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# Computational Study of the Mechanism of the Oxidation of Hydrazine / Hydrazinium Ion by Iodine in the Gas Phase

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**Abstract:** The reaction mechanisms of the oxidation of hydrazine / hydrazinium ion by iodine have been studied using 6311+G** basis set of the density functional theory (DFT) method at the B3LYP level of computation. The study shows that the oxidation reactions can proceed via four independent routes or pathways that can be separately monitored. Two of the proposed pathways involved a two-step reaction mechanism each, in which two transition states were produced while each of the other two routes involved three-step reaction mechanism in which three activated complexes were produced. The results obtained were based on the analyses of the computational energetics of the optimized reactants, intermediates, transition states and products of the reaction of iodine with hydrazine / hydrazinium ion. The study showed that all the four proposed routes were possible by comparing the enthalpies of reactions of the four proposed pathways as well as the activation barriers of the respective rate determining steps which were found to be reasonably acceptable. Rate laws, which were consistent with the written mechanisms, were also derived for each of the proposed mechanisms.

**Keywords:** DFT Calculations, Reaction Mechanisms, Rate Laws, Iodine, Hydrazine, Transition States

## 1. Introduction

Iodine is an essential micronutrient for mammals including humans and, in fact, appears to be the heaviest required element in a diet [1, 2, 3]. Iodine compounds are useful in medicine and lack of iodine in the diet, is a cause of goitre. Iodine is absolutely necessary for a healthy thyroid as well as ovaries, breasts and prostate. Iodine deficiency, though easily treated, continues to be a problem for approximately a fifth of the world population [4, 5]. Goitre, or enlargement of the thyroid, has been recognized for many years as symptom of iodine deficiency. These pathological conditions are normally grouped under the common name of iodine deficiency disorders (IDD) [6]. Iodine deficiency is, in fact, the largest preventable cause of mental retardation worldwide [3]. In severe cases, it can result in cretinism, a form of mental retardation. Mshelia *et al,* [7] reported in their studies that volatization from oceans and precipitation of ocean water is the origin of most iodine content of diet and is considered critical to compensate for metabolic losses. Goitre surveys so far are limited to clinical symptoms, urinary iodine output and, to some extent, plasma thyroid hormone levels.

Iodine is used to prevent iodine deficiency and its consequences, including goiter. It is also used for treating a skin disease caused by a fungus (*cutaneous sporotrichosis*); treating fibrocystic breast disease; preventing breast cancer, eye disease, diabetes, and heart disease and stroke; and as an expectorant [8, 9, 10, 11]. Iodine is applied to the skin to kill germs, prevent soreness inside the mouth (*mucositis*) caused by chemotherapy, and treat diabetic ulcers [12, 13]. It is also reported that iodine has very specific protective effects against several common poisons like fluoride and bromide and, to a lesser extent, helps eliminate lead and mercury from the body [14]. These are just a few of the reasons why the study of iodine is quite interesting.

It is also well known that hydrazine and its derivatives play important role in biological activity studies. A number of hydrazide-hydrazone are claimed to possess interesting antibacterial, antifungal [14], anticonvulsant [16], anti-inflammatory [17], antimalarial [17] and antituberculosis activities [18]. It is also well known that iodine

quantitatively oxidizes substances containing the -NH-NH group. This reaction is the basis of one of the standard analytical procedures to titrate hydrazine and related substances, in particular isonicotinoyl-hydrazide which is widely used in the pharmaceutical industry because of its bacteriostatic properties against *Mycobacterium tuberculosis [3, 7, 19, 20, 21, 22]*.

The study of the mechanisms of oxidation of substrates by iodine has been the subject of several studies, but among which no complete agreement is found [1, 7, 20, 23, 24,25, 26]. The mechanisms of the oxidation of substances by iodine is not only as varied as the number of authors who have published such works, but also as the number of internationally recognized peer reviewed journals in which such work were published [2, 7, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29]. A further investigation seemed desirable [30, 31].

The present paper desired to report the results of computational studies on the mechanism of the oxidation of hydrazine / hydrazinium ion by iodine. The computational analyses of the structures using DFT (B3LYP) are reported. Computational chemistry methods can be used to explore the theoretical chemistry behind reactive systems, to compare the relative chemical reactivity of different systems, and, by extension, to predict the reactivity of new systems. Transition states for reaction of hydrazine / hydrazinium ion with iodine were determined and equilibrium states of reactants, intermediates and products were searched by computational means. In theoretical studies, using *ab initio* or density functional theory (DFT) methods, adequate choices of a theoretical method and a basis set are very important in obtaining reliable results. Theoretical studies on compounds containing iodine, a 5th period halogen element, are less abundant compared to those containing F, Cl or Br which are 2nd, 3rd and 4th period elements, respectively [1, 23]. Heavy elements like iodine have a large number of core electrons which are in general less important for the chemical reactivity and bonding modes. However, it needs a large number of basis sets or functions to describe the corresponding orbitals. This makes computations with heavy elements like iodine very time consuming and expensive [32, 33, 34]. However, compounds containing iodine atom play very interesting and important roles in many chemical reactions, especially in the life sciences. Despite the challenges therefore, this makes the study of iodine quite interesting, especially when using the more exact method of DFT.

## 2. Materials and Methods

### 2.1. Materials

The Spartan '14 v1.1.0 density functional theory (DFT) method was used on Microsoft window XP professional version 2002 SP3 computer system, with Intel(R) Pentium(R) Dual CPU,E2200@2.20 GHz 219GHz, 3.24GB of RAM. All equations were written using Design Science MathType 6.9 program. All graphs were drawn using Microsoft Excel 2010,

while the structures in Schemes 2-5, were produced using ChemBio Office 2008 software.
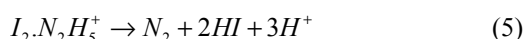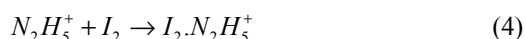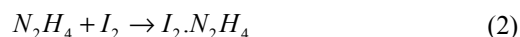
### 2.2. Geometry Optimization of Reactants, Intermediates, Transition States and Products

All the electronic structure calculations reported in this work were performed using the Spartan '14 v1.1.0 program packages. The geometries included in the reaction of hydrazine / hydrazinium ion with iodine were fully optimized using density functional theory (DFT) method [35, 36, 37]. To check the influence of basis set, PM3 of semi empirical method and 6-311+G** basis set of DFT at the B3LYP levels of computation were employed to optimize the geometries of the reactants, intermediates, transition states and products. There were marked differences between the semi empirical method and the DFT method. It thus indicated that the geometrical parameters were sensitive to the sizes of the basis sets or computational levels. The starting geometries for all of the DFT calculations were at first optimized in the Spartan '14 v1.1.0 Global calculations environment work space at the PM3 level, and then followed by the DFT B3LYP calculations at 6311+G** basis set level. The optimized geometries of the reactants, intermediates, transition states and products were confirmed in terms of vibrational analysis [35, 38]. The transition state for each step was located and confirmed by animating the vibration corresponding to the reaction coordinate by selecting the imaginary frequency at the top of the list of frequencies on the IR tab. No arbitrary assumptions were imposed on finding the most likely geometries for the transition state in each case.

## 3. Results Section

### 3.1. Published Mechanism

The outline of the published mechanism of the oxidation of hydrazine / hydrazinium ion with iodine as given by past workers [6] is shown in scheme1below.

$$N_2H_5^+ \qquad N_2H_4 + H^+ \qquad\qquad (1)$$

$$N_2H_4 + I_2 \rightarrow I_2.N_2H_4 \qquad\qquad (2)$$

$$I_2.N_2H_4 \rightarrow N_2 + 4HI \qquad\qquad (3)$$

$$N_2H_5^+ + I_2 \rightarrow I_2.N_2H_5^+ \qquad\qquad (4)$$

$$I_2.N_2H_5^+ \rightarrow N_2 + 2HI + 3H^+ \qquad\qquad (5)$$

**Scheme 1.** *The reaction mechanism as proposed by Mshelia et al [7].*

Mshelia *et al* [6] gave the stoichiometry of their reaction as (6) below.

$$N_2H_5^+ + 2I_2 \rightarrow N_2 + 4HI \qquad\qquad (6)$$
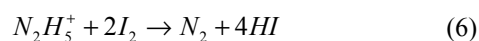
The mechanism as proposed in Scheme 1 by Mshelia et al

[7] was not consistent with their stated stoichiometric equation. Whereas the number of all atoms on the reactants side and those on the products side were balanced, the number of positive charges on the products was twice that on the reactants side. However, it was noted that their stoichiometry was consistent with their other data. It, therefore, showed the problem was with the mechanism they proposed. It is the desire of this work to find out if mechanisms that are consistent with the stoichiometry or, better still, mechanisms that are more favourable energetically than the one proposed by Mshelia *et al* [7] could be formulated in current study. Four mechanisms were proposed and presented in schemes 2 - 5 as routes I, II, III and IV, respectively.

### 3.2. Geometry Optimization of Intermediates and Transition States; and Validity of the Generally Accepted Mechanism

Geometry optimization of the reactants, intermediates, transition states and products in the hydrazine / hydrazinium ion reaction with iodine was executed. The geometry optimizations of all these species were successfully completed and the heat of formation ($\Delta H^o$) at standard condition of 1 atmosphere and 298.15K were evaluated and presented together with other thermodynamic parameters in Table 1 for route I, Table 2 for route II, Table 3 for route III and Table 4 for route IV. The activation parameters for all the routes proposed were given in Tables 5 and 6.

**Table 1.** *Heat of formation at standard condition of 1 atmosphere and 298.15K of reacting species for route I for hydrazine / hydrazinium ion – iodine system.*

| S/N | Reacting Specie | Heat of formation together with other thermodynamic parameters at 1 Atm and 298.15K for route I | | |
|---|---|---|---|---|
| | | $\Delta H^o$ (kJ/mol) | $\Delta G^o$ (kJ/mol) | $\Delta S^o$ (kJ/mol.K) |
| 1 | $I_2$ | -36,334,465.70 | -36,334,542.14 | 260.55 |
| 2 | $H_2O$ | -200,678.03 | -200,732.28 | 188.64 |
| 3 | $H_3O^+$ | -201,317.55 | -201,375.65 | 194.90 |
| 4 | $Hyd^+$ | -294,265.02 | -294,343.59 | 263.55 |
| 5 | Hyd | -293,512.76 | -293,585.77 | 244.93 |
| 6 | HI | -18,168,774.40 | -18,168,835.99 | 206.59 |
| 7 | Int. | -290,042.75 | -290,100.30 | 364.75 |
| 8 | $N_2$ | -287,570.90 | -287,627.96 | 191.57 |
| 9 | $TS_F$ | -494,142.06 | -494,634.72 | |
| 10 | $TS_1$ | -36,527,976.45 | -36,528,075.41 | 331.95 |
| 11 | $TS_2$ | -36,618,245.67 | -36,625,511.49 | |
| 12 | $R_1$ | -494,943.05 | | |
| 13 | $P_1$ | -494,830.31 | | |
| 14 | $R_2$ | -36,627,978.46 | | |
| 15 | $P_2$ | -36,627,591.55 | | |
| 16 | $R_3$ | -36,624,508.45 | | |
| 17 | $P_3$ | -72,962,668.50 | | |
| 18 | $E_{a1}$ | 800.99 | | |
| 19 | $E_{a2}$ | 100,002.01 | | |
| 20 | $E_{a3}$ | 6,262.78 | | |

Where $I_2$ was iodine molecule, $H_2O$ was water molecule, $Hyd^+$ was hydrazinium ion, Hyd was hydrazine, HI was hydrogen iodide molecule, HOI was hypoiodous acid, Int was intermediate (diazine), $TS_1$ was transition state for step 1, $N_2$ was nitrogen molecule, $R_1$ and $R_2$ were all the reactants for step 1 and step 2, $P_1$ and $P_2$ were all the products for step 1 and step 2, $E_{a1}$ and $E_{a2}$ were the activation energies for steps 1 and 2.

**Table 2.** *Heat of formation at standard condition of 1 atmosphere and 298.15K of reacting species for route 2 for hydrazine / hydrazinium ion –iodine system.*

| S/N | Reacting Specie | Heat of formation together with other thermodynamic parameters at 1 Atm and 298.15K for route 2 | | |
|---|---|---|---|---|
| | | $\Delta H^o$ (kJ/mol) | $\Delta G^o$ (kJ/mol) | $\Delta S^o$ (kJ/mol.K) |
| 1 | $I_2$ | -36,334,465.70 | -36,334,542.14 | 260.55 |
| 2 | $H_2O$ | -200,678.03 | -200,732.28 | 188.64 |
| 3 | $H_3O^+$ | -201,317.55 | -201,375.65 | 194.90 |
| 4 | $Hyd^+$ | -294,265.02 | -294,343.59 | 263.55 |
| 5 | Hyd | -293,512.76 | -293,585.77 | 244.93 |
| 6 | HI | -18,168,774.40 | -18,168,835.99 | 206.59 |
| 7 | $N_2$ | -287,570.90 | -287,627.96 | 191.57 |
| 8 | $TS_F$ | -494,142.06 | -494,634.72 | |
| 9 | $TS_B$ | -72,948,708.06 | -72,963,181.09 | |
| 10 | $R_1$ | -494,943.05 | | |
| 11 | $P_1$ | -494,830.31 | | |
| 12 | $R_B$ | -72,962,444.16 | | |
| 13 | $P_B$ | -72,962,668.50 | | |
| 14 | $E_{a1}$ | 800.99 | | |
| 15 | $E_{aB}$ | 13,736.10 | | |

Where $I_2$ was iodine molecule, $H_2O$ was water molecule, $Hyd^+$ was hydrazinium ion, Hyd was hydrazine, HI was hydrogen iodide molecule, HOI was hypoiodous acid, Int was intermediate (diazine), $TS_1$ was transition state for step 1, $N_2$ was nitrogen molecule, $R_1$ and $R_2$ were all the reactants for step 1 and step 2, $P_1$ and $P_2$ were all the products for step 1 and step 2, $E_{a1}$ and $E_{a2}$ were the activation energies for steps 1 and 2.

***Table 3.*** *Heat of formation at standard condition of 1 atmosphere and 298.15K of reacting species for route 3 for hydrazine / hydrazinium ion – iodine system.*

| S/N | Reacting Specie | Heat of formation together with other thermodynamic parameters at 1 Atm and 298.15K for route 3 | | |
| --- | --- | --- | --- | --- |
| | | $\Delta H^o$ (kJ/mol) | $\Delta G^o$ (kJ/mol) | $\Delta S^o$ (kJ/mol.K) |
| 1 | $I_2$ | -36,334,465.70 | -36,334,542.14 | 260.55 |
| 2 | $H_2O$ | -200,678.03 | -200,732.28 | 188.64 |
| 3 | $H_3O^+$ | -201,317.55 | -201,375.65 | 194.90 |
| 4 | $Hyd^+$ | -294,265.02 | -294,343.59 | 263.55 |
| 5 | Hyd | -293,512.76 | -293,585.77 | 244.93 |
| 6 | HI | -18,168,774.40 | -18,168,835.99 | 206.59 |
| 7 | $N_2$ | -287,570.90 | -287,627.96 | 191.57 |
| 7 | $TS_F$ | -494,142.06 | -494,634.72 | |
| 8 | $TS_1$ | -36,527,976.45 | -36,528,075.41 | 331.95 |
| 9 | $TS_C$ | -72,948,830.75 | -72,963,303.79 | 451.51 |
| 10 | $R_1$ | -494,943.05 | | |
| 11 | $P_1$ | -494,830.31 | | |
| 12 | $R_C$ | -72,962,444.16 | | |
| 13 | $P_C$ | -72,962,668.50 | | |
| 14 | $E_{a1}$ | 800.99 | | |
| 15 | $E_{aC}$ | 13,613.41 | | |

Where $I_2$ was iodine molecule, $H_2O$ was water molecule, $Hyd^+$ was hydrazinium ion, Hyd was hydrazine, HI was hydrogen iodide molecule, HOI was hypoiodous acid, Int was intermediate (diazine), $TS_1$ was transition state for step 1, $N_2$ was nitrogen molecule, $R_1$ and $R_2$ were all the reactants for step 1 and step 2, $P_1$ and $P_2$ were all the products for step 1 and step 2, $E_{a1}$ and $E_{a2}$ were the activation energies for steps 1 and 2.

***Table 4.*** *Heat of formation at standard condition of 1 atmosphere and 298.15K of reacting species for route 4 for hydrazine / hydrazinium ion – iodine system.*

| S/N | Reacting Specie | Heat of Formation together with other activation parameters at 1 Atm and 298.15K for route 4 | | |
| --- | --- | --- | --- | --- |
| | | $\Delta H^o$ (kJ/mol) | $\Delta G^o$ (kJ/mol) | $\Delta S^o$ (kJ/mol.K) |
| 1 | $I_2$ | -36,334,465.70 | -36,334,542.14 | 260.55 |
| 2 | $H_2O$ | -200,678.03 | -200,732.28 | 188.64 |
| 3 | $H_3O^+$ | -201,317.55 | -201,375.65 | 194.90 |
| 4 | HOI | -18,366,219.67 | -18,366,295.58 | 254.58 |
| 5 | $Hyd^+$ | -294,265.02 | -294,343.59 | 263.55 |
| 6 | Hyd | -293,512.76 | -293,585.77 | 244.93 |
| 7 | HI | -18,168,774.40 | -18,168,835.99 | 206.59 |
| 8 | $N_2$ | -287,570.90 | -287,627.96 | 191.57 |
| 9 | $TS_F$ | -494,142.06 | -494,634.72 | |
| 10 | $TS_D$ | -36,534,957.18 | -36,535,052.36 | 319.24 |
| 11 | $TS_E$ | -37,019,091.68 | -37,056,036.73 | |
| 12 | $R_1$ | -494,943.05 | | |
| 13 | $P_1$ | -494,830.31 | | |
| 14 | $R_D$ | -36,535,143.73 | | |
| 15 | $P_D$ | -36,534,994.07 | | |
| 16 | $R_E$ | -37,025,952.10 | | |
| 17 | $P_E$ | -37,026,475.76 | | |
| 18 | $E_{a1}$ | 800.99 | | |
| 19 | $E_{aD}$ | 186.55 | | |
| 20 | $E_{aC}$ | 6,860.42 | | |

Where $I_2$ was iodine molecule, $H_2O$ was water molecule, $Hyd^+$ was hydrazinium ion, Hyd was hydrazine, HI was

hydrogen iodide molecule, HOI was hypoiodous acid, Int was intermediate (diazine), $TS_1$ was transition state for step 1, $N_2$ was nitrogen molecule, $R_1$ and $R_2$ were all the reactants for step 1 and step 2, $P_1$ and $P_2$ were all the products for step 1 and step 2, $E_{a1}$ and $E_{a2}$ were the activation energies for steps 1 and 2.

**Table 5.** *Heat of formation and other activation parameters at standard condition of 1 atmosphere and 298.15K of reacting species for routes I and II for hydrazine / hydrazinium ion – iodine reaction system.*

| Route | Reacting Species | Heat of formation together with other activation parameters at 1 Atm and 298.15K for routes 1 and 2 | | | |
| | | $\Delta_r H^o$ (kJ/mol) | $\Delta^{\ddagger}G$ (kJ/mol) | $\Delta^{\ddagger}S$ (kJ/mol.K) | $\Delta^{\ddagger}E_a$ (kJ/mol) |
|---|---|---|---|---|---|
| Route I | $R_1$ | -494,943.05 | | | |
| | $P_1$ | -494,830.31 | | | |
| | $TS_1$ | -36,527,976.45 | | | |
| | Step I | | $2.76 \times 10^4$ | $-1.75 \times 10^3$ | $8.01 \times 10^2$ |
| | $R_2$ | -36,627,978.46 | | | |
| | $P_2$ | -36,627,591.55 | | | |
| | $TS_2$ | -36,618,245.67 | | | |
| | Step II | | $-2.70 \times 10^4$ | $-1.73 \times 10^5$ | $1.00 \times 10^5$ |
| | $R_3$ | -36,624,508.45 | | | |
| | $P_3$ | -72,962,668.50 | | | |
| | $TS_3 (TS_F)$ | -494,142.06 | | | |
| | Step III | | $-1.52 \times 10^7$ | $-3.66 \times 10^7$ | $6.26 \times 10^3$ |
| Route II | $R_1$ | -494,943.05 | | | |
| | $P_1$ | -494,830.31 | | | |
| | $(TS_1) TS_F$ | -494,142.06 | | | |
| | Step I | | $2.76 \times 10^4$ | $-1.75 \times 10^3$ | $8.01 \times 10^2$ |
| | $R_B$ | -72,962,444.16 | | | |
| | $P_B$ | -72,962,668.50 | | | |
| | $TS_B$ | -72,948,708.06 | | | |
| | Step II | | $5.91 \times 10^4$ | $-2.45 \times 10^5$ | $1.37 \times 10^4$ |

**Table 6.** *Heat of formation and other activation parameters at standard condition of 1 atmosphere and 298.15K of reacting species for routes III and IV for hydrazine / hydrazinium ion – iodine reaction System.*

| Route | Reacting species | Heat of formation together with other activation parameters at 1 Atm and 298.15K for routes 3 and 4 | | | |
| | | $\Delta_r H^o$ (kJ/mol) | $\Delta^{\ddagger}G$ (kJ/mol) | $\Delta^{\ddagger}S$ (kJ/mol.K) | $\Delta^{\ddagger}E_a$ (kJ/mol) |
|---|---|---|---|---|---|
| Route III | $R_1$ | -494,943.05 | | | |
| | $P_1$ | -494,830.31 | | | |
| | $(TS_1) TS_F$ | -494,142.06 | | | |
| | Step I | | $2.76 \times 10^4$ | $-1.75 \times 10^3$ | $8.01 \times 10^2$ |
| | $R_C$ | -72,962,444.16 | | | |
| | $P_C$ | -72,962,668.50 | | | |
| | $TS_C$ | -72,948,830.75 | | | |
| | Step II | | $7.37 \times 10^4$ | $-1.23 \times 10^5$ | $1.37 \times 10^4$ |
| | | | | | |
| Route IV | $R_1$ | -494,943.05 | | | |
| | $P_1$ | -494,830.31 | | | |
| | $(TS_1) TS_F$ | -494,142.06 | | | |
| | Step I | | $2.76 \times 10^4$ | $-1.75 \times 10^3$ | $8.01 \times 10^2$ |
| | $R_D$ | -36,535,143.73 | | | |
| | $P_D$ | -36,534,994.07 | | | |
| | $TS_D$ | -36,534,957.18 | | | |
| | Step II | | $1.57 \times 10^9$ | $-5.40 \times 10^6$ | $1.87 \times 10^2$ |
| | $R_E$ | -37,025,952.10 | | | |
| | $P_E$ | -37,026,475.76 | | | |
| | $TS_E$ | -37,019,091.68 | | | |
| | Step II | | $8.01 \times 10^4$ | $-1.24 \times 10^6$ | $6.86 \times 10^3$ |

In all the four routes proposed, the first step always started with the hydrolysis of the hydrazinium ion or abstraction of hydrogen ion by water to yield hydrazine. In fact, the abstraction of hydrogen ion or the hydrolysis of hydrazinium ion by water to yield hydrazine has been reported by several authors [39, 40, 41].

All the transition states in the schemes proposed in this work were found to be true transition states or activated complexes. They all have higher energies compared to other species in their respective elementary steps as can be seen in Tables 1 – 6. They all occupied saddle points on scaled potential energy surface diagrams as drawn in Figures 1 – 4. The trueness of the transition states were also confirmed by animating the vibration corresponding to the reaction coordinate by selecting the imaginary frequency at the top of the list of frequencies on the IR tab.
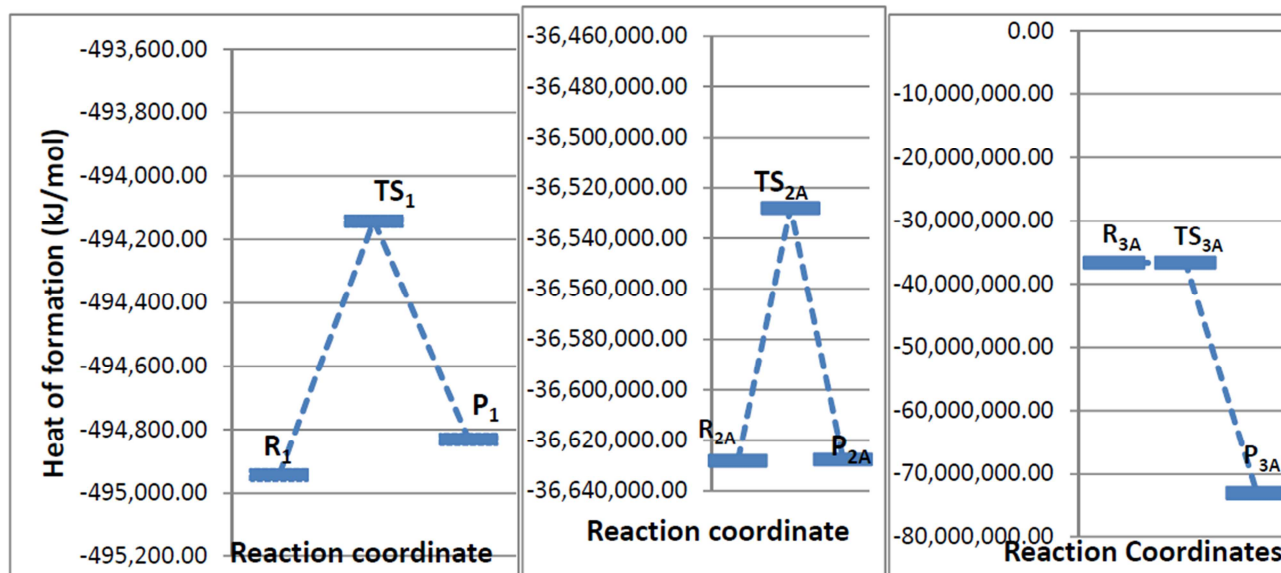


*Figure 1. Energy profile of the oxidation of hydrazine / hydrazinium ion by iodine according to the route I proposed mechanism.*

Where $R_1$, $TS_1$ and $P_1$ were reactants, transition state and products, respectively, for the first step; while $R_{2A}$ and $R_{3A}$ were reactants, $TS_{2A}$ and $TS_{3A}$ were transition states, in second and third steps, respectively. $P_2$ and $P_3$ were the products of the reaction in steps 2 and 3, respectively.
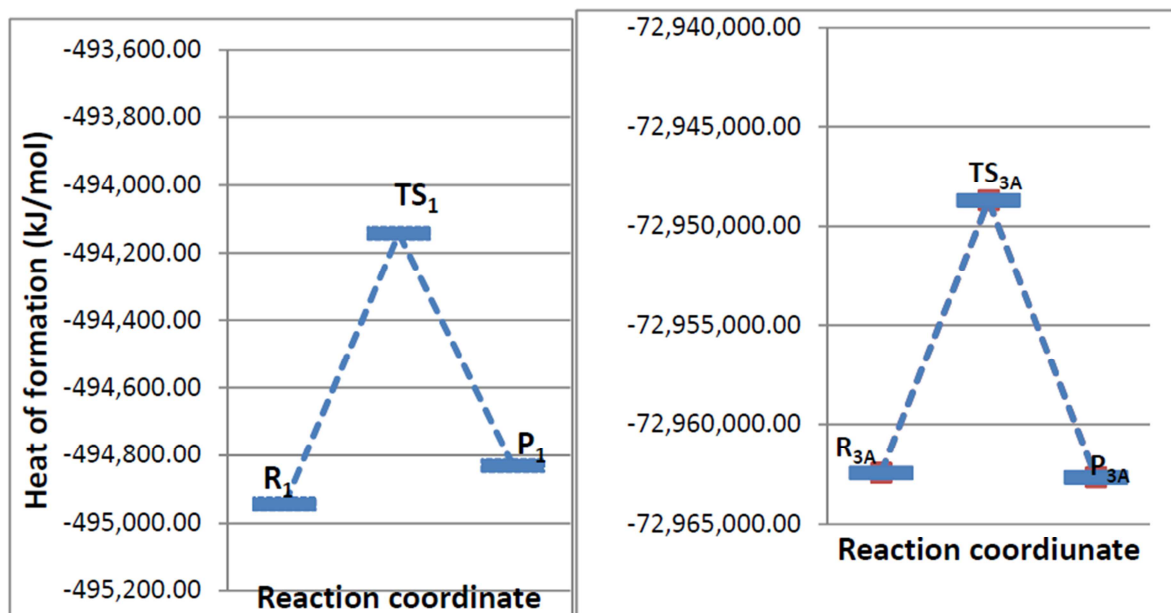


*Figure 2. Energy profile of the oxidation of hydrazine / hydrazinium ion by iodine according to the route II proposed mechanisms.*

Where $R_1$, $TS_1$ and $P_1$ were reactants, transition state and products, respectively, for the first step; while $R_{3A}$ were reactants and $TS_{3A}$ was transition state, in second step. $P_{3A}$ were the products of the reaction the step.
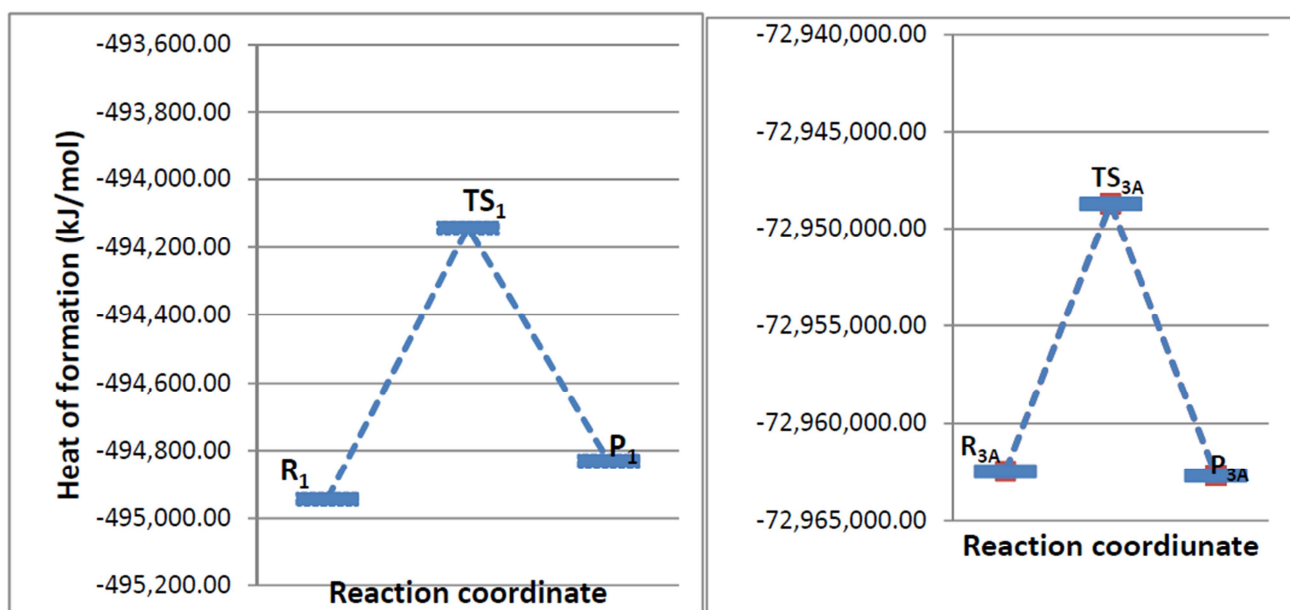
*Figure 3. Energy profile of the oxidation of hydrazine / hydrazinium ion by iodine according to the route III proposed mechanisms.*

Where $R_1$, $TS_1$ and $P_1$ were reactants, transition state and products, respectively, for the first step; while $R_{3A}$ were reactants and $TS_{3A}$ was transition state, in second step. $P_{3A}$ were the products of the reaction the step.
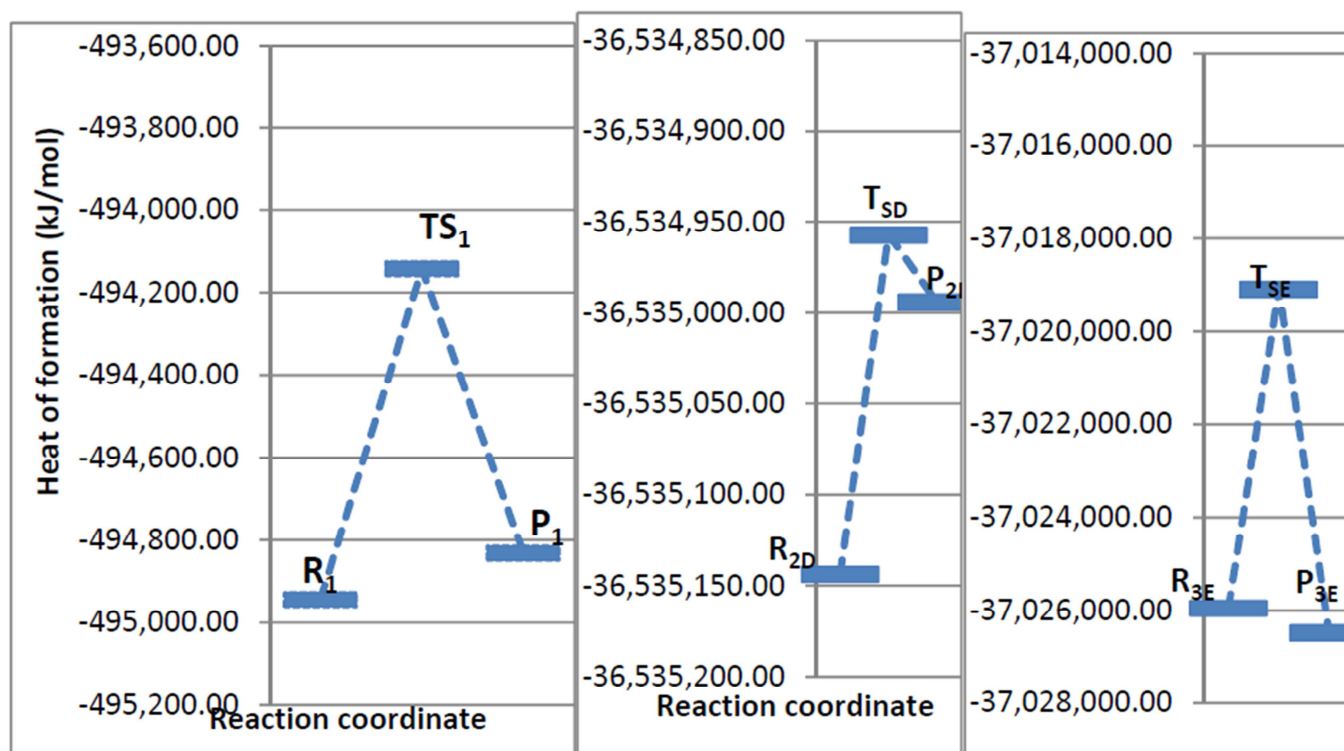


*Figure 4. Energy profile of the oxidation of hydrazine / hydrazinium ion by iodine according to the route IV proposed mechanism.*
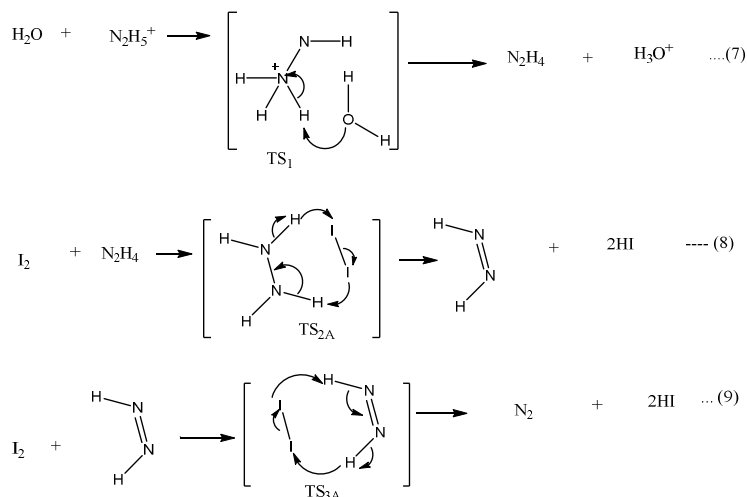
Where $R_1$, $TS_1$ and $P_1$ were reactants, transition state and products, respectively, for the first step; while $R_{2D}$ and $R_{3E}$ were reactants, $T_{SD}$ and $T_{SE}$ were transition states, in second and third steps, respectively. $P_{2D}$ and $P_{3E}$ were the products of the reaction in steps 2 and 3, respectively.

## 3.3. Proposal of a More Plausible Mechanism for the Reaction

Based on the discussion of the DFT calculations of the various optimized reacting species, the four reaction routes or mechanisms shown in Schemes 2 - 5 are more plausible than

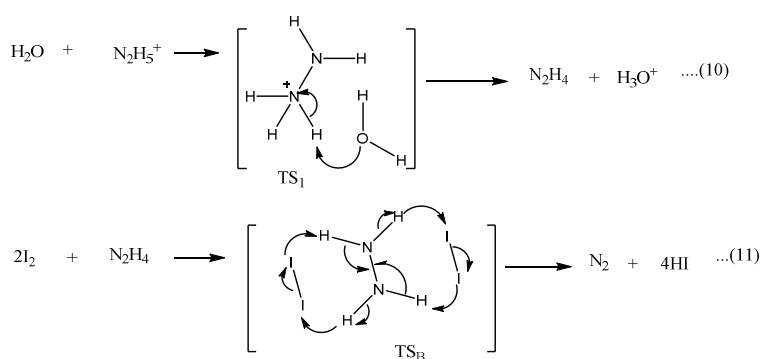the mechanism version published by Mshelia *et al* [6].

### 3.3.1. Route I



$$H_2O \ + \ N_2H_5^+ \longrightarrow [TS_1] \longrightarrow N_2H_4 \ + \ H_3O^+ \quad ....(7)$$

$$I_2 \ + \ N_2H_4 \longrightarrow [TS_{2A}] \longrightarrow \ + \ 2HI \quad ----(8)$$

$$I_2 \ + \longrightarrow [TS_{3A}] \longrightarrow N_2 \ + \ 2HI \quad ...(9)$$

**Scheme 2.** *The first proposed mechanism for the hydrazine / hydrazinium ion reaction with iodine.*

In this scheme (equations 7-9), water molecule reacted with the hydrazinium ion to yield hydrazine and hydroxonium ion via the transition state $TS_1$. The hydrazine molecule formed in the first step then reacted with an iodine molecule via transition state $TS_2$ to give a diazine molecule and two molecules of HI. Finally, the diazine molecule reacted with another iodine molecule via transition state $TS_3$ to give a nitrogen molecule plus two molecules of HI.

### 3.3.2. Route II



$$H_2O \ + \ N_2H_5^+ \longrightarrow [TS_1] \longrightarrow N_2H_4 \ + \ H_3O^+ \quad ....(10)$$

$$2I_2 \ + \ N_2H_4 \longrightarrow [TS_B] \longrightarrow N_2 \ + \ 4HI \quad ...(11)$$
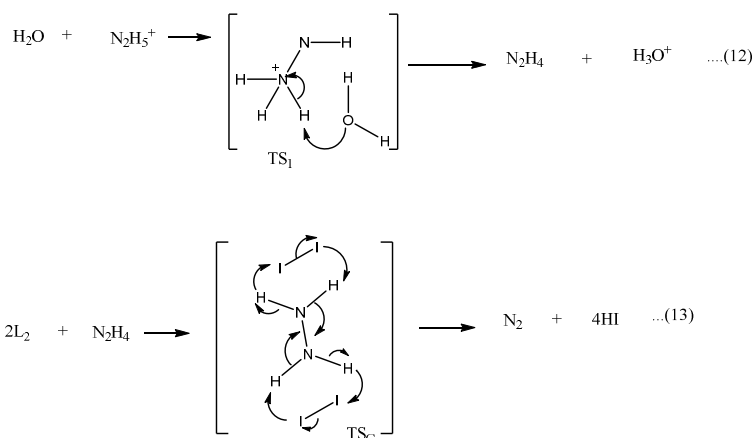
**Scheme 3.** *The second proposed mechanism for the hydrazine / hydrazinium ion reaction with iodine.*

In this scheme (equations 10 and 11), water molecule reacted with the hydrazinium ion to yield hydrazine and hydroxonium ion via the transition state $TS_1$. The hydrazine formed is then attacked concurrently by two molecules of iodine via the transition state $TS_B$ to yield the products of nitrogen molecule plus four molecules of HI.

### 3.3.3. Route III



$$H_2O \ + \ N_2H_5^+ \longrightarrow [TS_1] \longrightarrow N_2H_4 \ + \ H_3O^+ \quad ....(12)$$

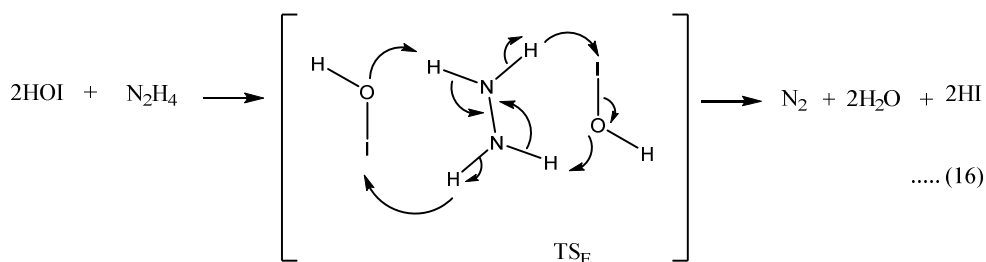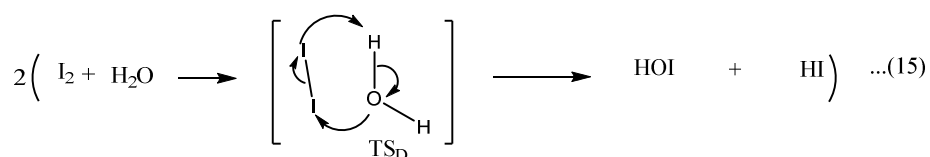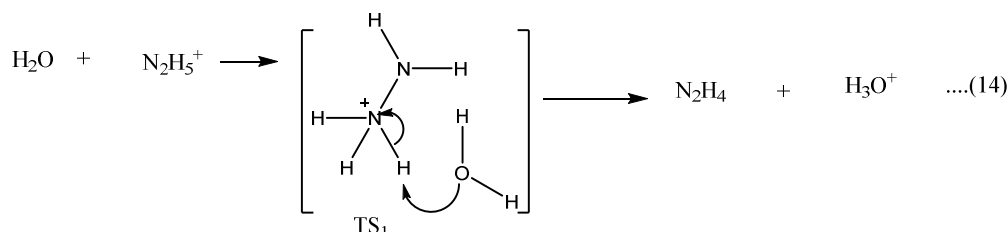$$2L_2 \ + \ N_2H_4 \longrightarrow [TS_C] \longrightarrow N_2 \ + \ 4HI \quad ...(13)$$

**Scheme 4.** *The second proposed mechanism for the hydrazine / hydrazinium ion reaction with iodine.*

This was another two-step pathway scheme (equations 12 and 13) just like the previous one. The only difference was that each of the two molecules of iodine attacked and abstracted two hydrogen atoms attached to the same nitrogen atoms of the hydrazine molecule. In the previous route, each iodine molecule attacked and abstracted two hydrogen atoms attached to different nitrogen atoms of the hydrazine molecule.

### 3.3.4. Route IV



Scheme 5. *The second proposed mechanism for the hydrazine / hydrazinium ion reaction with iodine.*

This scheme (equations 14 - 16), a three-step process, started, as usual, with water molecule reacting with the hydrazinium ion to yield hydrazine and hydroxonium ion via the transition state $TS_1$ in the first step. In the second step, two molecules of iodine reacted with two molecules water via the transition state $TS_D$ to yield two molecules of hypoiodous acid plus two molecules of HI. In the final step, two molecules of hypoiodous acid intermediate attacked and abstracted two hydrogen atoms attached to different nitrogen atoms of the hydrazine molecule via transition state $TS_D$ to give back the two water molecules, used as catalyst in step two, plus the products of nitrogen molecule and two molecules of HI.

The stoichiometries of the four proposed mechanisms are the same, and are consistent with each of the proposed scheme. In the scheme published by Mshelia *et al* [7] their stoichiometry was not consistent with their proposed mechanism, in relation to the net charges carried by reacting species. The stoichiometric equation of all the proposed mechanisms is as given below in equation (17).

$$H_2O + N_2H_5^+ + 2I_2 \rightarrow H_3O^+ + N_2 + 4HI \qquad (17)$$
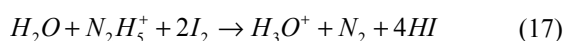
Route I of the four mechanisms proposed had three saddle points, $TS_F$, $TS_1$ and $TS_2$ as can be seen in Table 1 and Figure 1. Evidently, step 2 was the rate determining step with an activation barrier, $E_{a2}$, of 100,002.01kJ/mol. Routes II and III were both two-step mechanisms. Step 2 for both schemes were the rate determining steps with respective activation energies, $E_{aB}$ and $E_{aC}$, of 13,736.10kJ/mol and 13,613.41 kJ/mol respectively. The forth route proposed, a water molecule catalyzed mechanism scheme, had three elementary steps with the third step being the rate determining step. The rate determining step had an activation barrier, $E_{aE}$, of 6,860.4 kJ/mol. In comparing the rate determining steps of the four proposed schemes, the fourth route had the least activation barrier of 6,860.42 kJ/mol, followed by the third with activation energy of 13,613.41 kJ/mol, then the second route with activation energy of 13,736.10 kJ/mol, and lastly, the first route with highest activation barrier of 100,002.01 kJ/mol. Evidently, the fourth scheme proposed would be the most favorable mechanism energetically, and the reaction, in every likelihood, would follow the path of least energy [42].

### 3.4. Enthalpy of Reaction and Rate Constant Calculations [42, 43, 44, 45]

The enthalpies of reaction were calculated by using the Spartan software package to calculate heats of formation at standard temperature of 298.15K and pressure of 1 atmosphere. The calculations were done by taking the appropriate sums and differences as given in equation (18).

$$\Delta_r H^o \left(298.15K\right) = \sum_{products} \Delta_f H^o_{prod} \left(298.15K\right) - \sum_{reac\tan ts} \Delta_f H^o_{react} \left(298.15K\right) \tag{18}$$

The computed enthalpy of reaction at standard conditions was 357.96kJ/mol for each of the four proposed pathways. This is because they all have the same stoichiometry. The computed enthalpy of reaction also showed the reactions were endothermic. The potential energy surface diagrams (Figures 1 – 4) also confirmed this. $\Delta G^o$ and $\Delta S^o$ were also computed by using the Spartan software package, but for some species where there was no convergence, these parameters were calculated by using the Eyring [44] equation (19).

$$\ln K = -\frac{\Delta G^o}{RT} = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{19}$$

The rate constant calculations were computed according to (20).

$$k\left(298.15K\right) = \frac{k_B T}{hc^o} e^{-\Delta\ddagger G^o / RT} \tag{20}$$

Where k (298.15K) = reaction rate at temperature (298.15K), $k_B$= Boltzmann constant (1.380662 X $10^{-23}$ J/K), T = temperature (298.15K), h = Planck's constant (6.626176 x $10^{-34}$Js), $C^o$ = concentration (taken to be 1), $\Delta\ddagger G^o$ = Gibbs free energy of activation (kJ/mol),R = gas constant (8.31441 J/mol. K).

The first step for all the four proposed schemes is the same. The rate constants, $k_1$, for this step was calculated to be 68.02 x $10^3$ $dm^3mol^{-1}sec^{-1}$. However, $k_2$ was calculated as 1.84 x $10^{-5}$ $dm^3mol^{-1}sec^{-1}$ for route I. $k_2$for routes II, III, and IV were calculated as 22.29 x $10^9$ $dm^3mol^{-1}$ $sec^{-1}$, 8.02 x $10^{12}$ $dm^3mol^{-1}$ $sec^{-1}$ and 5.68 x $10^{12}$ $dm^3mol^{-1}$ $sec^{-1}$, respectively. The fourth scheme proposed, which incidentally, is the most preferred mechanism, energetically, had the third step as the rate determining step. The rate constant, $k_3$ for this scheme was calculated as 108.48 x $10^{12}$ $dm^3mol^{-1}sec^{-1}$. Again, in comparing the rate constants for the rate determining steps for the four proposed pathways, it showed that even kinetically, the fourth scheme was the most favoured yet, as it was reported that the larger the value of the rate constant, the faster the reaction [46].
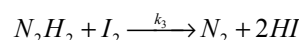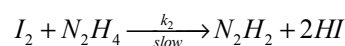
The overall rate constant, k, for each of the proposed pathways were also calculated after the rate laws were derived. The overall rate constant, k = 1.00 x $10^{-4}$ $dm^3mol^{-1}$ $sec^{-1}$for route I, k = 1.21 x $10^{13}$ $dm^3mol^{-1}$ $sec^{-1}$for route II, k = 4.36 x $10^{13}$ $dm^3mol^{-1}$ $sec^{-1}$for route III and, k = 4.19 x $10^{31}$ $dm^3mol^{-1}$ $sec^{-1}$ for route IV

### 3.5. Rate Laws for the Four Proposed Pathways

Four different mechanisms were proposed for the hydrazine / hydrazinium ion – iodine reaction system, tagged route I to route IV (schemes 2 – 5). The rate laws for the various mechanisms are as derived below.

### 3.5.1. Route I

Route I is a three - steps reaction mechanism as given in scheme 2.

$$H_2O + N_2H_5^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2H_4 + H_3O^+$$

$$I_2 + N_2H_4 \xrightarrow[slow]{k_2} N_2H_2 + 2HI$$

$$N_2H_2 + I_2 \xrightarrow{k_3} N_2 + 2HI$$

The second step is the slowest and this is the rate determining step. Therefore, rate,

$$r = k_2 \left[I_2\right]\left[N_2H_4\right]$$

At the steady state, rate of formation of [$N_2H_2$] = rate of consumption of [$N_2H_2$].

$$k_1\left[H_2O\right]\left[N_2H_5^+\right] = k_{-1}\left[N_2H_4\right]\left[H_3O^+\right]$$

$$Hence, \left[N_2H_4\right] = \frac{k_1\left[H_2O\right]\left[N_2H_5^+\right]}{k_{-1}\left[H_3O^+\right]}$$

Therefore,

$$r = k_2\left[I_2\right]\left(\frac{k_1\left[H_2O\right]\left[N_2H_5^+\right]}{k_{-1}\left[H_3O^+\right]}\right)$$

$$r = \frac{k_1 k_2}{k_{-1}} \frac{\left[I_2\right]\left[H_2O\right]\left[N_2H_5^+\right]}{\left[H_3O^+\right]}$$

$$r = k\left(\frac{\left[I_2\right]\left[H_2O\right]\left[N_2H_5^+\right]}{\left[H_3O^+\right]}\right)$$

$$Where, k = \frac{k_1 k_2}{k_{-1}}$$

Therefore, k = 1.00 x $10^{-4}$ $dm^3mol^{-1}$ $sec^{-1}$.

### 3.5.2. Route II

Route II is a two-step reaction mechanism as given in scheme 3.

$$H_2O + N_2H_5^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2H_4 + H_3O^+$$

$$2I_2 + N_2H_4 \xrightarrow[slow]{k_2} N_2 + 4HI$$
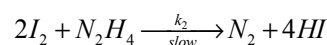
The second step is the slowest and this is the rate determining step. Therefore, the rate,

$$r = k_2 \left[ I_2 \right]^2 \left[ N_2 H_4 \right]$$

At the steady state, equilibrium is set up and, therefore,

$$\left[ N_2 H_4 \right] = \frac{k_1 \left[ H_2 O \right] \left[ N_2 H_5^+ \right]}{k_{-1} \left[ H_3 O^+ \right]}$$

$$Hence, r = k_2 \left[ I_2 \right]^2 \left( \frac{k_1 \left[ H_2 O \right] \left[ N_2 H_5^+ \right]}{k_{-1} \left[ H_3 O^+ \right]} \right)$$

$$r = \frac{k_1 k_2}{k_{-1}} \frac{\left[ I_2 \right]^2 \left[ H_2 O \right] \left[ N_2 H_5^+ \right]}{\left[ H_3 O^+ \right]}$$

$$r = k \left( \frac{\left[ I_2 \right]^2 \left[ H_2 O \right] \left[ N_2 H_5^+ \right]}{\left[ H_3 O^+ \right]} \right)$$

$$Where, k = \frac{k_1 k_2}{k_{-1}}$$

Therefore, k = 1.21 x $10^{13}$ dm$^3$mol$^{-1}$ sec$^{-1}$for route II.

### 3.5.3. Route III

Route III is another two-step reaction mechanism as given in scheme 4. The rate law is exactly the same as that of route II. That is,

$$H_2 O + N_2 H_5^+ \quad \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} \quad N_2 H_4 + H_3 O^+$$

$$2 I_2 + N_2 H_4 \xrightarrow[slow]{k_2} N_2 + 4 HI$$
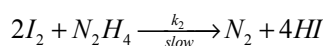
The second step is the slowest and, therefore, the rate-determining, with the rate,

$$r = k_2 \left[ I_2 \right]^2 \left[ N_2 H_4 \right]$$

At the steady state, equilibrium is set up and, therefore,

$$\left[ N_2 H_4 \right] = \frac{k_1 \left[ H_2 O \right] \left[ N_2 H_5^+ \right]}{k_{-1} \left[ H_3 O^+ \right]}$$

$$Hence, r = k_2 \left[ I_2 \right]^2 \left( \frac{k_1 \left[ H_2 O \right] \left[ N_2 H_5^+ \right]}{k_{-1} \left[ H_3 O^+ \right]} \right)$$

$$r = \frac{k_1 k_2}{k_{-1}} \frac{\left[ I_2 \right]^2 \left[ H_2 O \right] \left[ N_2 H_5^+ \right]}{\left[ H_3 O^+ \right]}$$

$$r = k \left( \frac{\left[ I_2 \right]^2 \left[ H_2 O \right] \left[ N_2 H_5^+ \right]}{\left[ H_3 O^+ \right]} \right)$$

$$Where, k = \frac{k_1 k_2}{k_{-1}}$$

Therefore, k = 4.36 x $10^{13}$ dm$^3$mol$^{-1}$ sec$^{-1}$for route III

### 3.5.4. Route IV

Route IV is a three-step reaction mechanism as given in scheme 5.

$$H_2 O + N_2 H_5^+ \quad \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} \quad N_2 H_4 + H_3 O^+$$

$$2 I_2 + 2 H_2 O \quad \overset{k_2}{\underset{k_{-2}}{\rightleftharpoons}} \quad 2 HOI + 2 HI$$

$$2 HOI + N_2 H_4 \xrightarrow[slow]{k_3} N_2 + 2 H_2 O + 2 HI$$
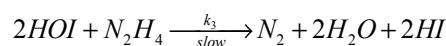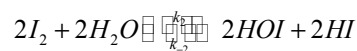
The third step is the slowest and this is the rate determining step. Therefore,

$$r = k_3 \left[ HOI \right]^2 \left[ N_2 H_4 \right]$$

At the steady state, equilibrium is set up and, therefore,

$$\left[ HOI \right]^2 = \frac{k_2 \left[ I \right]^2 \left[ H_2 O \right]^2}{k_{-2} \left[ HI \right]^2}$$

and

$$\left[ N_2 H_4 \right] = \frac{k_1 \left[ H_2 O \right] \left[ N_2 H_5^+ \right]}{k_{-1} \left[ H_3 O^+ \right]}$$

$$Hence, r = k_3 \left( \frac{k_2 \left[ I_2 \right]^2 \left[ H_2 O \right]^2}{k_{-2} \left[ HI \right]^2} \right) \left( \frac{k_1 \left[ H_2 O \right] \left[ N_2 H_5^+ \right]}{k_{-1} \left[ H_3 O^+ \right]} \right)$$

$$r = \frac{k_1 k_2 k_3}{k_{-1} k_{-2}} \left( \frac{\left[ I_2 \right]^2 \left[ H_2 O \right]^3 \left[ N_2 H_5^+ \right]}{\left[ HI \right]^2 \left[ H_3 O^+ \right]} \right)$$

$$r = k \left( \frac{\left[ I_2 \right]^2 \left[ H_2 O \right]^3 \left[ N_2 H_5^+ \right]}{\left[ HI \right]^2 \left[ H_3 O^+ \right]} \right)$$

$$Where, \ k = \frac{k_1 k_2 k_3}{k_{-1} k_{-2}}$$

$k_{-2}$ is approx. zero
Therefore, k = 4.19 x $10^{31}$ dm$^3$mol$^{-1}$ sec$^{-1}$ for route IV.

## 4. Conclusion

The mechanism of the reaction of hydrazine / hydrazinium ion with iodine was studied using 6311+G** basis set of DFT at the B3LYP level of computation method. The results of this study were compared with previously published work on the reaction of hydrazine / hydrazinium ion with iodine. This work proposed four different reaction mechanisms for the reaction of hydrazine / hydrazinium ion with iodine. The study was also able to demonstrate that the reaction can follow any of the four routes proposed because the activation energies for the rate determining steps in all pathways were

comparable. Rate laws for the four proposed mechanisms were also derived, and each of the derived rate laws was consistent with mechanisms proposed. Rate constants for the various reactions were also calculated.

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