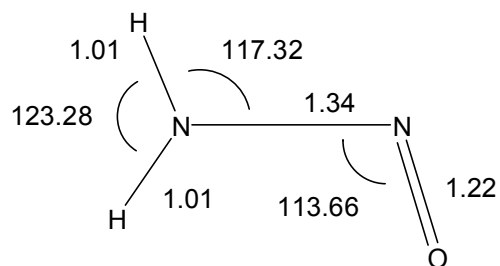
H₂N₂O – INT3
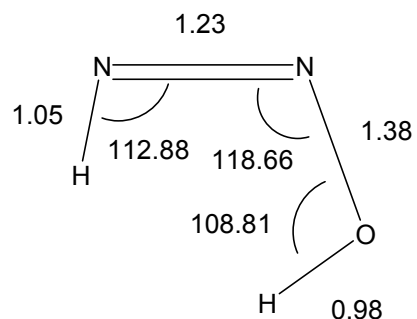
cis-cis HN₂OH – INT4
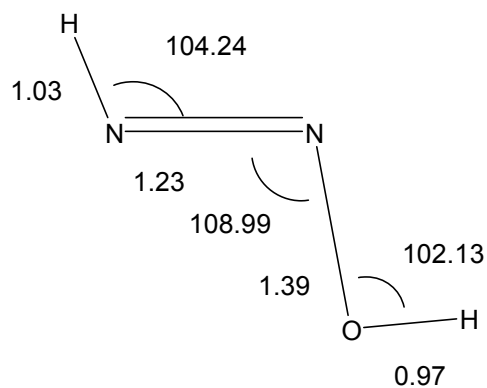
trans-trans HN₂OH – INT5
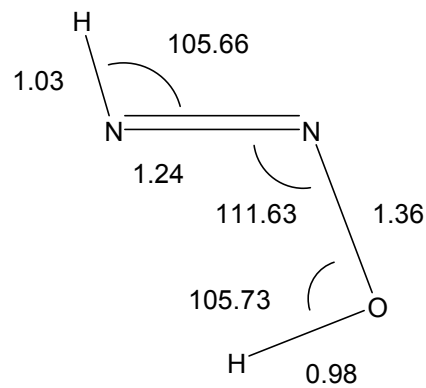
trans-cis HN₂OH – INT6

Figure 3-2. The Geometry of Intermediate Structures

Bond lengths in Å and bond angles in degree

28
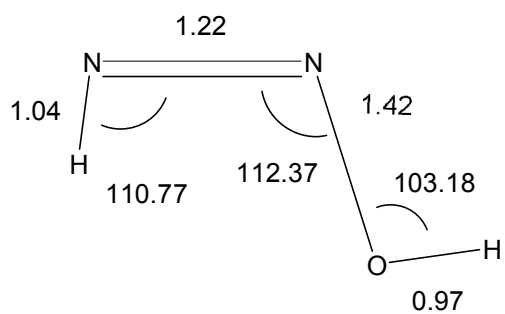
cis-trans HN₂OH – INT7
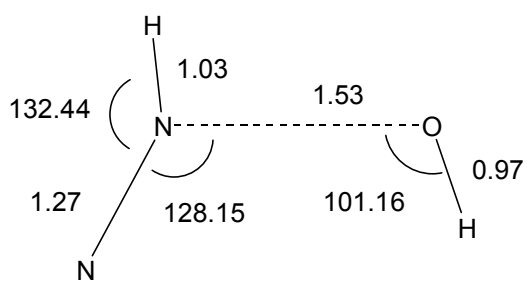
N₂HOH – INT8
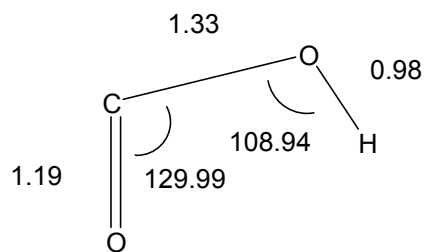
OCOH – INT9

Figure 3-2 (Cont'd). The Geometry of Intermediate Structures

Bond lengths in Å and bond angles in degree

H₂NCO – TS1

H₂NCO – TS2

H₂NCO₂–TS3

H₂N₂O – TS4

H₂N₂O – TS5
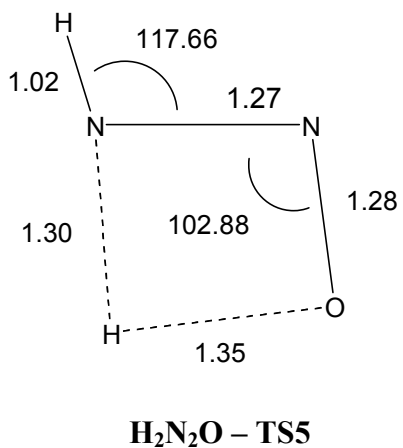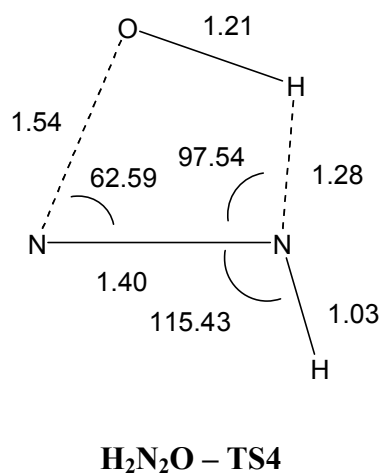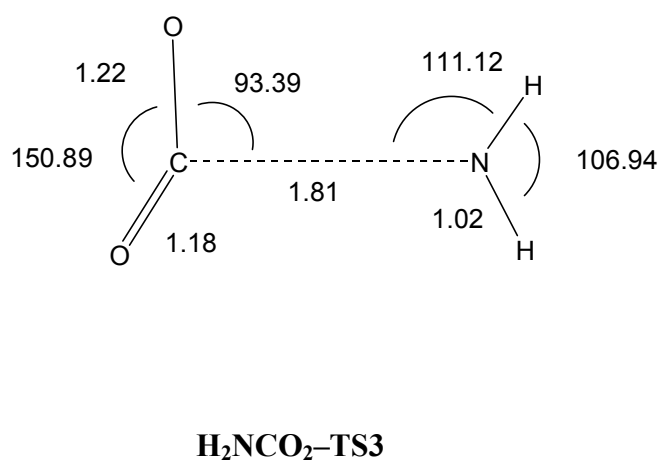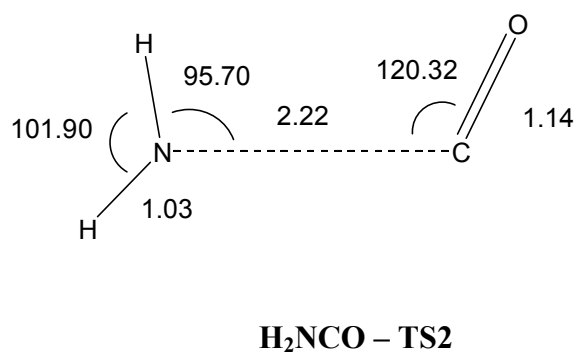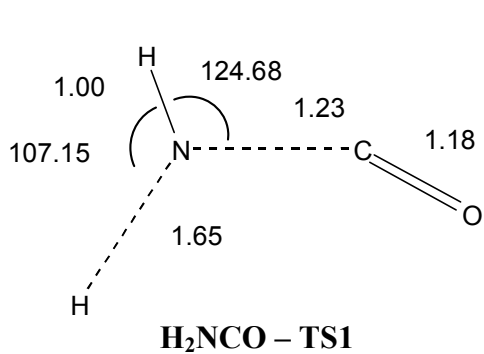
Figure 3-3. The Geometry of Transition State Structures

Bond lengths in Å and bond angles in degree

30

H₂N₂O – TS6

1.17
N══N
94.34
1.17
1.84
112.46
60.54
H
1.50
O
0.97

N₂H – TS7

1.12
N══N
118.93
1.55
H

N₂HOH – TS8

H
1.01
1.59
167.76
89.08
N
1.87
O
0.84
N
1.13
115.86
H

HOCO – TS9

1.26
C
O
1.26
116.89
1.35
O
H
1.35

H₂O – TS10

179.94
H
O
H
0.93
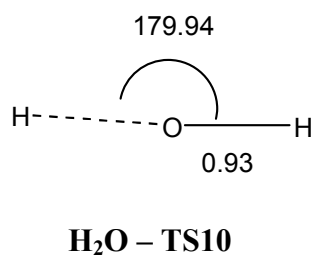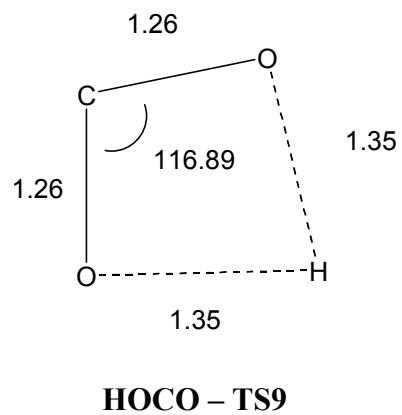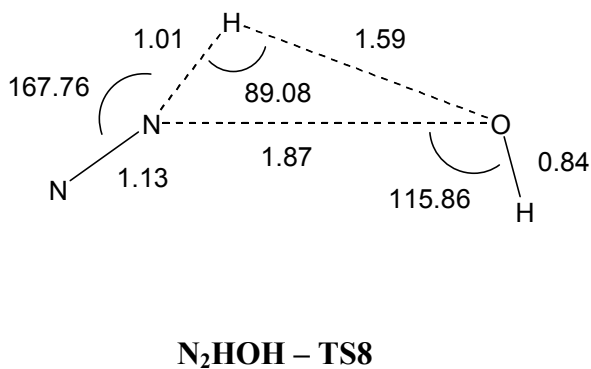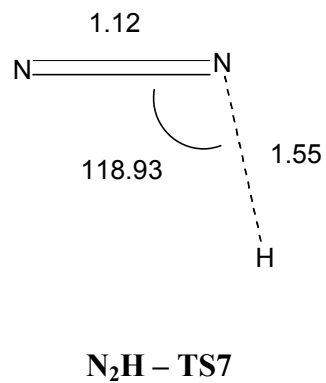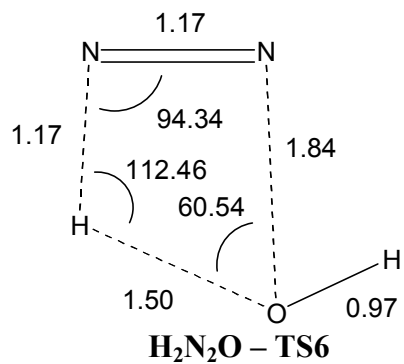
Figure 3-3 (Cont'd). The Geometry of Transition State Structures
Bond lengths in Å and bond angles in degree

Potential Energy Diagrams

Electronic energies computed for all reactants, products, intermediates, and transition states have been provided in Table 3-1. Zero point vibrational energies were taken into account for calculating the relative energies of the species. The potential energy diagrams for possible reaction schemes (scheme 3-1 to 3-9) were made respectively.

Table 3-1: Electronic Energies of Reactants, Products, Intermediates and Transition State Structures
All energies are given in Hartree

Structure	Electronic Energy (EE)	Zero Point Energy (ZPE)	EE + ZPE
H	-0.500272784	0.000000	-0.500272784
HNCO	-168.681499342	0.021318	-168.660181342
CO	-113.309454336	0.005032	-113.304422336
NH_2	-55.878980501	0.018967	-55.860013501
OH	-75.728482297	0.008421	-75.720061297
CO_2	-188.580940224	0.011593	-188.569347224
N_2H	-110.032726159	0.013248	-110.019478159
H_2O	-76.419736621	0.021370	-76.398366621
N_2	-109.524129072	0.005599	-109.518530072
NO	-129.888156193	0.004537	-129.883619193
INT1	-169.238908112	0.032939	-169.205969112
INT2	-244.423905039	0.036876	-244.387029039
INT3	-185.850169440	0.032236	-185.817933440
INT4	-185.836590247	0.032297	-185.804293247
INT5	-185.844311255	0.033534	-185.810777255
INT6	-185.847449553	0.033523	-185.813926553
INT7	-185.846535242	0.032865	-185.813670242
INT8	-185.816082673	0.032023	-185.784059673
INT9	-189.093405752	0.020650	-189.072755752
TS1	-169.176438450	0.023086	-169.153352450
TS2	-169.190864933	0.027473	-169.163391933
TS3	-244.445896543	0.034714	-244.411182543
TS4	-185.630946598	0.025624	-185.605322598
TS5	-185.797592275	0.028289	-185.769303275
TS6	-185.800693810	0.026163	-185.774530810
TS7	-110.013307113	0.006594	-110.006713113
TS8	-185.790545469	0.027130	-185.763415469
TS9	-189.018707023	0.015556	-189.003151023
TS10	-76.366850867	0.019729	-76.347121867

Energy Calculation for the Reaction of HNCO and H

According to our calculation at B3LYP/6-31G** level, there are two possible pathways for the reaction of hydrogen radical with Isocyanic acid that lead to the production of NH_2 and CO. The relevant energies of the species involved have been provided in schemes 3-1 and 3-2.

In scheme 3-1, the reaction goes through a second-order transition state TS1. While hydrogen radical is attacking the nitrogen, the N-C bond breaks. The energy barrier for this thermoneutral reaction (ΔE= -2.5 Kcal/mol) is predicted to be 4.45 Kcal/mol.

Scheme 3-2 displays the absence of any barrier energy for the association of HNCO and H to form a stable intermediate INT1. The bond energy produced due to the formation of INT1 further makes adequate energy to overcome the energy barrier of 26.72 Kcal/mol for N-C bond cleavage. The dissociation of INT1 goes through transition state TS2 that lies 1.84 Kcal/mol below the reactants.

As there is no high-energy barrier involved in the above two schemes, we predicted that both pathways are likely to happen.

Energy Calculation for the Reaction of HNCO and OH

The relative energy calculation, scheme 3-3, shows that the reaction of OH radical with Isocyanic acid is exothermic by –30.82 Kcal/mol. We were able to locate one intermediate INT2 and one transition state TS3 on the potential energy surface of this reaction. INT2 shows a structure resulted from the simultaneous attachment of oxygen atom of OH radical to C atom of HNCO. We expected that the formation of INT2 would go through a cyclic transition state but our extensive calculations failed to locate the designated transition state.

In the meantime, based on the first order saddle point characteristic of transition state, we also predicted that TS3 was a preceding species of a more stable intermediate structure. However, our careful search was not successful in finding the expected intermediate.

Energy Calculation for the Reaction of HNCO and N_2H

Our investigation to locate any transition state or intermediate species for a SN2 reaction of HNCO and N_2H was not successful. Because the two molecules are relatively large, it is

expected that the reaction is collision sensitive. Meanwhile, based on the experimental data[19], as well as theoretical calculation done in this research, N_2H is a very unstable species. Hence, it is more likely that it dissociates to N_2 and H before colliding with HNCO or reacts with much smaller molecules such as OH.

Energy Calculation for the Reaction of NH_2 and NO

The reaction of NH_2 and NO is of major importance in RAPRENOx process. In agreement with numerous experimental investigations[18], our study of reaction mechanism analysis indicated three different pathways for this bimolecular reaction as indicated below:

$$NO + NH_2 \rightarrow N_2H + OH \qquad (1)$$
$$NO + NH_2 \rightarrow H_2O + N_2 \qquad (2)$$
$$NO + NH_2 \rightarrow N_2 + H + OH \qquad (3)$$
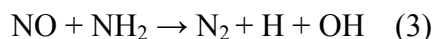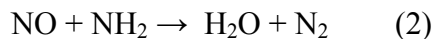
The total electronic energies of the reactants and products for each pathway calculated at B3LYP/6-31G** shows that reactions number (1) and (3) are thermoneutral ($\Delta E_1 = +2.57$ Kcal/mol and $\Delta E_2 = +2.99$ kcal/mol) while reaction number (2) is exothermic by -108.723 Kcal/mol.

The potential energy diagrams for reactions (1) and (2) have been displayed in schemes 3-4 and 3-5. Scheme 3-4 shows the reaction of NH_2 and NO radicals to give N_2H and OH as products. This reaction goes through a four-member ring transition state TS4. The relative energy calculation, while ZPE has been taken into account, indicates a rather high-energy barrier of 86.79 Kcal/mol.

On the other hand, scheme 3-5 shows the association of NH_2 and NO without any energy barrier to produce a stable intermediate INT3. The bond energy is predicted to be -46.63 Kcal/mol. The resulted intermediate can further undergo 1,3 H migration going through a four-member ring transition state TS5 to give different conformers of hydroxydiimide intermediate.

The possibility for production of four isomers of cis-cis (INT4), trans-trans (INT5), trans-cis (INT5), and cis-trans (INT7) - discussed in reference No.21- have been considered in this research. Based on the results obtained from energy comparison, trans-cis hydroxydiimide is the most stable conformer. cis-trans is the next stable one with a negligible energy difference of 0.16 Kcal/mol with respect to trans-cis. This is not completely in agreement with the results provided by Abou Rashid[21] which shows cis-trans as the most favorable conformer.

However, after transition state calculation, we noticed that cis-trans isomer is the conformer which can go through a cyclic transition state TS6 and ultimately produce H_2O and N_2. The possibility for the formation of N_2H and OH from cis-trans isomer has also been considered. Nevertheless, we failed to find the designated transition state.

Meanwhile, we did numerous calculations on transition state structures of tran-cis, trans-trans, and cis-cis isomers to predict a direct pathway to give one of the product sets of N_2H + OH, $H_2O + N_2$ or $N_2 + H + OH$. The attempts were not satisfactory. The only possibility that could be considered is through the conversion of above-mentioned isomers into cis-trans isomer, which eventually leads to H_2O and N_2.

Based on our calculation, it seems unlikely that reaction (3) takes place in one single step. To explain reaction (3), it is more reasonable to consider the dissociation of N_2H following its production via reaction (1). Another alternative could be the breakup of the H_2O molecule after passing through the activated complex for the elimination of water in reaction (2). This is only possible under conditions in which the H_2O molecule contains excess energy[22].

Energy Calculation for the Dissociation of N_2H

The potential energy diagram for the dissociation of N_2H is shown in scheme 3-6. Based on the results of our calculation at B3LYP/6-31G** level, ΔE and the energy barrier for this reaction are predicted as 0.42 Kcal/mol and 8.01 Kcal/mol, respectively. The low energy barrier indicates that N_2H species has a short lifetime and consequently bears minor importance as an intermediate in RAPRENOx process.

Energy Calculation for the Reaction of OH and N_2H

        Potential energy scheme 3-7 shows that the reaction of OH and N_2H is exothermic by –111.29 Kcal/mol. It is likely that the reaction between these radicals goes to a rather stable intermediate INT8 without any activation energy. The reaction will further go through a three-member ring transition state TS8 which leads to H migration from nitrogen atom to oxygen. TS8 lies 14.98 Kcal/mol below the reactants. The energy barrier for INT8 $\rightarrow$ TS8 is calculated to be 12.96 Kcal/mol, which can be provided by the bond energy of –27.94 Kcal/mol resulting from the formation of INT8.

Energy Calculation for the Reaction of OH and CO

        Relative energies of the species involved in this step are presented in scheme 3-8. It is predicted that the reaction of OH and CO goes to a very stable intermediate INT9 in the absence of any activation energy. The bond energy for INT9 formation is calculated to be –30.29 Kcal/mol. The INT9 further rearrange to a cyclic transition state structure TS9 with a high-energy barrier of 43.67 Kcal/mol. TS9 lies 13.38 Kcal/mol above the reactant level.

Energy Calculation for the Reaction of OH and H

        The potential energy diagram for the formation of water is shown in scheme 3-9. According to the results of our calculation at B3LYP/6-31G** level, the reaction is exothermic by –111.72 Kcal/mol. It also seems that the reaction goes through a transition state ST10 which lies 79.56 Kcal/mol below the reactants.
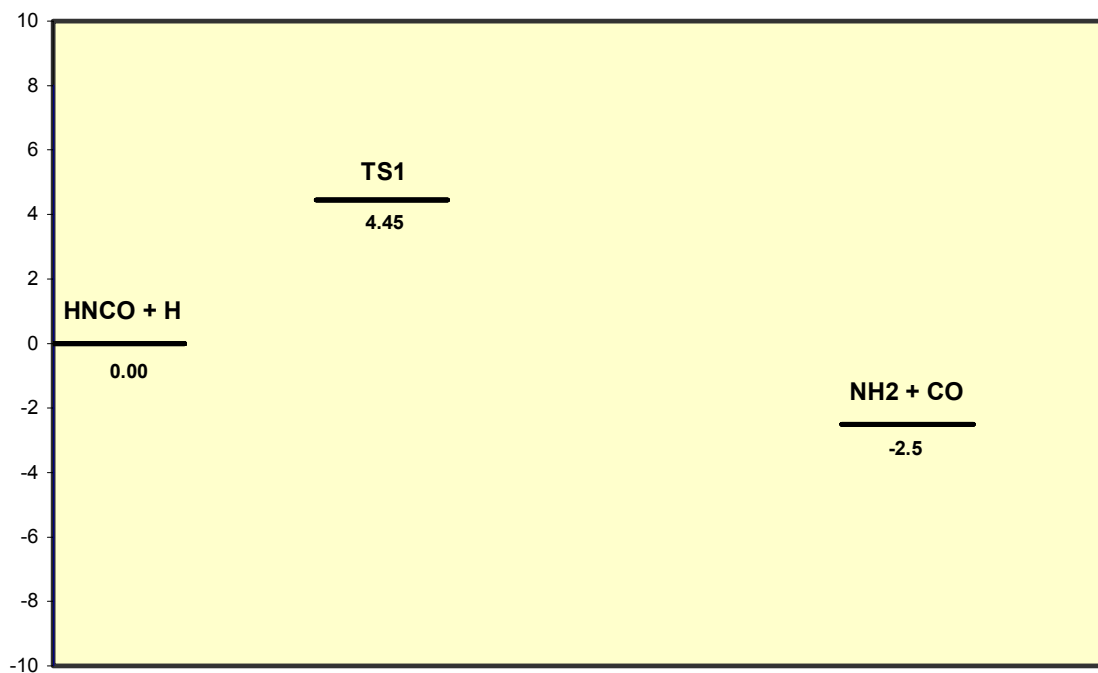
Scheme 3-1 Relevant Energies given in Kcal/mol for the Reaction of HNCO & H
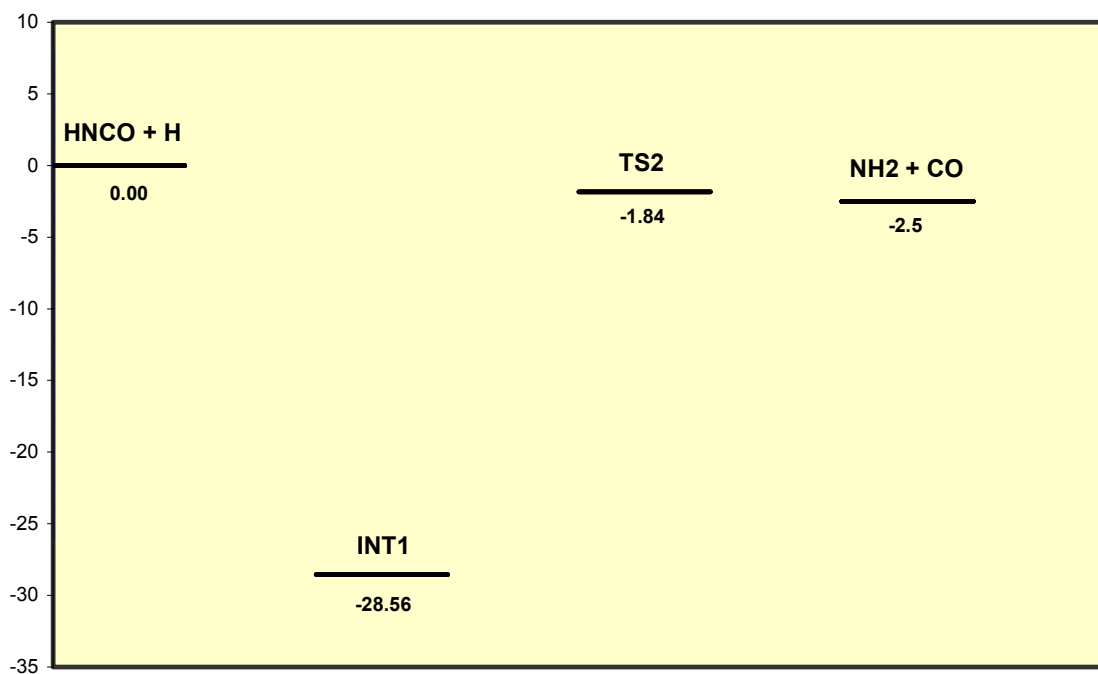
Scheme 3-2 Relevant Energies given in Kcal/mol for the Reaction of HNCO & H
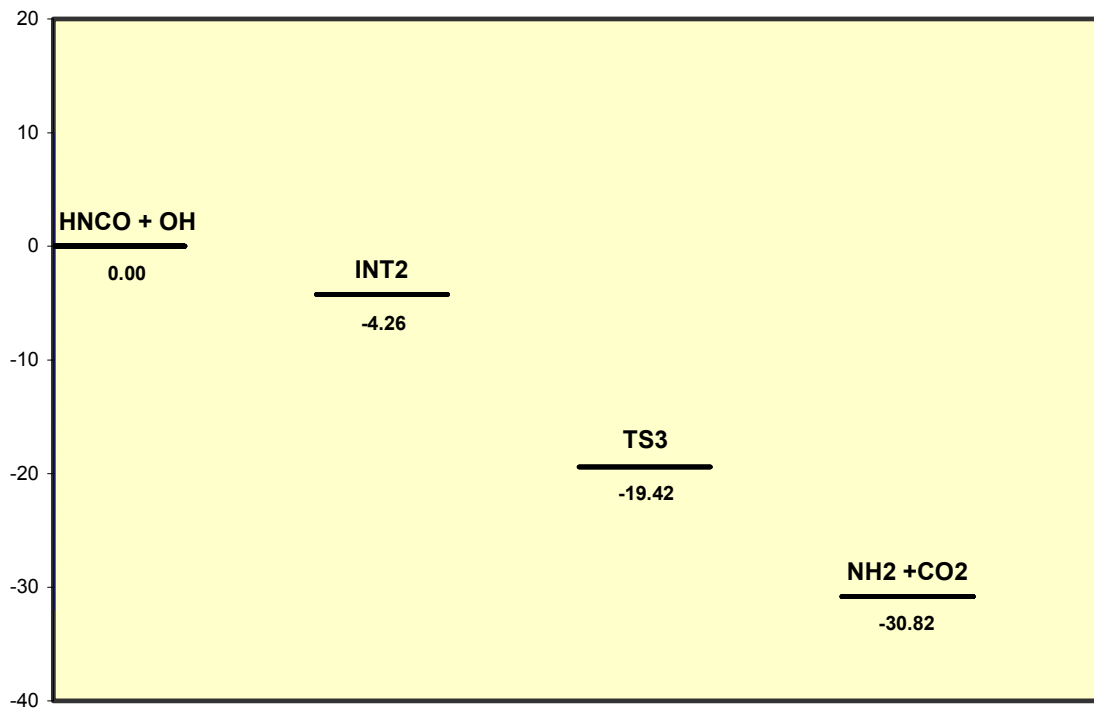
Scheme 3-3 Relevant Energies given in Kcal/mol for the Reaction of HNCO & OH
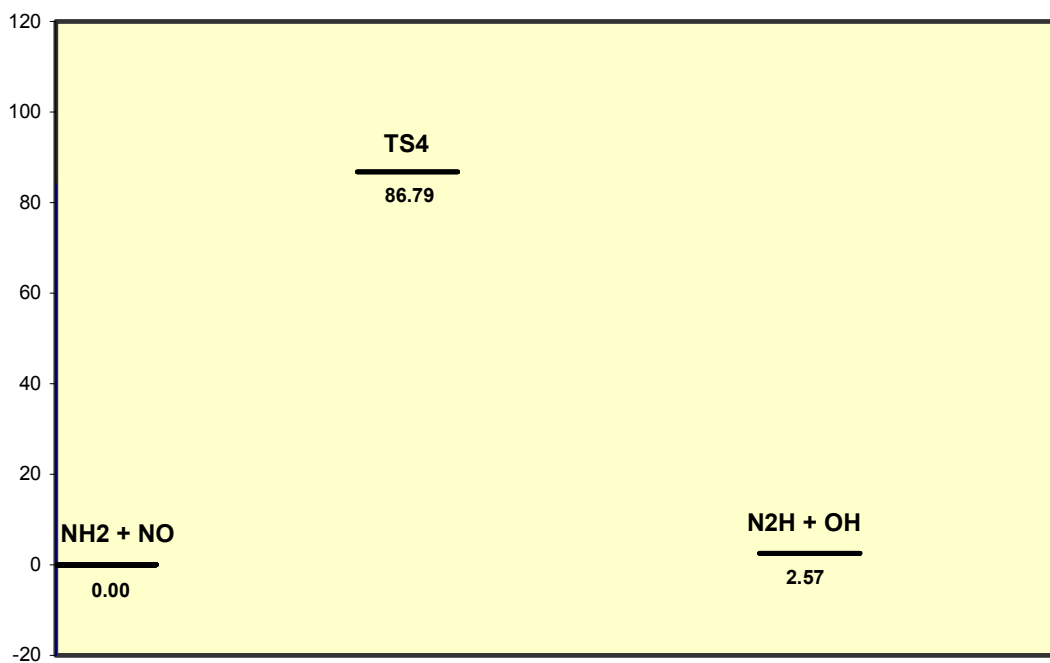
Scheme 3-4 Relevant Energies given in Kcal/mol for the Reaction of NH2 & NO
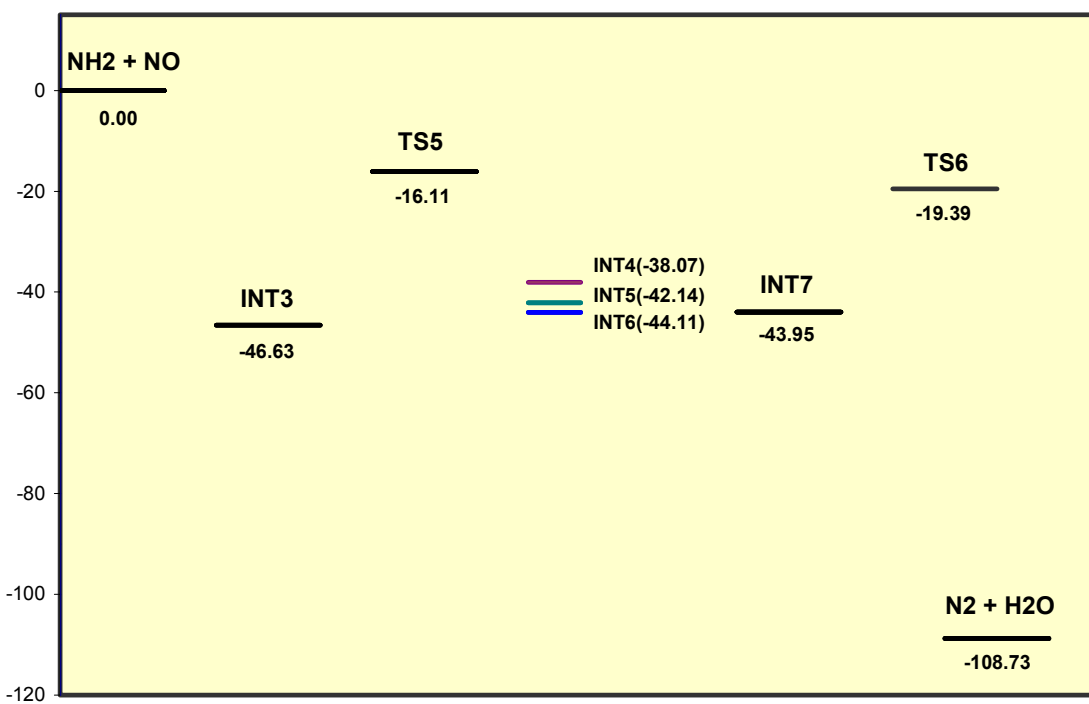
Scheme 3-5 Relevant Energies given in Kcal/mol for the Reaction of NH2 & NO

39
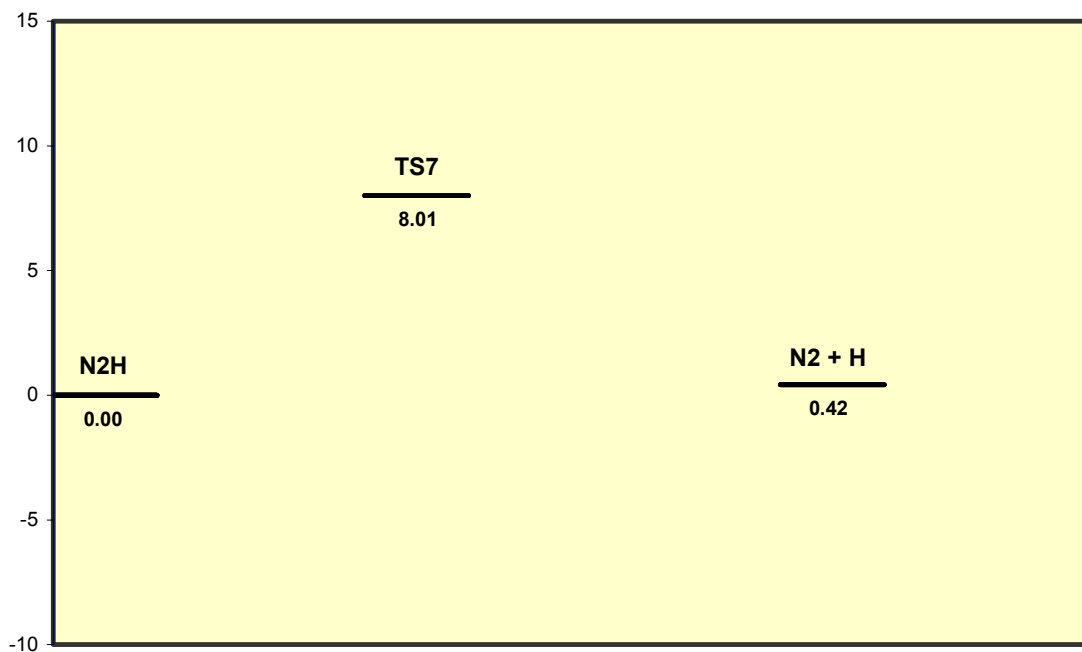
Scheme 3-6 Relevant Energies given in Kcal/mol for the Dissociation of N2H
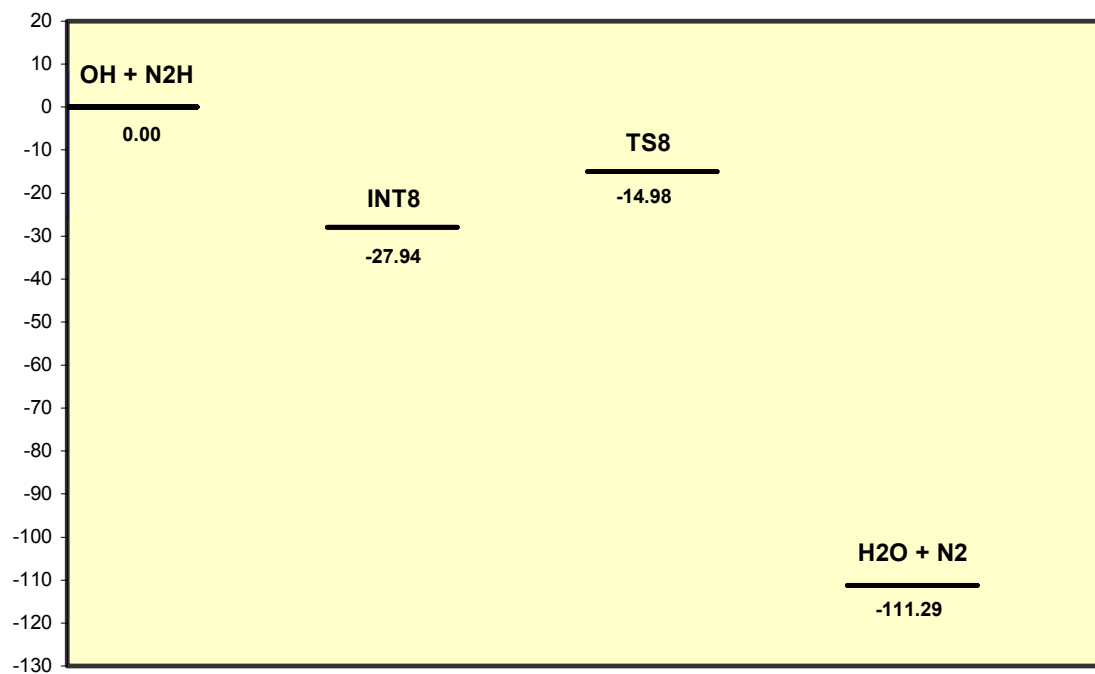
Scheme 3-7 Relevant Energies given in Kcal/mol for the Reaction of N2H & OH
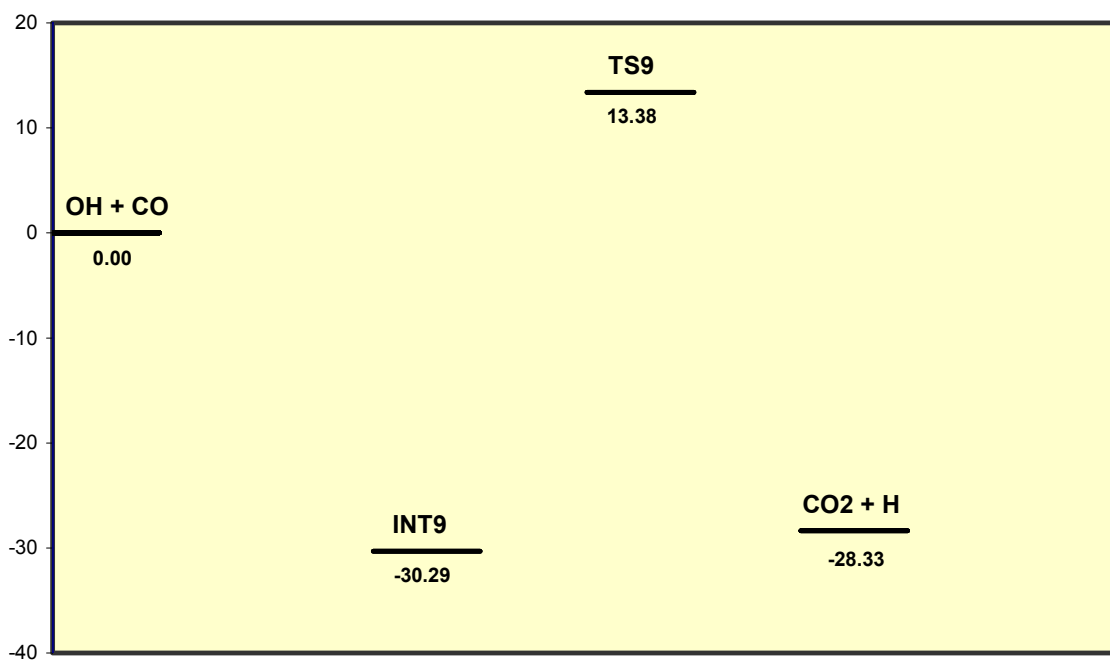
Scheme 3-8 Relevant Energies given in Kcal/mol for the Reaction of OH & CO
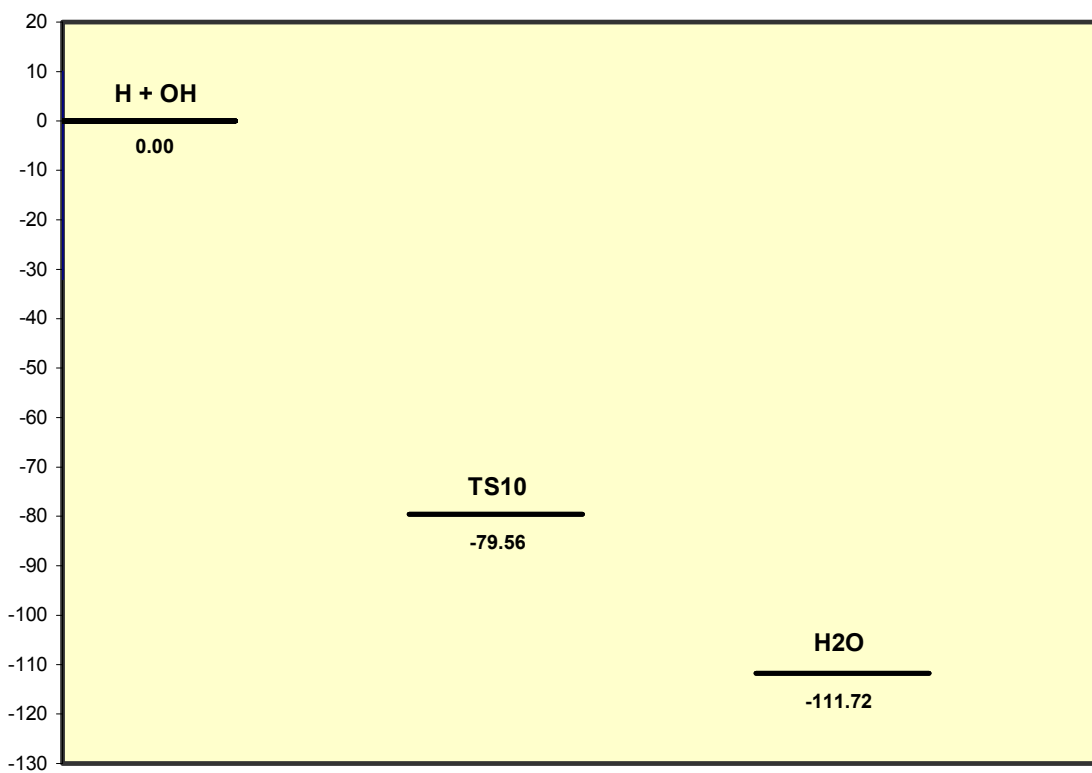
Scheme 3-9 Relevant Energies given in Kcal/mol for the Reaction of OH & H

<p align="center">Concluding Remarks</p>

Energy calculations based on Density Functional Theory and the study of potential energy diagrams for the proposed elementary steps (page 25) indicated that all elementary steps except No.3 and No.4 could be possible. The unsatisfactory results on locating any transition state for these two steps led us to conclude that they may be unlikely to happen in one single step and therefore none can be considered as an independent step in the reaction mechanism. As a consequence the proposed reaction schemes of A, C, and D, which include one of these steps, must be disregarded at the present time. Further experimental study could be useful for more certain clarification.

Moreover, the energy barrier comparisons made for the possible schemes of B, E, and F indicated that the highest activation energy for all three mechanisms is related to a single elementary step provided below. Therefore, it is reasonable to conclude that each of the schemes could be the actual reaction mechanism for RAPRENOx process, while it is also probable that all the schemes happen at the same time.

$NO + NH_2 \rightarrow N_2H + OH$ Energy barrier : 86.79 Kcal/mol

In the meantime, it is noticeable that the energy barrier for this rate-determining reaction step is rather high. We expect it to happen in combustion processes at high temperature. Nevertheless, because there is another pathway for the reaction of NH_2 and NO with lower energy level ($NO + NH_2 \rightarrow H_2O + N_2$), more efforts are needed to understand the branching ratio between these two pathways.

Further attempts to find direct reaction pathways through other conformers of hydroxydiimide (Cis-Cis, Trans-Trans, Trans-Cis) could be helpful in finding a lower energy pathway for $NO + NH_2 \rightarrow N_2H + OH$.

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    Yu, J; Baker,J.; Carpernter, J.; Dixon, R.; Fielder, S.; Johnson, H.; Kahn, S.;
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APPENDIX A

Sample Procedure for Reaction Mechanism Analysis Using Chemist

After initiating Chemist, we selected "Enter unbalanced equation" from the menu and input the unbalanced equation of $HNCO + NO \rightarrow CO_2 + H_2O + N_2 + CO$ from the keyboard. Processing the unbalanced reaction, Chemist provided us with the balanced equation and reaction channels as below:

unbalanced equation:

   HNCO+NO->CO2+H2O+N2+CO

balanced equation:

   2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press ENTER . . .

reaction channel(s):

   4HNCO + 6NO -> 4CO2 + 2H2O + 5N2
   4HNCO + 2NO -> 2H2O + 3N2 + 4CO

Press ENTER . . .

Having selected "Enter intermediates" from the menu , we suggested H, OH, NH_2 and N_2H as the intermediates to be analyzed in the reaction mechanism. All mathematically possible elementary steps were produced and a complete list was displayed as below:

Elementary steps: (HNCO+NO->CO2+H2O+N2+CO)

    N2H + CO2 -> HNCO + NO
    HNCO + NO -> CO2 + N2H
    H + N2 -> N2H
    HNCO + H -> CO + NH2
    OH + NH2 -> NO + 3H
    OH + N2H -> NO + NH2
    HNCO + OH -> CO2 + NH2
    HNCO + OH -> NO + CO + 2H
    NH2 + CO2 -> HNCO + OH
    NO + NH2 -> H2O + N2
    NH2 + H2O -> NO + 4H
    2NH2 -> N2 + 4H
    NH2 + CO -> HNCO + H
    2NH2 -> 3H + N2H
    NO + NH2 -> OH + N2H
    N2H -> N2 + H
    HNCO + NO -> CO2 + N2 + H
    HNCO + CO2 -> NO + 2CO + H
    H2O + N2 -> NO + NH2
    HNCO + H2O -> NO + CO + 3H

Press any key to continue . . .

    H2O -> H + OH
    2HNCO -> N2 + 2CO + 2H
    HNCO + NO -> N2 + CO + OH
    2HNCO -> 2CO + H + N2H
    H + OH -> H2O
    H + CO2 -> CO + OH
    OH + N2H -> H2O + N2
    OH + CO -> CO2 + H
    H2O + CO -> CO2 + 2H
    CO2 + H2O -> CO + 2OH
    HNCO + H2O -> CO2 + H + NH2
    HNCO + H2O -> CO + OH + NH2
    NH2 + CO2 -> NO + CO + 2H
    N2H + CO2 -> N2 + CO + OH
    N2H + H2O -> NO + H + NH2
    HNCO + NH2 -> CO + 2H + N2H
    H2O + N2 -> OH + N2H
    HNCO + NH2 -> N2 + CO + 3H
    HNCO + N2H -> N2 + CO + NH2
    NO + NH2 -> N2 + H + OH

Press any key to continue . . .

    N2H + H2O -> N2 + 2H + OH

Press ENTER . . .

46

Once the elementary steps were produced, we carried out "Reaction mechanism analysis" by highlighting those elementary steps that might be chemically possible. The highlighted elementary steps and the respective results for one of our trials are presented below.

```
  N2H + CO2 ->  HNCO + NO
  HNCO + NO ->  CO2 + N2H
  H + N2 ->  N2H
* HNCO + H ->  CO + NH2
* OH + NH2 ->  NO + 3H
* OH + N2H ->  NO + NH2
* HNCO + OH ->  CO2 + NH2
* HNCO + OH ->  NO + CO + 2H
  NH2 + CO2 ->  HNCO + OH
* NO + NH2 ->  H2O + N2
* NH2 + H2O ->  NO + 4H
* 2NH2 ->  N2 + 4H
  NH2 + CO ->  HNCO + H
* 2NH2 ->  3H + N2H
  NO + NH2 ->  OH + N2H
* N2H ->  N2 + H
* HNCO + NO ->  CO2 + N2 + H
* HNCO + CO2 ->  NO + 2CO + H
* H2O + N2 ->  NO + NH2
  HNCO + H2O ->  NO + CO + 3H
* H2O ->  H + OH
* 2HNCO ->  N2 + 2CO + 2H
* HNCO + NO ->  N2 + CO + OH
* 2HNCO ->  2CO + H + N2H
* H + OH ->  H2O
* H + CO2 ->  CO + OH
* OH + N2H ->  H2O + N2
* OH + CO ->  CO2 + H
* H2O + CO ->  CO2 + 2H
* CO2 + H2O ->  CO + 2OH
* H2O + CO ->  CO2 + 2H
* CO2 + H2O ->  CO + 2OH
* HNCO + H2O ->  CO2 + H + NH2
* HNCO + H2O ->  CO + OH + NH2
  NH2 + CO2 ->  NO + CO + 2H
* N2H + CO2 ->  N2 + CO + OH
  N2H + H2O ->  NO + H + NH2
* HNCO + NH2 ->  CO + 2H + N2H
* H2O + N2 ->  OH + N2H
* HNCO + NH2 ->  N2 + CO + 3H
* HNCO + N2H ->  N2 + CO + NH2
* NO + NH2 ->  N2 + H + OH
  N2H + H2O ->  N2 + 2H + OH
```

Maximum number of elementary steps: 6

2
. . . . 3
. . . . 4

                    analysis #: 1

CHAIN
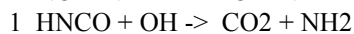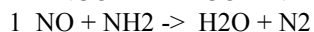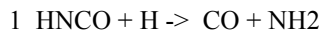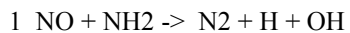
   1 NO + NH2 -> N2 + H + OH
   1 HNCO + H -> CO + NH2
   1 NO + NH2 -> H2O + N2
   1 HNCO + OH -> CO2 + NH2

  2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

                    analysis #: 2

CHAIN

   1 NO + NH2 -> H2O + N2
   1 NO + NH2 -> N2 + H + OH
   1 HNCO + H -> CO + NH2
   1 HNCO + OH -> CO2 + NH2

  2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

                    analysis #: 3

CHAIN

   1 HNCO + OH -> CO2 + NH2
   1 NO + NH2 -> H2O + N2
   1 NO + NH2 -> N2 + H + OH
   1 HNCO + H -> CO + NH2

  2HNCO + 2NO -> CO2 + H2O + 2N2 + CO
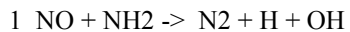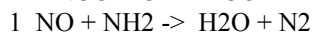
Press I for initialization step or any other key to continue . . .

analysis #: 4

CHAIN

  1 HNCO + H -> CO + NH2
  1 HNCO + OH -> CO2 + NH2
  1 NO + NH2 -> H2O + N2
  1 NO + NH2 -> N2 + H + OH

 2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

analysis #: 5

CHAIN

  1 HNCO + N2H -> N2 + CO + NH2
  1 HNCO + OH -> CO2 + NH2
  1 NO + NH2 -> OH + N2H
  1 NO + NH2 -> H2O + N2

 2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

analysis #: 6

CHAIN

  1 NO + NH2 -> OH + N2H
  1 HNCO + N2H -> N2 + CO + NH2
  1 HNCO + OH -> CO2 + NH2
  1 NO + NH2 -> H2O + N2

 2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

analysis #: 7

CHAIN

  1 NO + NH2 -> H2O + N2
  1 NO + NH2 -> OH + N2H
  1 HNCO + N2H -> N2 + CO + NH2
  1 HNCO + OH -> CO2 + NH2

49

2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

                    analysis #: 8

CHAIN

  1 HNCO + OH -> CO2 + NH2
  1 NO + NH2 -> H2O + N2
  1 NO + NH2 -> OH + N2H
  1 HNCO + N2H -> N2 + CO + NH2

 2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . . .
. . . . 5

                    analysis #: 9

CHAIN

  1 N2H -> N2 + H
  1 HNCO + H -> CO + NH2
  1 NO + NH2 -> H2O + N2
  1 HNCO + OH -> CO2 + NH2
  1 NO + NH2 -> OH + N2H

 2HNCO + 2NO -> CO2 + H2O + 2N2 + CO
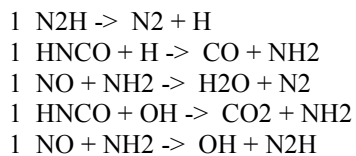
Press I for initialization step or any other key to continue . . .

                    analysis #: 10

CHAIN
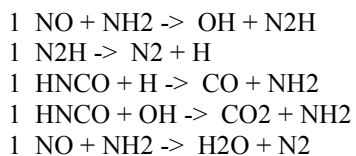
  1 NO + NH2 -> OH + N2H
  1 N2H -> N2 + H
  1 HNCO + H -> CO + NH2
  1 HNCO + OH -> CO2 + NH2
  1 NO + NH2 -> H2O + N2

 2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

CHAIN

  1 NO + NH2 -> H2O + N2
  1 NO + NH2 -> OH + N2H
  1 N2H -> N2 + H
  1 HNCO + H -> CO + NH2
  1 HNCO + OH -> CO2 + NH2

  2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

analysis #: 12

CHAIN

  1 HNCO + OH -> CO2 + NH2
  1 NO + NH2 -> H2O + N2
  1 NO + NH2 -> OH + N2H
  1 N2H -> N2 + H
  1 HNCO + H -> CO + NH2

  2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

analysis #: 13

CHAIN

  1 HNCO + H -> CO + NH2
  1 HNCO + OH -> CO2 + NH2
  1 NO + NH2 -> H2O + N2
  1 NO + NH2 -> OH + N2H
  1 N2H -> N2 + H

  2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

analysis #: 14

CHAIN

  1 NO + NH2 -> N2 + H + OH
  1 HNCO + H -> CO + NH2

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1 HNCO + OH -> CO2 + NH2
1 NO + NH2 -> OH + N2H
1 OH + N2H -> H2O + N2

 2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

analysis #: 15

CHAIN

1 OH + N2H -> H2O + N2
1 NO + NH2 -> N2 + H + OH
1 HNCO + H -> CO + NH2
1 HNCO + OH -> CO2 + NH2
1 NO + NH2 -> OH + N2H

 2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

analysis #: 16

CHAIN

1 NO + NH2 -> OH + N2H
1 OH + N2H -> H2O + N2
1 NO + NH2 -> N2 + H + OH
1 HNCO + H -> CO + NH2
1 HNCO + OH -> CO2 + NH2

 2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

analysis #: 17

CHAIN

1 HNCO + OH -> CO2 + NH2
1 NO + NH2 -> OH + N2H
1 OH + N2H -> H2O + N2
1 NO + NH2 -> N2 + H + OH
1 HNCO + H -> CO + NH2

 2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

analysis #: 18

CHAIN

  1 HNCO + H -> CO + NH2
  1 HNCO + OH -> CO2 + NH2
  1 NO + NH2 -> OH + N2H
  1 OH + N2H -> H2O + N2
  1 NO + NH2 -> N2 + H + OH

 2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

analysis #: 19

CHAIN

  1 HNCO + N2H -> N2 + CO + NH2
  1 HNCO + H -> CO + NH2
  1 NO + NH2 -> OH + N2H
  1 NO + NH2 -> H2O + N2
  1 OH + CO -> CO2 + H

 2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

analysis #: 20

CHAIN

  1 OH + CO -> CO2 + H
  1 HNCO + N2H -> N2 + CO + NH2
  1 HNCO + H -> CO + NH2
  1 NO + NH2 -> H2O + N2
  1 NO + NH2 -> OH + N2H

 2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

53

analysis #: 21

CHAIN

    1 NO + NH2 -> OH + N2H
    1 OH + CO -> CO2 + H
    1 HNCO + N2H -> N2 + CO + NH2
    1 HNCO + H -> CO + NH2
    1 NO + NH2 -> H2O + N2

  2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

analysis #: 22

CHAIN

    1 NO + NH2 -> H2O + N2
    1 NO + NH2 -> OH + N2H
    1 OH + CO -> CO2 + H
    1 HNCO + N2H -> N2 + CO + NH2
    1 HNCO + H -> CO + NH2

  2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

analysis #: 23

CHAIN

    1 HNCO + H -> CO + NH2
    1 NO + NH2 -> H2O + N2
    1 NO + NH2 -> OH + N2H
    1 OH + CO -> CO2 + H
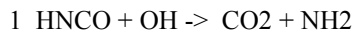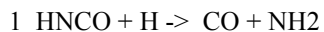   1 HNCO + N2H -> N2 + CO + NH2

  2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

Press I for initialization step or any other key to continue . . .

analysis #: 24

CHAIN

    1 NO + NH2 -> N2 + H + OH
    1 HNCO + OH -> CO2 + NH2

54

```
    1  NO + NH2 ->  OH + N2H
    1  HNCO + N2H ->  N2 + CO + NH2
    1  H + OH ->  H2O


  2HNCO + 2NO ->  CO2 + H2O + 2N2 + CO
```
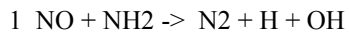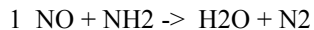
Press I for initialization step or any other key to continue . . .

analysis #: 25

CHAIN

```
    1  HNCO + N2H ->  N2 + CO + NH2
    1  NO + NH2 ->  N2 + H + OH
    1  HNCO + OH ->  CO2 + NH2
    1  NO + NH2 ->  OH + N2H
    1  H + OH ->  H2O


  2HNCO + 2NO ->  CO2 + H2O + 2N2 + CO
```
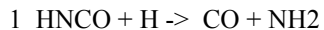
Press I for initialization step or any other key to continue . . .

analysis #: 26

CHAIN

```
    1  H + OH ->  H2O
    1  HNCO + N2H ->  N2 + CO + NH2
    1  NO + NH2 ->  N2 + H + OH
    1  HNCO + OH ->  CO2 + NH2
    1  NO + NH2 ->  OH + N2H


  2HNCO + 2NO ->  CO2 + H2O + 2N2 + CO
```

Press I for initialization step or any other key to continue . . .

analysis #: 27

CHAIN

```
    1  NO + NH2 ->  OH + N2H
    1  H + OH ->  H2O
    1  HNCO + N2H ->  N2 + CO + NH2
    1  NO + NH2 ->  N2 + H + OH
    1  HNCO + OH ->  CO2 + NH2


  2HNCO + 2NO ->  CO2 + H2O + 2N2 + CO
```

Press I for initialization step or any other key to continue . . .
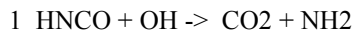
<div align="center">analysis #: 28</div>

CHAIN

  1 HNCO + OH -> CO2 + NH2
  1 NO + NH2 -> OH + N2H
  1 H + OH -> H2O
  1 HNCO + N2H -> N2 + CO + NH2
  1 NO + NH2 -> N2 + H + OH

  2HNCO + 2NO -> CO2 + H2O + 2N2 + CO

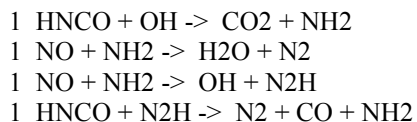Press I for initialization step or any other key to continue . . .

     To check out more possibilities, we repeated this last procedure for several trials, each time selecting some different elementary steps.

APPENDIX B

Sample Input & Output Files for Electronic Energy Calculation Using Gaussian 98

Sample input files for geometry optimization and transition state calculation are presented below. Input files were created using the Gaussian 98 manual as well as reference No.15. The command "runG98 filename.dat>&out&" was used in order to submit the input file for computation.

Input file for Geometry Optimization:


```
%mem=3000000
%chk=HNCO.chk
#B3LYP/6-31G** opt

Isocyanic Acid

0 1
O   0         -0.0343730      0.0000000      1.2690168
N   0          0.1117557      0.0000000     -1.2331228
C   0          0.0371888      0.0000000      0.0444393
H   0         -0.7304384      0.0000000     -1.7869106

--link1--
%mem=3000000
%chk=HNCO.chk
#B3LYP/6-31G** freq geom=check guess=read

Isocyanic Acid

0 1
```

Input file for Transition State:

```
%mem=3000000
%chk=n2h-ts.chk
# B3LYP/6-31G** opt=(addredund, maxcycle=150)

N2H - Transition State

0 2
H   0    -0.5293903    0.0000000    -1.2504522
N   0     0.1241563    0.0000000    -0.4800863
N   0    -0.0485291    0.0000000     0.6587223

1 2 1.43 f

--link1--
%mem=3000000
%chk=n2h-ts.chk
# B3LYP/6-31G** freq geom=check

N2H - Transition State

0 2

--link1--
%mem=3000000
%chk=n2h-ts.chk
# B3LYP/6-31G** opt=(ts,readfc,noeigentest,nofreeze,maxcycle=150) geom=check

N2H - Transition State

0 2

--link1--
%mem=3000000
%chk=n2h-ts.chk
# B3LYP/6-31G** freq geom=check

N2H - Transition State

0 2
```

Collected parts of sample output files for geometry optimization and transition state calculation have also been provided as follows:

Output file for Geometry Optimization:

```
Entering Gaussian System, Link 0=g98
Input=test.dat
Output=test.log
Initial command:
/work1/g98/l1.exe /work1/Gau-14466.inp -scrdir=/work1/
Entering Link 1 = /work1/g98/l1.exe PID=      13700.


                                    .
                                    .
                                    .


    ************************************************
    Gaussian 98:   IBM-RS6000-G98RevA.7 11-Apr-1999
                   11-May-2001
    ************************************************
    %mem=3000000
    %chk=HNCO.chk
    ------------------------
    #T B3LYP/6-31G** opt freq
    ------------------------
    --------------
    Isocyanic Acid
    --------------
    Symbolic Z-matrix:
    Charge =  0 Multiplicity = 1
    O                0    -0.03437   0.        1.26902
    N                0     0.11176   0.       -1.23312
    C                0     0.03719   0.        0.04444
    H                0    -0.73044   0.       -1.78691

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    Initialization pass.
                         ----------------------------
                         !     Initial Parameters    !
                         ! (Angstroms and Degrees)   !
    ------------------------                          ------------------------
    ! Name  Definition            Value          Derivative Info.          !
    ------------------------------------------------------------------------
    ! R1    R(1,3)                1.2267         estimate D2E/DX2          !
    ! R2    R(2,3)                1.2797         estimate D2E/DX2          !
    ! R3    R(2,4)                1.008          estimate D2E/DX2          !
    ! A1    A(3,2,4)            119.9867         estimate D2E/DX2          !
    ! A2    L(1,3,2,4,-1)       179.9959         estimate D2E/DX2          !
    ! A3    L(1,3,2,4,-2)       180.            estimate D2E/DX2          !
    ------------------------------------------------------------------------
    Number of steps in this run=  20 maximum allowed number of steps= 100.
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```

```
                               .
                               .
                 Distance matrix (angstroms):
                       1          2          3          4
     1  O      .000000
     2  N     2.387134    .000000
     3  C     1.174421   1.218322    .000000
     4  H     3.116566   1.007754   1.974339    .000000
Framework group  CS[SG(CHNO)]

Deg. of freedom    5
                      Standard orientation:
----------------------------------------------------------------------
Center     Atomic     Atomic              Coordinates (Angstroms)
Number     Number      Type         X           Y           Z
----------------------------------------------------------------------
   1          8          0        -.622657    1.046243     .000000
   2          7          0         .498812   -1.061057     .000000
   3          6          0         .000000     .050471     .000000
   4          1          0        1.489569   -1.245368     .000000
----------------------------------------------------------------------
Rotational constants (GHZ):    862.2749714    10.9585439    10.8210209
Isotopes: O-16,N-14,C-12,H-1
   50 basis functions        91 primitive gaussians
   11 alpha electrons        11 beta electrons
      nuclear repulsion energy        58.9270592082 Hartrees.
Initial guess read from the read-write file:
Initial guess orbital symmetries:
      Occupied  (A') (A') (A') (A') (A') (A') (A') (A") (A') (A')
                (A")
      Virtual   (A') (A") (A') (A') (A') (A") (A') (A') (A') (A")
                (A') (A') (A') (A") (A') (A') (A') (A") (A') (A")
                (A') (A") (A') (A') (A') (A") (A") (A') (A') (A")
                (A') (A') (A") (A') (A') (A') (A') (A') (A')
SCF Done:  E(RB+HF-LYP) =  -168.681499342     A.U. after    9 cycles
           Convg  =      .3628D-08            -V/T =  2.0092
           S**2   =      .0000


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Internal  Forces:  Max     .000241002 RMS        .000115736
Step number   6 out of a maximum of  20
All quantities printed in internal units (Hartrees-Bohrs-Radians)
Trust test= 1.04D+00 RLast= 1.01D-02 DXMaxT set to 4.24D-01
     Eigenvalues ---      .06042    .17041    .25000    .46231    .84295
     Eigenvalues ---    1.06336
Quartic linear search produced a step of   .13995.
Iteration  1 RMS(Cart)=   .00060416 RMS(Int)=   .00000039
Iteration  2 RMS(Cart)=   .00000042 RMS(Int)=   .00000000
Variable       Old X    -DE/DX    Delta X    Delta X    Delta X     New X
                                 (Linear)    (Quad)     (Total)
   R1        2.21933   -.00013    .00010    -.00017    -.00007    2.21926
   R2        2.30229   -.00006   -.00029     .00009    -.00020    2.30209
   R3        1.90438    .00000   -.00016     .00011    -.00005    1.90433
   A1        2.17655    .00000    .00125    -.00084     .00042    2.17697
   A2        3.27858   -.00024   -.00054    -.00092    -.00145    3.27713
   A3        3.14159    .00000    .00000     .00000     .00000    3.14159
```

```
         Item                  Value      Threshold  Converged?
Maximum Force                  .000241      .000450     YES
RMS      Force                 .000116      .000300     YES
Maximum Displacement           .001197      .001800     YES
RMS      Displacement          .000604      .001200     YES
Optimization completed.
   -- Stationary point found.


-------------------------------------------------------
#T Geom=AllCheck Guess=TCheck RB3LYP/6-31G(d,p) Freq
-------------------------------------------------------
--------------
Isocyanic Acid
--------------
Redundant internal coordinates taken from checkpointfile:
HNCO.chk
Charge =  0 Multiplicity = 1
O,0,0.0270319227,0.,1.2172082679
N,0,0.0880633308,0.,-1.1691456581
C,0,-0.0248423708,0.,0.0439334699
H,0,-0.6836444728,0.,-1.8172473556
Recover connectivity data from disk.


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 Initialization pass.
                                 .
                                 .
                                 .


 Full mass-weighted force constant matrix:
 Low frequencies ---  -16.9370    .0011    .0012    .0014    7.4234
16.6200
 Low frequencies ---  559.1840  610.4572  791.1691
 Harmonic frequencies (cm**-1), IR intensities (KM/Mole),
 Raman scattering activities (A**4/AMU), Raman depolarization ratios,
 reduced masses (AMU), force constants (mDyne/A) and normal coordinates:
                      1                   2                   3
                      A'                  A"                  A'
 Frequencies --    559.1839            610.4528            791.1691
 Red. masses --      2.3791              6.2667              1.8195
 Frc consts  --       .4383             1.3759               .6710
 IR Inten    --     72.8357             2.9112             222.1789
 Raman Activ --       .0000               .0000               .0000
 Depolar     --       .0000               .0000               .0000
 Atom AN      X    Y     Z      X    Y     Z      X    Y     Z
   1   8     .12  .08   .00    .00  .00   .24    .03  .04   .00
   2   7     .07 -.02   .00    .00  .00   .18    .11  .11   .00
   3   6    -.26 -.15   .00    .00  .00  -.60   -.17 -.11   .00
   4   1     .27  .90   .00    .00  .00   .74   -.14 -.96   .00
```

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```
                    4                        5                        6
                    A'                       A'                       A'
 Frequencies --  1338.9560                2356.2663                3701.5178
 Red. masses --    10.0716                  10.3685                   1.0849
 Frc consts  --    10.6386                  33.9168                   8.7580
 IR Inten    --      .3776                 595.5261                 135.9011
 Raman Activ --      .0000                    .0000                    .0000
 Depolar     --      .0000                    .0000                    .0000
 Atom AN      X      Y      Z        X      Y      Z        X      Y      Z
   1   8     .28   -.47    .00      .17   -.27    .00      .00    .00    .00
   2   7    -.27    .53    .00      .14   -.25    .00      .07   -.02    .00
   3   6    -.03   -.04    .00     -.41    .67    .00      .00    .01    .00
   4   1    -.37    .46    .00      .24   -.38    .00     -.97    .21    .00


 Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
 Zero-point correction=                             .021318 (Hartree/Particle)
 Thermal correction to Energy=                      .024579
 Thermal correction to Enthalpy=                    .025524
 Thermal correction to Gibbs Free Energy=          -.001602
 Sum of electronic and zero-point Energies=          -168.660181
 Sum of electronic and thermal Energies=             -168.656920
 Sum of electronic and thermal Enthalpies=           -168.655976
 Sum of electronic and thermal Free Energies=        -168.683101


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 Job cpu time:  0 days  0 hours  5 minutes 38.7 seconds.
  File lengths (MBytes):  RWF=     6 Int=     0 D2E=     0 Chk=     3 Scr=     1
  Normal termination of Gaussian 98.
```

Output file for Transition State:

```
 Entering Gaussian System, Link 0=g98
 Input=test1.dat
 Output=test1.log
 Initial command:
 /work1/g98/l1.exe /work1/Gau-14788.inp -scrdir=/work1/
 Entering Link 1 = /work1/g98/l1.exe PID=     14534.


 ***********************************************
 Gaussian 98:  IBM-RS6000-G98RevA.7 11-Apr-1999
                 11-May-2001
 ***********************************************
 %mem=3000000
 %chk=n2h-ts.chk
 ------------------------------------------------
 #T B3LYP/6-31G** opt=(addredund, maxcycle=150)
 ------------------------------------------------
 ----------------------
 N2H - Transition State
 ----------------------
 Symbolic Z-matrix:
 Charge =  0 Multiplicity = 2
 H                  0    -0.52939   0.       -1.25045
 N                  0     0.12416   0.       -0.48009
 N                  0    -0.04853   0.        0.65872
 The following ModRedundant input section has been read:
 B    1    2 1.4300 F
 Iteration  1 RMS(Cart)=   .09128958 RMS(Int)=   .34250815
 Iteration  2 RMS(Cart)=   .09177750 RMS(Int)=   .22703773
 Iteration  3 RMS(Cart)=   .09201478 RMS(Int)=   .11156762
 Iteration  4 RMS(Cart)=   .08909842 RMS(Int)=   .00047249
 Iteration  5 RMS(Cart)=   .00051780 RMS(Int)=   .00000016
 Iteration  6 RMS(Cart)=   .00000016 RMS(Int)=   .00000000
 Iteration  1 RMS(Cart)=   .00000000 RMS(Int)=   .00000000


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 Initialization pass.
                                  .
                                  .
                                  .
 Full mass-weighted force constant matrix:
 Low frequencies ----1109.4890   -9.7846   -7.7562     .0014      .0014
 .0017
 Low frequencies ---   23.1428  647.7564 2246.7541
 ******    1 imaginary frequencies (negative Signs) ******
 Harmonic frequencies (cm**-1), IR intensities (KM/Mole),
 Raman scattering activities (A**4/AMU), Raman depolarization ratios,
 reduced masses (AMU), force constants (mDyne/A) and normal coordinates:
```

```
                         1                         2                         3
                        A'                        A'                        A'
Frequencies -- -1109.4890                  647.7564                  2246.7541
Red. masses --     1.0928                    1.3764                    10.0225
Frc consts  --      .7926                     .3403                    29.8084
IR Inten    --   268.4140                    2.2104                    75.7614
Raman Activ --      .0000                     .0000                      .0000
Depolar     --      .0000                     .0000                      .0000
Atom AN      X        Y        Z        X        Y        Z        X        Y        Z
  1   1     .85     -.52      .00      .44      .88      .00     -.46      .31      .00
  2   7    -.06      .05      .00     -.13     -.03      .00      .03      .58      .00
  3   7     .00     -.02      .00      .10     -.03      .00      .00     -.60      .00

                                        .
                                        .
                                        .

Job cpu time:  0 days  0 hours  4 minutes  3.6 seconds.
File lengths (MBytes): RWF=     6 Int=     0 D2E=     0 Chk=     3 Scr=     1
Normal termination of Gaussian 98.
```

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VITA

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	Chemistry, B.Sc., 1989
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Professional
Experience:

Cosmetic Manager
   Micronized Powder Co., Tehran, 1991-1992
Marketing Assistant in Industrial Measuring Systems Dept.
   Geotech Company, Tehran, 1992-1994
Contract Expert in Export and Representatives Section
   Petrochemical Commercial Co., Tehran, 1995-1996
Marketing Manager for Plastic Field, Kumho chemicals Inc., Korea
   Tehran Representative Office, 1996-1999
Teaching Assistant, East Tennessee State University,
   Chemistry Dept., 1999-2001

Honors and
Awards:

International Student Outstanding Scholastic Achievement,
ETSU, 1999-2000 & 2000-2001